Characterization and manipulation of individual defects in insulating hexagonal boron nitride using scanning tunnelling microscopy

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Defects play a key role in determining the properties and technological applications of nanoscale materials and, because they tend to be highly localized, characterizing them at the singledefect level is of particular importance. Scanning tunnelling microscopy has long been used to image the electronic structure of individual point defects in conductors¹, semiconductors²⁻⁴ and ultrathin films⁵⁻⁹, but such single-defect electronic characterization remains an elusive goal for intrinsic bulk insulators. Here, we show that individual native defects in an intrinsic bulk hexagonal boron nitride insulator can be characterized and manipulated using a scanning tunnelling microscope. This would typically be impossible due to the lack of a conducting drain path for electrical current. We overcome this problem by using a graphene/boron nitride heterostructure, which exploits the atomically thin nature of graphene to allow the visualization of defect phenomena in the underlying bulk boron nitride. We observe three different defect structures that we attribute to defects within the bulk insulating boron nitride. Using scanning tunnelling spectroscopy we obtain charge and energy-level information for these boron nitride defect structures. We also show that it is possible to manipulate the defects through voltage pulses applied to the scanning tunnelling microscope tip.

Boron nitride (BN) is an essential component in many new and technologically promising devices that incorporate two-dimensional materials¹⁰⁻¹² and so it is crucial to understand the nature of intrinsic defects in BN layers. Previous cathodoluminescence and elemental analysis of high-purity single-crystal BN synthesized at high pressure and temperature indicated the existence of residual impurities and defects^{12,13}. Optoelectronic experiments have revealed that these defects give rise to photoactive states within the BN bandgap^{14,15}. So far, however, these studies have been limited to spatially averaged defect behavior, and the investigation of individual defects at the nanoscale remains an outstanding challenge.

Here, we visualize individual BN defects by capping a BN crystal with a monolayer of graphene. Figure 1a shows a typical scanning tunnelling microscopy (STM) topographic image of our graphene/ BN heterostructures, where a 7 nm moiré pattern can be seen on top of long-range height fluctuations spanning tens of nanometres, similar to previous imaging of graphene on BN^{16,17}. Localized shallow dips and a protrusion are also visible ($\Delta z < 0.1$ Å). More revealing, however, are the differential conductance (dI/dV) maps shown in Fig. 1b. Striking new features are visible in these data. We observe randomly distributed bright (high dI/dV) and dark (low d*I*/d*V*) circular dots (~20 nm in diameter) that have varying degrees of intensity (see Supplementary Sections 1 and 2 for intensities and densities). Another common feature, as seen at the right edge of the map in Fig. 1b, is a sharp ring structure with an interior that does not obscure the moiré pattern. Close-up topographic studies of these defects reveal unblemished atomically resolved graphene honeycomb structure with occasional slight dips or a protrusion with $|\Delta z| < 0.1$ Å (Supplementary Section 3). Maps obtained at numerous locations with many tips across three different devices replicate these observations.

Figure 2a,b presents higher-resolution dI/dV maps of representative bright and dark dot defects. These maps show clearly that the graphene moiré pattern is not obscured by the defects. To determine the effect of these defects on the electronic structure of graphene, we performed dI/dV spectroscopy at varying distances from the dot centres (each spectrum was started with the same tunnel current I and sample bias $V_{\rm s}$). These data are plotted in Fig. 2c,d for the bright and dark dots, respectively. The spectra are characteristic of undamaged graphene¹⁸, but show an electron/hole asymmetry that is dependent on the tip position relative to the centre of a defect. In Fig. 2c, for example, we see that dI/dV ($V_s > 0$) increases as the tip approaches the bright-dot centre. Figure 2d shows the opposite trend, as seen by the decrease in dI/dV ($V_s > 0$) as the STM tip approaches the dark-dot centre. These basic trends were seen for all bright and dark dot defects, regardless of the intensity and tip-height configuration (Supplementary Section 4). These observations can be understood by recalling that dI/dV reflects the graphene local density of states (LDOS). The distance-dependent enhancement of d*I*/d*V* above the Dirac point ($V_s \approx -0.17$ V) as the tip nears a bright dot in Fig. 2c can therefore be interpreted as arising from the attraction of negatively charged Dirac fermions to the dot centre. We thus conclude that the bright dot in Fig. 2a reflects a positively charged defect in BN19,20. Similarly, the distance-dependent reduction of dI/dV above the Dirac point in Fig. 2d arises from the repulsion of negatively charged Dirac fermions from the defect. We thus conclude that the dark dots are negatively charged^{19,20}.

We now focus on the ring defects, as displayed at the right edge of Fig. 1b. We find that the ring radius depends on the values of V_s and backgate voltage V_g . Figure 3 shows that the ring radius changes from 2 nm (Fig. 3a) to 11 nm (Fig. 3b) as V_g is changed from $V_g = 17$ V to 9 V (with constant $V_s = -0.3$ V). Figure 3 c shows the dependence of the ring radius on V_g for various V_s values (denoted by distinct symbols). These data were obtained by measuring the

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Figure 1 | STM topography and corresponding dI/dV **map for a graphene/BN device. a**, STM topographic image of a clean graphene/BN area. **b**, A dI/dV map (I = 0.4 nA, $V_s = -0.25$ V) acquired simultaneously with **a** exhibits various new features: bright dots, a dark dot and a ring.

ring radius from dI/dV maps taken at the same location as Fig. 3a,b, but with different V_s and V_g configurations. Although the precise ring radius depends on the sharpness of the STM tip³, the qualitative behaviour shown in Fig. 3c is typical of the vast majority of ring defects observed here. In general, for fixed V_s , the ring radius increases with decreasing V_g until a critical backgate voltage ($V_c = 6 \pm 1$ V) is reached, whereupon the ring vanishes.

We now discuss the origin of the 'dot' and 'ring' defects observed in our dI/dV maps. Three general scenarios are possible: (1) adsorbates bound to the surface of graphene; (2) adsorbates trapped at the interface between the graphene and BN; and (3) intrinsic defects within the insulating BN substrate. Our data imply that (3) is the correct scenario, for the following reasons. First we rule out scenario (1), because weakly bound adsorbates would have a higher height profile than the topographically small features observed^{19,21} (Supplementary Section 3) and would also probably get swept away by the STM tip when it is brought close enough to observe the graphene honeycomb structure²⁰. Strongly bound adsorbates in scenario (1) would also probably have taller height profiles as



Figure 2 | d*I*/dV maps and spatially dependent d*I*/dV spectroscopy determining the defect charge state. **a**,**b**, d*I*/dV maps (I = 0.4 nA, $V_s = -0.3 \text{ V}$, $V_g = 5 \text{ V}$) for bright- and dark-dot defects. **c**, d*I*/dV spectroscopy (initial tunnelling parameters: I = 0.4 nA, $V_s = -0.5 \text{ V}$, $V_g = 20 \text{ V}$) measured on graphene at different lateral distances from the centre of the bright dot in **a**. **d**, Same as in **c**, but for the dark dot in **b**. Distance-dependent d*I*/dV spectroscopy reveals that **a** and **b** represent positively and negatively charged defects in BN, respectively.

seen for other graphene adsorbates (Supplementary Section 3) and should disrupt the graphene honeycomb lattice²² (which was not observed). Also, strongly bound adsorbates should lead to changes in the graphene spectroscopy due to the formation of localized bonding states²², which are not seen. Scenario (2) can be ruled out because an adsorbate trapped beneath graphene would cause a bump in graphene at least an order of magnitude larger than the $\Delta z < 0.1$ Å feature observed here. We would also expect a trapped adsorbate to locally delaminate the graphene from the BN substrate, thus disrupting the moiré pattern, which is not seen.

Scenario (3)-intrinsic charged BN defects-is thus the most likely explanation for the defects observed here. Polycrystalline BN has been shown to host several varieties of charged defects, as seen from electron paramagnetic resonance²³ and luminescence experiments^{24,25}, as well as theoretical investigations²⁶. In those studies the most abundantly reported defects were nitrogen vacancies, which were shown to act as donors, and carbon impurities substituted at nitrogen sites, which were shown to act as acceptors. Secondary ion mass spectroscopy studies of high-purity single-crystal BN synthesized at high pressure and temperature have also identified oxygen and carbon impurities¹³. A comparison between optoelectronic experiments^{14,15} on new, high-purity singlecrystal BN and recent theoretical work²⁷ shows that the nature of the defects in the new, high-purity BN crystals is consistent with observations of carbon impurities and nitrogen vacancies in previous polycrystalline studies (although the influence of oxygen impurities remains ambiguous). Such defects, when ionized, could induce the bright and dark dots observed in graphene/BN via a graphene screening response²⁸ (Figs 1 and 2). The fact that these defects are embedded in the BN explains why the dots have such a small topographic deflection, as well as why the graphene lattice and moiré pattern are not disrupted, and also why no new states arise in the graphene spectroscopy^{21,22}. Variations in the intensity of bright and dark defects are explained by BN defects lying at different depths relative to the top graphene layer.

It is possible to extract quantitative information regarding the electronic configuration of BN defects from the STM dI/dV signal measured from the graphene capping layer. This can be achieved for the ring defects by analysing the gate (V_g) and bias (V_s) dependent ring radius, shown in Fig. 3c. Similar rings have been observed in other systems and have been attributed to the charging of an adsorbate or defect^{3,21,29,30}. Because the ring in Fig. 3 is highly responsive to the presence of the STM tip and displays no charge hysteresis, we expect that it lies in the topmost BN layer and is strongly coupled to the graphene electronic structure. The STM tip is capacitively coupled to the graphene directly above the defect through the equation $|e|\delta n = C(r)V_{tip}$, where δn is the local change in graphene electron density, C(r) is a capacitance (per area) that increases with decreasing lateral tip–defect distance r,

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Figure 3 | *dl/dV* maps of ring defect enable energy-level characterization. **a**,**b**, *dl/dV* maps (I = 0.4 nA, $V_s = -0.3$ V) of the same ring defect at backgate voltages of $V_g = 17$ V and 9 V, respectively. **c**, Ring radius *R* for different V_s and V_g . The ring radius was extracted from *dl/dV* maps taken at the same location as in **a** and **b**. **d**,**e**, Schematic model (energies not to scale) for ring formation due to charge transfer between graphene and a defect in the top layer of BN. When the distance *r* between the tip and the defect is larger than the ring radius *R* (**d**), the defect level is filled and negatively charged. When r < R (**e**), local gating from the tip lowers the local electron density so that the Fermi level is below the defect level, neutralizing the defect. For negative tip potentials and n-doped graphene, *R* increases as reduced V_g shifts the unperturbed defect level closer to the Fermi energy.

 V_{tip} is the tip electrostatic potential ($V_{\text{tip}} = -V_{\text{s}} + \text{constant}$, Supplementary Section 6), and |e| is the charge of an electron. For the dI/dV maps in Fig. 3, $V_{\rm tip}$ < 0, so the electrostatic gating from the tip lowers the electron density of the (n-doped) graphene directly beneath the tip. Figure 3d schematically depicts the local electronic structure of the graphene immediately above the defect when r is large and V_{g} is set such that the defect level is filled and carries negative charge. As the tip approaches the defect, C(r)increases and thus δn becomes more negative. Eventually, the defect level crosses the Fermi level (and switches to a neutral state) when the tip is at a distance R away from the defect, thus causing a perturbation in the tunnel current that leads to the observation of a ring of radius *R*. Figure 3e shows the case (r < R) where the defect is in a neutral charge state through interaction with the tip. The energy level of the defect can be found by tuning V_{g} such that the Fermi level matches the defect level in the absence of the tip. This will cause the radius of the charging ring to diverge. As seen in Fig. 3c, this occurs for the observed ring defects when $V_{\rm g} = 6 \pm 1$ V, thus resulting in a defect level $\sim 30 \pm 10$ meV above the graphene Dirac point energy (because the Dirac point energy can be measured with respect to the Fermi level), which is expected to be ~4 eV below the BN conduction band-edge³¹. Interestingly, this is similar to a previously observed carbon substitution defect level²⁴, suggesting that the ring defect arises from a carbon impurity.

Additional microscopic information regarding the observed BN defects can be obtained by directly manipulating their charge state with the STM tip. Similar manipulation has been performed previously to switch the charge state of defects in semiconductors³² as well as adatoms on top of ultrathin insulating films⁵, but this type of STM-based manipulation is unprecedented for defects inside bulk insulators. Figure 4a presents a dI/dV map exhibiting numerous charged defects. To manipulate the charge state of the observed BN defects, the STM tip was positioned 1 nm over the centre point of this area and a bias of $V_8 = 5$ V was applied for

10 s (Supplementary Section 8). After applying this voltage pulse, a dI/dV map was acquired over the same region at low bias, as shown in Fig. 4b. Figure 4c shows the same region after similar application of a second pulse. Inspection of Fig. 4b,c shows that the BN defect configurations are significantly altered by application of such voltage pulses. The defects are seen to reversibly switch between charged and neutral states, as well as between states having opposite charge. To highlight this behaviour, we denote changes to defect states (compared to the preceding image) with coloured arrows. A red arrow signifies the disappearance of a charged defect, a blue arrow represents the appearance of a charged defect, and a green arrow indicates where a defect has changed the sign of its charge. We find that defects that disappear after a tip pulse always reappear in the same location after subsequent tip pulses. Additionally, dark dots tend to switch into metastable neutral states (that is, disappear) at a higher rate than bright dots. Ring defects, as well as the darkest and brightest dots, remain unchanged by tip pulses.

This tip-induced manipulation of BN defects can be explained by electric-field-induced emission of charge carriers from BN defect states. By tilting the local potential landscape, the STM tip causes charge carriers to tunnel through the ionization barrier between different defects, charging some while neutralizing others (Supplementary Section 9). This accounts for the disappearance and reappearance of the dots in the same location, which cannot be described by defect migration through the BN lattice. In addition, the observation of a higher rate of switching for the dark dots (acceptors) than bright dots (donors) suggests it is more energetically favourable for neutral acceptors to emit holes than for neutral donors to emit electrons (and the same for the reverse processes). Hence, the acceptor states are probably closer to the valence band than the donor states are to the conduction band. Because the rings, as well as the darkest and brightest dots, never change under tip pulses, we surmise that they are in the top layers of BN and in

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Figure 4 | Manipulating defects in BN with an STM tip. Tip pulses with $V_s = 5 V$ and $\Delta t = 10 s$ are used to toggle the charge states of the dot defects. **a**, dI/dV map (I = 0.4 nA, $V_s = -0.25 V$) of graphene/BN reveals various dots and rings. **b**, dI/dV map of the same region after a tip pulse is applied at the centre of the region in **a. c**, dI/dV map of the same region after another tip pulse. Red arrows mark the disappearance of dots relative to the previous image, blue arrows mark the appearance of dots, and green arrows mark dot defects that have changed the sign of their charge.

direct electrical contact with the graphene. Their charge states thus depend only on graphene's local chemical potential and show no hysteresis or metastability with the electric field (for example, the ring defects smoothly and reversibly alter their charge in response to the passage of the STM tip and always return to the same charge state). The defects that switch into new metastable charge states (that is, exhibit hysteresis) must thus be in lower BN layers, out of direct contact with the graphene.

In conclusion, we have shown that a single graphene capping layer enables STM imaging and manipulation of individual point defects in an insulating bulk BN substrate. We were able to identify the charge state of individual defects and we have quantitatively extracted the energy level location for one species of defect (suggesting that it is a carbon impurity). We find that voltage pulses applied to our STM tip enable ionization, neutralization and even toggling of the charge state for defects in BN. This new method of using an atomically thin conducting capping layer to probe and control defects in bulk insulators might be extended to other insulator/defect systems previously inaccessible to STM, such as diamond with nitrogen-vacancy centres.

Methods

Methods and any associated references are available in the online version of the paper.

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References

- Madhavan, V., Chen, W., Jamneala, T., Crommie, M. F. & Wingreen, N. S. Tunneling into a single magnetic atom: spectroscopic evidence of the Kondo resonance. *Science* 280, 567–569 (1998).
- Feenstra, R. M., Woodall, J. M. & Pettit, G. D. Observation of bulk defects by scanning tunneling microscopy and spectroscopy: arsenic antisite defects in GaAs. *Phys. Rev. Lett.* **71**, 1176–1179 (1993).
- Teichmann, K. *et al.* Controlled charge switching on a single donor with a scanning tunneling microscope. *Phys. Rev. Lett.* **101**, 076103 (2008).
- Lee, D. H. & Gupta, J. A. Tunable field control over the binding energy of single dopants by a charged vacancy in GaAs. *Science* 330, 1807–1810 (2010).
- Repp, J., Meyer, G., Olsson, F. E. & Persson, M. Controlling the charge state of individual gold adatoms. *Science* 305, 493–495 (2004).
- Pradhan, N. A., Liu, N. & Ho, W. Vibronic spectroscopy of single C₆₀ molecules and monolayers with the STM. J. Phys. Chem. B 109, 8513–8518 (2005).
- Avouris, P. & Wolkow, R. Scanning tunneling microscopy of insulators: CaF₂ epitaxy on Si(111). *Appl. Phys. Lett.* 55, 1074–1076 (1989).
- Repp, J., Meyer, G., Paavilainen, S., Olsson, F. E. & Persson, M. Scanning tunneling spectroscopy of Cl vacancies in NaCl films: strong electron-phonon coupling in double-barrier tunneling junctions. *Phys. Rev. Lett.* **95**, 225503 (2005).
- Choi, T., Ruggiero, C. D. & Gupta, J. A. Incommensurability and atomic structure of c(2×2)N/Cu(100): a scanning tunneling microscopy study. *Phys. Rev. B* 78, 035430 (2008).
- Dean, C. R. et al. Boron nitride substrates for high-quality graphene electronics. Nature Nanotech. 5, 722–726 (2010).
- 11. Britnell, L. *et al.* Strong light–matter interactions in heterostructures of atomically thin films. *Science* **340**, 1311–1314 (2013).
- Watanabe, K., Taniguchi, T. & Kanda, H. Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal. *Nature Mater.* 3, 404–409 (2004).
- 13. Taniguchi, T. & Watanabe, K. Synthesis of high-purity boron nitride single crystals under high pressure by using Ba–BN solvent. *J. Cryst. Growth* **303**, 525–529 (2007).
- Remes, Z., Nesladek, M., Haenen, K., Watanabe, K. & Taniguchi, T. The optical absorption and photoconductivity spectra of hexagonal boron nitride single crystals. *Phys. Status Solidi A* 202, 2229–2233 (2005).
- Ju, L. et al. Photoinduced doping in heterostructures of graphene and boron nitride. Nature Nanotech. 9, 348–352 (2014).
- Xue, J. *et al.* Scanning tunnelling microscopy and spectroscopy of ultra-flat graphene on hexagonal boron nitride. *Nature Mater.* 10, 282–285 (2011).
- Decker, R. G. et al. Local electronic properties of graphene on a BN substrate via scanning tunneling microscopy. Nano Lett. 11, 2291–2295 (2011).
- Zhang, Y. et al. Giant phonon-induced conductance in scanning tunneling spectroscopy of gate-tunable graphene. Nature Phys. 4, 627–630 (2008).
- Wang, Y. *et al.* Mapping Dirac quasiparticles near a single Coulomb impurity on graphene. *Nature Phys.* 8, 653–657 (2012).
- 20. Wang, Y. *et al.* Observing atomic collapse resonances in artificial nuclei on graphene. *Science* **340**, 734–737 (2013).
- 21. Brar, V. W. *et al.* Gate-controlled ionization and screening of cobalt adatoms on a graphene surface. *Nature Phys.* **7**, 43–47 (2011).
- 22. Scheffler, M. et al. Probing local hydrogen impurities in quasi-free-standing graphene. ACS Nano 6, 10590–10597 (2012).
- Fanciulli, M. & Moustakas, T. D. Study of defects in wide band gap semiconductors by electron paramagnetic resonance. *Physica B* 185, 228–233 (1993).
- Katzir, A., Suss, J. T., Zunger, A. & Halperin, A. Point defects in hexagonal boron nitride. I. EPR, thermoluminescence, and thermally-stimulated-current measurements. *Phys. Rev. B* 11, 2370–2377 (1975).
- Andrei, E. Y., Katzir, A. & Suss, J. T. Point defects in hexagonal boron nitride. III. EPR in electron-irradiated BN. *Phys. Rev. B* 13, 2831–2834 (1976).

- Zunger, A. & Katzir, A. Point defects in hexagonal boron nitride. II. Theoretical studies. *Phys. Rev. B* 11, 2378–2390 (1975).
- Attaccalite, C., Bockstedte, M., Marini, A., Rubio, A. & Wirtz, L. Coupling of excitons and defect states in boron-nitride nanostructures. *Phys. Rev. B* 83, 144115 (2011).
- Das Sarma, S., Adam, S., Hwang, E. H. & Rossi, E. Electronic transport in twodimensional graphene. *Rev. Mod. Phys.* 83, 407–470 (2011).
- 29. Woodside, M. T. & McEuen, P. L. Scanned probe imaging of single-electron charge states in nanotube quantum dots. *Science* **296**, 1098–1101 (2002).
- Pradhan, N. A., Liu, N., Silien, C. & Ho, W. Atomic scale conductance induced by single impurity charging. *Phys. Rev. Lett.* 94, 076801 (2005).
- Kharche, N. & Nayak, S. K. Quasiparticle band gap engineering of graphene and graphone on hexagonal boron nitride substrate. *Nano Lett.* 11, 5274–5278 (2011).
- Garleff, J. K., Wijnheijmer, A. P., v. d. Enden, C. N. & Koenraad, P. M. Bistable behavior of silicon atoms in the (110) surface of gallium arsenide. *Phys. Rev. B* 84, 075459 (2011).

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Author contributions

L.J. and J.V.J. conceived the work and designed the research strategy. J.V.J., D.W., S.K. and J.L. performed data analysis. J.V.J., S.K., L.J. and A.Z. facilitated sample fabrication. D.W., J.L. and J.V.J. carried out STM/ scanning tunnelling spectroscopy (STS) measurements. J.V.J. and S.K. carried out electron transport measurements. K.W. and T.T. synthesized the hBN samples. D.W., J.V.J. and L.J. formulated the theoretical model with advice from F.W. and M.F.C. M.F.C. supervised the STM/STS experiments. J.V.J., D.W. and M.F.C. co-wrote the manuscript. J.V.J. and M.F.C. coordinated the collaboration. All authors discussed the results and commented on the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.F.C.

Competing financial interests

The authors declare no competing financial interests.

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Methods

The samples were fabricated using the transfer technique developed by Zomer and colleagues³³ with standard electron-beam lithography. We used high-purity BN crystals synthesized by Taniguchi and colleagues¹³, exfoliated to 60–100 nm thickness and with a SiO₂ thickness of 285 nm as the dielectric for electrostatic gating. Monolayer graphene was exfoliated from graphite and deposited onto methyl methacrylate polymer and transferred onto BN (also annealed) sitting on a SiO₂/Si wafer. Completed devices were annealed in flowing Ar/H₂ forming gas at 350 °C and their electrical conductance was measured with a standard a.c. voltage bias lock-in technique with a 50 μ V signal at 97.13 Hz. Samples that exhibited bipolar transport within a gate voltage range of –30 to 30 V were then transferred into an Omicron ultrahigh-vacuum (UHV) low-temperature STM. A second anneal was then performed for several hours at ~300 °C and 10⁻¹¹ torr before moving the device into the STM chamber for measurements at T = 5 K. Before all STM measurements, the

platinum iridium STM tip was calibrated by measuring the surface state of an independent Au(111) crystal. All STM topographic images were acquired in constant current mode with a sample bias $V_{\rm s}$ defined as the voltage applied to the sample with respect to the STM tip. All scanning tunnelling spectroscopy measurements were obtained by lock-in detection of the a.c. tunnel current induced by a modulated voltage (6 mV at 613 Hz) added to $V_{\rm s}$. The uncertainty in the measurements of the ring radii plotted in Fig. 3c is smaller than ±0.22 nm for all data shown.

References

 Zomer, P. J., Dash, S. P., Tombros, N. & van Wees, B. J. A transfer technique for high mobility graphene devices on commercially available hexagonal boron nitride. *Appl. Phys. Lett.* 99, 232104–232107 (2011).