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► **To cite this version:**

Vishnu Ottapilakkal, Abhishek Juyal, Suresh Sundaram, Phuong Vuong, Collin Beck, et al.. High-quality hexagonal boron nitride selectively grown on patterned epigraphene by MOVPE. 2024. hal-04763687

HAL Id: hal-04763687

<https://hal.science/hal-04763687v1>

Preprint submitted on 4 Nov 2024

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High-quality hexagonal boron nitride selectively grown on patterned epigraphene by MOVPE

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VO and AJ contributed equally to this work.

KEYWORDS: Boron nitride, Graphene, MOVPE, van der Waals heterostructure, Epitaxial
growth

21 **ABSTRACT**

22 Hexagonal boron nitride encapsulation is the method of choice for protecting graphene
23 from environmental doping and impurity scattering. It was previously demonstrated that
24 metal-organic vapor phase epitaxy (MOVPE) grows epitaxially ordered, uniform BN layers
25 on epigraphene (graphene grown on SiC). Due to graphene's non-wetting properties, h-BN
26 growth starts preferentially from the graphene ledges. We use this fact here to selectively
27 promote growth of high-quality flat h-BN on epigraphene by patterning epigraphene
28 microstructures prior to BN growth. Thin h-BN films (down to 6 nm) grown by MOVPE
29 show smooth and pleated surface morphology on epigraphene, while crumpled BN is
30 observed on the SiC. Cross-sectional high-resolution transmission electron microscopy
31 images and fluorescence imaging confirm the higher BN quality grown on the epigraphene.
32 Transport measurements reveal p-doping as expected from hydrogen intercalation of
33 epigraphene and regions of high and low mobility. This method can be used to produce
34 structurally uniform high-quality h-BN/epigraphene micro/nano scale heterostructure.

35 **SYNOPSIS**

36 Using metal organic vapor phase epitaxy (MOVPE), we demonstrate the selective growth
37 of high-quality hexagonal boron nitride on patterned epigraphene and investigate its
38 electrical transport properties.

39

40 **INTRODUCTION**

41 Two-dimensional (2D) materials such as graphene, hexagonal boron nitride (h-BN), and
42 transition metal dichalcogenides (TMDCs) have attracted significant interest in recent
43 years due to their unique physical properties and potential for electronic and photonic
44 applications.^{1,2} Epigraphene (EG) is structurally high quality graphene grown epitaxially on
45 SiC³⁻⁶, with exceptional properties such as quantized ballistic electronic transport on length
46 scales of hundreds of micrometers⁷, highly efficient spin transport⁸, high frequency
47 transistor operation⁹, quantum Hall effect-based standard of resistance¹⁰ and it is compatible
48 with largescale nanoelectronics processing methods.³ Ultra-high mobility semiconducting
49 epigraphene was recently demonstrated in the epigraphene buffer layer, with mobilities up
50 to 5000 cm²/Vs¹¹, which is 20 times the theoretical limit of other 2D semiconductors. The
51 required single crystal SiC substrates are commercially available in up to 200 mm wafers,
52 as they are widely used for high temperature /high power electronics and compatible with
53 THz electronics applications.¹²

54 To fully exploit epigraphene potential properties, it requires to be integrated with
55 dielectrics, while sustaining graphene pristine properties in an industrially relevant
56 process. Exfoliated h-BN is a widely-used dielectric capping layer to protect graphene from
57 environmental doping and to mitigate impurity scattering¹³⁻¹⁵. h-BN is a 6 eV wide bandgap
58 semiconductor with a dielectric constant of about 4.¹⁶ It is isostructural with graphene
59 (1.7% lattice mismatch), charge neutral, doesn't form chemical bonds with graphene. It has
60 high temperature and chemical stability. We have previously demonstrated a process
61 where Migration Enhanced Metal Organic Vapor Phase Epitaxy (ME-MOVPE) of h-BN on
62 epigraphene by van der Waals growth produces epitaxially ordered h-BN/EG/SiC
63 heterostructures of excellent quality, with flat and clean interfaces.¹⁵ This process is scalable
64 and compatible with industrial methods so that it has significant advantages over the
65 conventional mechanical transfer processes.

66 The ME-MOVPE BN growth process has been explained by a lateral epitaxial deposition
67 mechanism involving a one-dimensional nucleation-free-energy-barrierless growth that
68 relies on the large mobilities of the B and N species on the graphene surface.¹⁵ The method

69 was inspired by our observation that on partially grown epigraphene on SiC, flat h-BN
70 layers grow from the graphene edge, whereas a large density of crumpled BN particles are
71 observed on (oxidized) SiC and also accumulate on defects and step edges.¹⁵ Here we use
72 this fact to promote growth of flat h-BN selectively on graphene by patterning epigraphene
73 microstructures prior to h-BN deposition. The process was specifically developed to coat
74 micro/nano scale devices (e.g. Hall-bars) with h-BN. Their small lateral size steers high-
75 quality h-BN growth, as growth of 2D materials on micrometre-sized patterned substrates
76 results in homogeneous nucleation, leading to improved crystal quality.¹⁷ The small size
77 will also make the underlying epigraphene more likely to be defects- and step- free.

78

79 **EXPERIMENTAL METHODS**

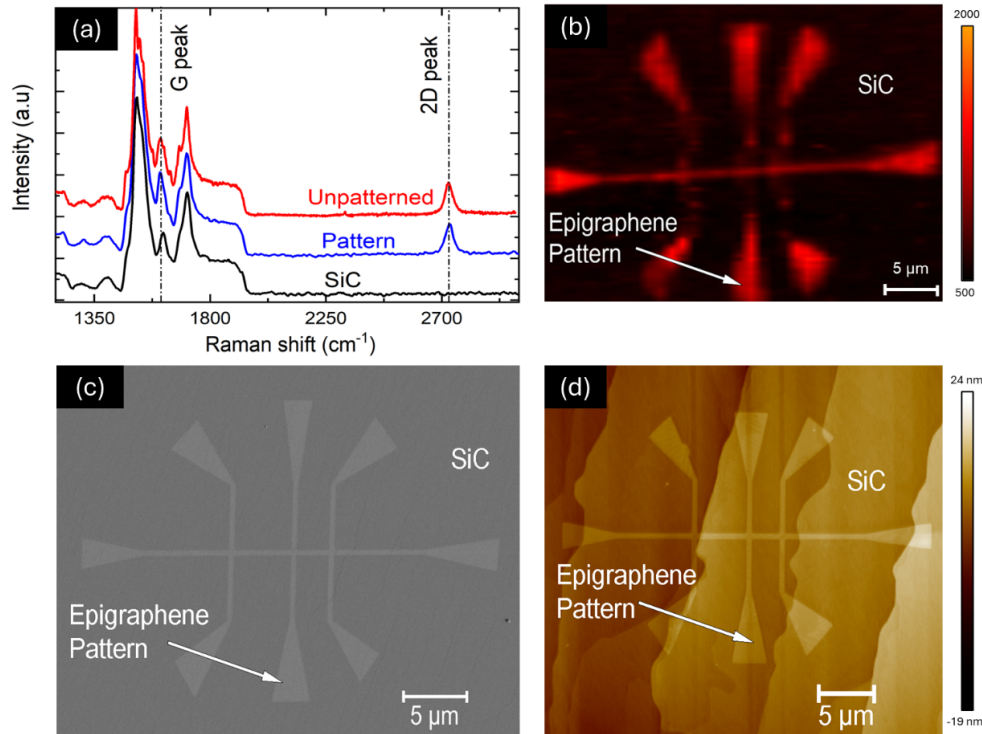
80 Epigraphene was produced on commercial chemical mechanical polished (CMP) insulating
81 4H-SiC substrates (from II-VI, now Coherent) by the polymer enhanced confinement-
82 controlled sublimation growth method.¹⁸ The growth temperature is adjusted around
83 1600°C under 1 atm Ar. Details of the epigraphene growth have been reported elsewhere.¹⁸⁻
84 ²⁰ Epigraphene microstructures were fabricated by standard lithography: a 300 nm thick
85 ma-N-2403 resist was patterned via electron beam lithography and epigraphene was etched
86 with oxygen plasma (RIE) at a pressure of 15 mTorr, an oxygen flow 4 sccm and an RIE
87 power of 16 W for 15s.

88 BN growth was carried out using an Aixtron MOVPE close-coupled showerhead (CCS)
89 3x2" reactor. Triethylboron and ammonia were used as the precursors for boron and
90 nitrogen, respectively. The growth was carried out at 1270°C in a hydrogen environment
91 at 85 mbar, following the similar growth conditions as previously reported.^{15,21,22} Raman
92 spectroscopy measurements and fluorescence emission mapping were performed using
93 Horiba Lab RAM HR equipment with an excitation wavelength of 532 nm. The
94 fluorescence emission mapping was acquired with a lateral resolution of 1 μm by exciting
95 the sample with a 532 nm laser and measuring the fluorescence emission spectra in the
96 range of 570 nm to 630 nm. High-resolution scanning transmission electron microscopy
97 (HR-STEM) was performed using a probe-corrected ThermoFisher Scientific Titan G2 on

98 cross-sections prepared by focused ion beam (FIB). Atomic force microscopy (AFM –
99 Bruker Edge) in non-contact mode and scanning electron microscopy (SEM – Zeiss Supra
100 55VP with an SE2 detector) was utilized for morphological characterization.

101

102 RESULTS AND DISCUSSION

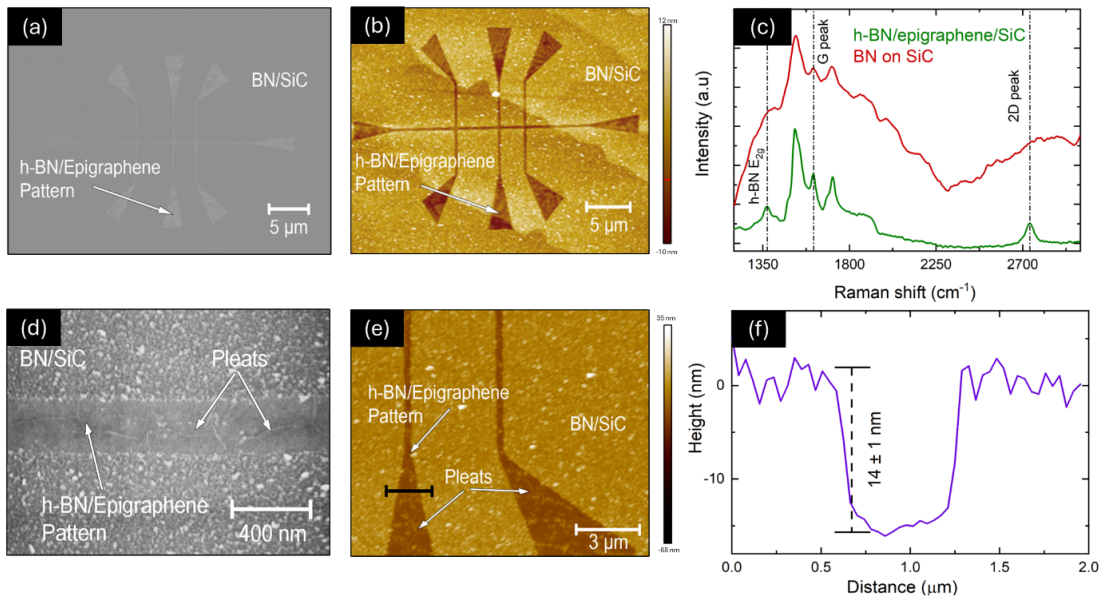


103

104 **Figure 1.** (a) comparison of Raman spectra before (red) and after (blue) patterning, highlighting
105 the unchanged characteristic epigraphene peaks after patterning. A bare SiC spectrum (black) is
106 shown for comparison, (b) Raman mapping (2D peak) of the sample revealing the Hall bar-shaped
107 epigraphene structure, (c) SEM and (d) AFM images of epigraphene Hall bar. The SiC terraces are
108 visible onto which the epigraphene grows continuously.

109 The structural characteristics and morphology of patterned epigraphene are presented in
110 Figure 1. The Raman spectrum remains the same before (red trace) and after (blue trace)
111 patterning process (Figure 1a), indicating that the quality of epigraphene is unaltered by
112 the patterning process. The characteristic 2D-peak²³ of graphene at 2738 cm⁻¹ show a
113 compressive strain as is usual for epigraphene on the Si-face^{24,25}, and a FWHM less than 40

114 cm^{-1} indicates monolayer graphene.^{23,24} The graphene G peak at 1600 cm^{-1} is well resolved,
 115 despite the large SiC peaks in that energy range. The absence of a Raman D-peak around
 116 1350 cm^{-1} on both spectra confirm the high quality of the epigraphene. A bare SiC Raman
 117 spectrum (black trace) is included for comparison. Raman mapping of the 2D peak, shown
 118 in Figure 1b, confirms the successful removal of epigraphene outside of the Hall bar. The
 119 SEM and AFM images in Figure 1c, d respectively, show a well-defined patterned Hall-bar
 120 structure, with the continuity of the epigraphene clearly visible in the AFM image despite
 121 the presence of SiC steps.²⁴ The AFM roughness of the epigraphene throughout the
 122 structure after patterning is less than 0.2 nm .



123
 124 **Figure 2.** (a) SEM and (b) AFM image of the BN grown on patterned epigraphene sample. (c) Raman
 125 spectra recorded on h-BN/epigraphene pattern and BN/SiC, showing significant fluorescence in the
 126 BN/SiC sample, high-magnification (d) SEM and (e) AFM image of the heterostructure showing the
 127 pleated h-BN on the patterned epigraphene and granular BN on SiC substrate. (f) Height profile
 128 measured along the black line in (e), showing a dip in the BN surface across the pattern.

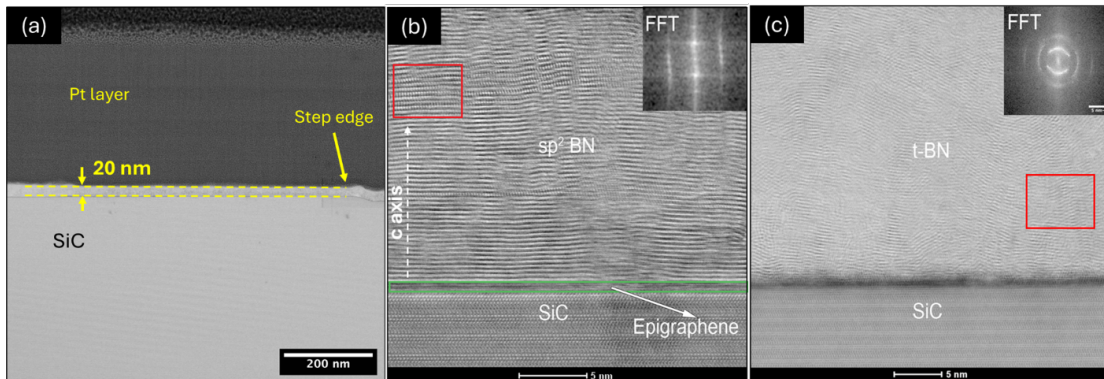
129 The patterned epigraphene samples were transferred to the MOVPE reactor for h-BN
 130 growth. The growth was adjusted to grow 6-30 nm thick h-BN, by tuning the deposition
 131 time. The Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)

132 images in Figure 2a, b respectively, reveal that after BN growth, on the epigraphene
133 patterned structure, a very smooth surface was obtained, which is different from the surface
134 deposits outside of the pattern (i.e. on O₂ plasma etched SiC). The flat surface on the
135 epigraphene structure is contrasted with granular and rough surface on the (oxidized) SiC,
136 as previously observed in ref 15.

137 We first confirm the presence of BN on the epigraphene patterns with Raman spectroscopy.
138 In addition to the graphene (2D peak at 2734 cm⁻¹ and G peak at 1600 cm⁻¹) and SiC peaks,
139 a prominent peak is observed at 1370 cm⁻¹ at the expected location of the h-BN E_{2g} peak (as
140 shown in Figure 2c). This peak is close to the position of the graphene D peak (1350 cm⁻¹),
141 superimposed with SiC features, making it difficult to resolve. However, the D peak is not
142 detectable in as-grown epigraphene samples (the observed peaks in the 1000-1350 cm⁻¹
143 range are SiC peaks, Figure 1a). Also, after peeling off the BN film, no significant D-peak
144 was observed in the underlying graphene (as shown in Figure S1).¹⁵ Therefore, we
145 confidently ascribe the peak observed at 1370 cm⁻¹ to h-BN E_{2g}. In addition, considerable
146 background fluorescence was observed in the Raman spectrum in the range 1200-2000 cm⁻¹
147 after BN growth, which is not seen in the Raman spectra of bare epigraphene shown in
148 Figure 1a, this also indicates the presence of h-BN and is probably due to point defects in
149 the h-BN layers.^{26,27} For h-BN/EG, an estimated FWHM value of the h-BN Raman E_{2g} peak
150 is 37 cm⁻¹. The peak is narrower than previously reported for h-BN grown on epigraphene¹⁵
151 and h-BN grown on sapphire²² under similar growth conditions. The E_{2g} peak of BN/SiC is
152 masked by a strong fluorescence, as shown in Figure 2c. Consequently, the E_{2g} peak cannot
153 be isolated, and the FWHM cannot be estimated for BN/SiC. Better FWHM of 12 cm⁻¹ have
154 been reported for BN on sapphire under PLD growth conditions²⁸. The reported FWHM 37
155 cm⁻¹ from BN on EG cannot be compared as this FWHM has significant contribution from
156 SiC peaks, a residual graphene D-peak (see Figure S1) and a broad fluorescence.

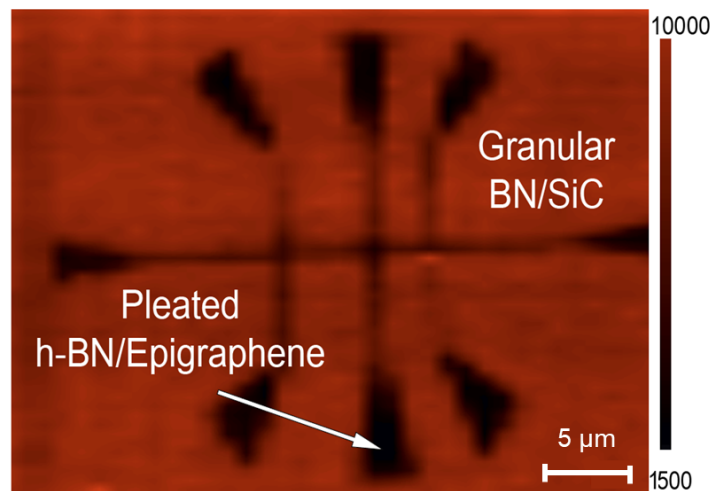
157 The high-magnification SEM and AFM images of Figure 2d, e show pleats on the h-BN on
158 the epigraphene surface. These pleats are characteristic of a thin 2D film grown at high
159 temperature on a substrate that contracts differently upon cooling, as expected for 2D h-
160 BN layers grown at 1270°C on epigraphene/SiC. Note that monolayer epigraphene on the

161 Si-face doesn't show pleats (strained graphene as indicated by the Raman 2D peak blue-
 162 shift) and graphene doesn't grow on SiC under the MOVPE h-BN deposition conditions.¹⁵
 163 An average surface roughness of approximately 0.7 nm was determined from 400 nm X 400
 164 nm AFM images in between the pleats on h-BN on patterned epigraphene, while the pleat
 165 height is approximately 5 ± 2 nm (as shown in Figure S2).
 166 In contrast, the granular BN on SiC has an AFM roughness of about 2.3 nm (for 400 nm X
 167 400 nm area). The granular morphology and the higher AFM roughness could be due to a
 168 higher nucleation density of BN because of the lower adatom mobility, which is consistent
 169 with the expected effects of the rough surface morphology of (oxidized) SiC.²⁹ The dip in
 170 the AFM height profile across the h-BN/epigraphene pattern (Figure 2f) is expected from
 171 the crumpled BN layers on the SiC taking up more space than flat layers on the
 172 epigraphene. Also bare SiC outside of the epigraphene swells upon oxidation during the O₂
 173 plasma process used to remove graphene and define the Hall bar. We cannot exclude a
 174 difference in growth rate of BN on epigraphene and SiC under these growth conditions
 175 that can be related to the change in surface free energy of the substrates/templates.^{30,31}



176
 177 **Figure 3.** Cross-sectional Bright Field-STEM images of (a) the 20 nm BN deposit covered by the
 178 Pt protective layer for FIB preparation, (b) h-BN/epigraphene/SiC heterostructure showing the
 179 BN layer on 2-layer graphene (buffer + graphene) and inset is the Fast Fourier transform (FFT) of
 180 the region enclosed in the red box, and (c) BN/SiC depicting the randomly oriented BN layers
 181 grown on SiC substrate (inset: FFT pattern of the region enclosed in the red box indicating the
 182 random arrangement of layers).

183 HR-STEM images on cross-sections of 20 nm thick h-BN grown on patterned epigraphene
184 prepared by Focused Ion Beam (FIB) and recorded in Bright-Field (BF) mode are shown in
185 Figure 3. The studies were conducted on both BN/epigraphene patterns on SiC and BN/SiC,
186 as depicted in Figure 3b, c, respectively. Figure 3a shows the cross-sectional TEM image of
187 the h-BN/EG/SiC heterostructure showing the thickness of BN approximately 20 nm, as
188 targeted. The BN grown on the epigraphene patterns exhibits a layered structure consisting
189 of a stacking of almost flat layers with interatomic spacing of $d=0.34$ nm, which is consistent
190 with interatomic distances reported in the literature.²² The FFT pattern clearly shows that
191 the layers have a long-range order. Although BN layers exhibit an orderly stacking
192 arrangement, determining the stacking sequence from the FFT pattern (shown in the inset
193 of Figure 3b) was difficult. In contrast, the BN layers grown outside of graphene (i.e. SiC)
194 showed turbostratic stacking as clearly observed in the HR-STEM image (Figure 3c), and
195 from the arcs of diffuse scattering in the FFT pattern (inset of Figure 3c). Bright field (BF),
196 annular bright-field (ABF) and dark field (DF) images of BN/EG and BN/SiC shown in
197 Figure S3 show the influence of the interface signal on the contrast. Indeed, in the first
198 layers above the SiC appears darker or brighter depending on the detector.



199

200 **Figure 4.** Fluorescence emission mapping performed on the heterostructure showing the different
201 intensity from h-BN/epigraphene and BN/SiC.

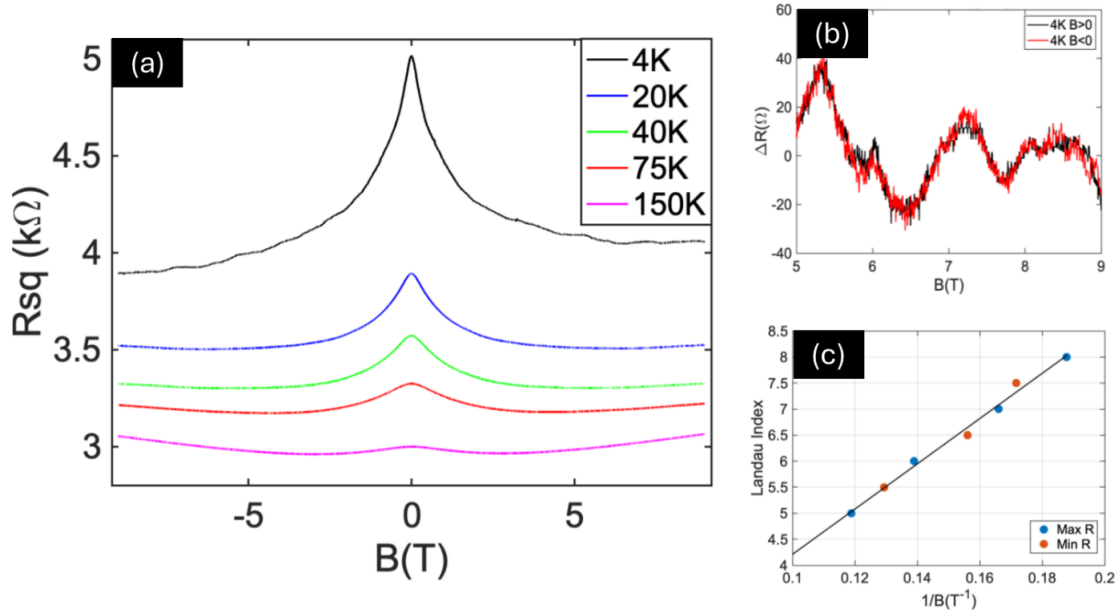
202 Fluorescence emission mapping was used to study the difference in quality between BN
203 grown on epigraphene and on SiC. The fluorescence emission intensity was measured range
204 (570–630 nm). Following Refs. 21,32,33 we attribute the fluorescence emission in this
205 range to defects (mostly due to the carbon incorporation³³) in the BN layer. Figure 4 shows
206 fluorescence emission map of a nominal 6 nm thick BN on patterned epigraphene on SiC
207 sample. A very low fluorescence intensity (almost 7 times) was observed on the h-
208 BN/epigraphene structure compared to the BN/SiC.

209 To further investigate, we have conducted fluorescence spectroscopy on thickness-
210 calibrated 20 nm BN samples grown on both epigraphene and SiC, with measurements
211 performed under identical conditions. The results shown in Figure S4 indicate that the
212 fluorescence intensity of BN/SiC is approximately twice that of h-BN/EG. It is known that
213 carbon impurities can be a source of photoluminescence³³, and in CVD processes, a larger
214 carbon impurities level is observed in grown turbostratic BN compared to grown h-BN³⁴.
215 This is in agreement with our observation of a lower fluorescence for BN/EG (h-BN type
216 ordered layers) compared to BN/SiC (more turbostratic). Therefore, we attribute the lower
217 fluorescence intensity observed in Figure 4 for h-BN/EG to the combined effect of a higher
218 quality (as also see in TEM images) and a thinner film.

219 The epitaxial growth of h-BN on EG does not involve direct polar bonding with the
220 substrate. As discussed previously, a growth model, supported by ab-initio calculations, was
221 proposed in Gigliotti et al. with a lateral epitaxial deposition mechanism involving a one-
222 dimensional nucleation-free-energy-barrierless growth that relies on the large mobilities
223 of the B and N species on the graphene surface¹⁵. The atomic arrangements and surface
224 properties of graphene and oxidized SiC differ significantly, influencing the adsorption,
225 diffusion, and nucleation of boron and nitrogen atoms during h-BN growth. Clearly the
226 one-dimensional nucleation-free-energy-barrierless growth mechanism doesn't apply to
227 SiO₂/SiC since, the underlying substrate provides orientational guidance for the growth of
228 h-BN.

229 For instance, related studies have reported differences in h-BN thickness and quality
230 depending on the orientation or substrate used.^{30,31,35–37} Moreover, Kobayashi et al. reported

231 the growth of h-BN on SiC substrates, which also resulted in a turbostratic BN structure²⁹.
 232 The premise of the epigraphene patterning is therefore to seed the BN growth on the edges
 233 of a graphene template, taking advantage of B and N atoms mobility on the graphene (and
 234 subsequent BN layers).



235
 236 **Figure 5.** Sample 1: 30 nm BN deposited on a graphene patterned Hall bar 6 x15 μ m. (a) square
 237 magnetoresistance at various temperatures showing a large zero field peak that decreases with
 238 temperature. (b) Shubnikov de Haas oscillations outlined by subtracting a smooth background
 239 from the data in (a). The traces for positive and negative field exactly superimpose at high field.
 240 (c) Fan plot of the field of the maxima and minima in (b). The index values are shifted by $1/2$ for
 241 the minima.

242 Transport measurements were performed on several samples patterned with Hall bar
 243 devices similar to that of Figure 2 and on a non-patterned sample. For sample 1, a 6 μ m x
 244 15 μ m Hall bar, we find a large resistivity $R_{sq} = 4k\Omega$, a positive charge density
 245 $n_s = 6 \times 10^{12} \text{cm}^{-2}$, determined from the linear in field Hall effect (Figure S5) and a
 246 relatively low mobility value $\mu \sim 250 \text{cm}^2/\text{Vs}$. The magnetoresistance (Figure 5a) presents a
 247 broad peak at zero field that decreases with temperature, suggestive of weak localization

248 (WL). According to WL theory, the peak width of about 3 T indicates a phase coherence l_ϕ
 249 of about 30 nm^{38,39}, larger, as required, than the scattering length calculated from the
 250 resistivity ($l_e \sim 5$ nm). Similar resistances and charge densities are measured by the Van der
 251 Pauw method⁴⁰ on a non-patterned macroscopic sample (Sample 2: 3 x 4 mm², see Figure
 252 S6), indicating that the low mobilities are not related to the graphene patterning process.
 253 At low temperature and for B larger than 4 T, small oscillations are superimposed to the
 254 broad peak, with maxima (minima) at the same magnetic field value for both field
 255 directions. Small deviation from linearity in field is also observed in the Hall effect at 4 K
 256 (note that, as expected at such high charge density, no quantum Hall effect is observed,
 257 Figure S5). Figure 5c is a plot of the Landau level index N as a function of the values of $1/B_N$
 258 corresponding to the resistance maxima after subtraction of a smooth background (Figure
 259 5b): $N + \gamma = \frac{B_0}{B_N}$. The B_N values for the resistance minima were also included on the figure,
 260 by shifting N by $\frac{1}{2}$. The linearity of the plot is a strong indication that these are Shubnikov
 261 de Haas oscillations. The charge density can be calculated from the slope $B_0 = n_s \frac{h}{4e}$. We
 262 find $n_s = 4.2 \times 10^{12} \text{ cm}^{-2}$, consistent with the charge density determined from the Hall
 263 effect (Figure S5). The lowest index level (N=5 at 8.5 Tesla) is also consistent with a
 264 projected $R_{xy} = (h/4e^2)(N + 1/2)^{-1} \approx 1 \text{ k}\Omega$, close to the measured value at that field. The
 265 $\gamma = 0.1$ value, found by extrapolation to $1/B_N=0$, is compatible with single layer
 266 graphene^{4,41,42} but this estimate is not very reliable, given the small number of points and
 267 the relatively broad maxima. The important point here is that Shubnikov de Haas
 268 oscillations can only be observed for $\mu B \gtrsim 1$ ⁴³. This indicates a mobility $\mu > 2,500 \text{ cm}^2/\text{Vs}$,
 269 inconsistent with the low mobility values found from the resistance. We therefore
 270 conclude that the samples present inhomogeneities, with regions of high and low mobility.
 271 Similar conclusion was reached for free standing bilayer epigraphene, where the SiC
 272 substrate was etched away under the graphene.⁴⁴
 273 Positive charge carrier could indicate hydrogen intercalated epigraphene (a.k.a. quasi-free-
 274 standing graphene).^{45,46} This is expected here from the BN deposition process, since by
 275 annealing above 900°C in a hydrogen containing environment, hydrogen atoms passivate

276 the SiC surface, decoupling the first graphene layer (buffer layer) at the SiC interface. This
277 results in a larger SiC-first graphene layer distance, as was indicated in previously measured
278 HR-STEM cross sectional image of similarly prepared BN/EG/SiC heterostructures.¹⁵
279 Further work will be necessary to understand the origin of electronic scattering. Cross-
280 sectional TEM indicates that the BN/epigraphene interface is epitaxial and clean. The high
281 temperature deposition process in a hydrogen carrier gas is beneficial to clean the graphene
282 surface from impurities deposited on the graphene during transfer from the growth furnace
283 to the deposition chamber. On the other, we cannot exclude damage to the epigraphene by
284 the hydrogen carrier gas, despite the absence of a noticeable Raman D-peak for the
285 graphene under BN.¹⁵ Inhomogeneous hydrogen intercalation is possible. Another
286 possibility would be scattering induced by defects in the as-deposited BN. The next step
287 will be measuring a high temperature annealed BN/patterned epigraphene/SiC
288 heterostructure as we know this results in higher quality BN layers (sharper BN X-ray peak
289 and no fluorescence in Raman spectroscopy).²¹

290

291 **CONCLUSION**

292 In summary, we have demonstrated the selective growth of smooth and continuous high-
293 quality h-BN on micrometer-sized monolayer epigraphene patterns by MOVPE method
294 down to a thickness of 6 nm. In between the h-BN/epigraphene heterostructures, the BN
295 layers are crumpled with granular morphology on the SiC substrate, denoting a high
296 nucleation rate. In particular, fluorescence mapping shows the higher quality and possibly
297 smaller thickness of h-BN layers grown on epigraphene than on SiC. Transport results
298 indicate inhomogeneities with low and high mobility regions and a high positive charge
299 density. The presence of high mobility areas in particular is extremely promising and
300 further improvement can be expected by high temperature annealing, which further
301 improves BN quality, and by depositing BN on step free graphene on atomically flat terraces
302 that can now be produced on mm scale.¹¹ These results show that MOVPE is a promising
303 technique for growing structurally uniform h-BN for graphene-based devices.

304

305 **ASSOCIATED CONTENT**

306 Supporting Information

307 Raman spectra of the epigraphene (Figure S1); Atomic force microscopy scans of the sample
308 (Figure S2); Cross-sectional transmission electron microscopy images of the heterostructure
309 (Figure S3); Emission spectra of the samples (Figure S4); Electrical measurements on the
310 samples (Figures S5 and S6).

311

312 **NOTE**

313 The authors have no conflicts to disclose.

314

315 **ACKNOWLEDGMENT**

316 This work is supported by a grant from the Agence Nationale de la Recherche, BONNEG
317 project, (No ANR-19-CE24-0025). CB, AJ and AL acknowledge funding from the European
318 Union Graphene Flagship grant agreements No. 696656 and No 785219. This work was also
319 made possible by the French American Cultural Exchange council through a Thomas
320 Jefferson grant.

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323

324 **REFERENCES**

- 325 1. Backes, C. *et al.* Production and processing of graphene and related materials. *2d Mater* **7**,
326 022001 (2020).
- 327 2. Bonaccorso, F. *et al.* Graphene photonics and optoelectronics. *Nature Photonics* **4**, 611–622
328 (2010).
- 329 3. Berger, C. *et al.* Ultrathin epitaxial graphite: 2D electron gas properties and a route toward
330 graphene-based nanoelectronics. *Journal of Physical Chemistry B* **108**, 19912–19916 (2004).
- 331 4. Berger, C. *et al.* Electronic Confinement and Coherence in Patterned Epitaxial Graphene.
332 *Science (1979)* **312**, 1191–1196 (2006).
- 333 5. Emtsev, K. V. *et al.* Towards wafer-size graphene layers by atmospheric pressure graphitization
334 of silicon carbide. *Nat Mater* **8**, 203–207 (2009).
- 335 6. Forti, S. *et al.* Epitaxial graphene on SiC: From carrier density engineering to quasi-free standing
336 graphene by atomic intercalation. *J Phys D Appl Phys* **47**, 094013 (2014).
- 337 7. Baringhaus, J. *et al.* Exceptional ballistic transport in epitaxial graphene nanoribbons. *Nature*
338 **506**, 349–254 (2014).
- 339 8. Dlubak, B. *et al.* Highly efficient spin transport in epitaxial graphene on SiC. *Nat Phys* **8**, 557–
340 561 (2012).
- 341 9. Lin, Y. M. *et al.* Wafer-scale graphene integrated circuit. *Science (1979)* **332**, 1294–1297 (2011).
- 342 10. Tzalenchuk, A. *et al.* Towards a quantum resistance standard based on epitaxial graphene. *Nat*
343 *Nanotechnol* **5**, 186–189 (2010).
- 344 11. Zhao, J. *et al.* Ultrahigh-mobility semiconducting epitaxial graphene on silicon carbide. *Nature*
345 **625**, 60–65 (2024).
- 346 12. Bresnehan, M. S. *et al.* Integration of hexagonal boron nitride with quasi-freestanding epitaxial
347 graphene: Toward wafer-scale, high-performance devices. *ACS Nano* **6**, 5234–5241 (2012).

- 348 13. Dean, C. R. *et al.* Boron nitride substrates for high-quality graphene electronics. *Nat*
349 *Nanotechnol* **5**, 722–726 (2010).
- 350 14. Fukamachi, S. *et al.* Large-area synthesis and transfer of multilayer hexagonal boron nitride for
351 enhanced graphene device arrays. *Nature Electronics* **2023** *6*:26, 126–136 (2023).
- 352 15. Gigliotti, J. *et al.* Highly ordered boron nitride/epigraphene epitaxial films on silicon carbide by
353 lateral epitaxial deposition. *ACS Nano* **14**, 12962–12971 (2020).
- 354 16. Lipp, A. *et al.* Hexagonal boron nitride: Fabrication, properties and applications. *J Eur Ceram*
355 *Soc* **5**, 3–9 (1989).
- 356 17. Kim, K. S. *et al.* Non-epitaxial single-crystal 2D material growth by geometric confinement.
357 *Nature* **614**, 88–94 (2023).
- 358 18. Kruskopf, M. *et al.* Comeback of epitaxial graphene for electronics: Large-area growth of
359 bilayer-free graphene on SiC. *2d Mater* **3**, 041002 (2016).
- 360 19. De Heer, W. A. *et al.* Large area and structured epitaxial graphene produced by confinement
361 controlled sublimation of silicon carbide. *Proc Natl Acad Sci U S A* **108**, 16900–16905 (2011).
- 362 20. Berger, C. *et al.* Epitaxial Graphene on SiC: 2D Sheets, Selective Growth, and Nanoribbons. in
363 *Growing Graphene on Semiconductors* 181–204 (Jenny Stanford Publishing, 2017).
- 364 21. Ottapilakkal, V. *et al.* Thermal stability of thin hexagonal boron nitride grown by MOVPE on
365 epigraphene. *J Cryst Growth* **603**, 127030 (2023).
- 366 22. Li, X. *et al.* Large-area two-dimensional layered hexagonal boron nitride grown on sapphire by
367 metalorganic vapor phase epitaxy. *Cryst Growth Des* **16**, 3409–3415 (2016).
- 368 23. Ferrari, A. C. *et al.* Raman spectrum of graphene and graphene layers. *Phys Rev Lett* **97**, 187401
369 (2006).
- 370 24. Hu, Y. *et al.* Structured epitaxial graphene: growth and properties. *J Phys D Appl Phys* **45**,
371 154010 (2012).
- 372 25. Röhrl, J. *et al.* Raman spectra of epitaxial graphene on SiC(0001). *Appl Phys Lett* **92**, 201918
373 (2008).

- 374 26. Dąbrowska, A. K. *et al.* Two stage epitaxial growth of wafer-size multilayer h-BN by metal-
375 organic vapor phase epitaxy - A homoepitaxial approach. *2d Mater***8**, 015017 (2020).
- 376 27. Pakuła, K. *et al.* Fundamental mechanisms of hBN growth by MOVPE. *arXiv preprint*
377 *arXiv:1906.05319* (2019).
- 378 28. Wang, G. *et al.* Wafer-Scale Single Crystal Hexagonal Boron Nitride Layers Grown by
379 Submicron-Spacing Vapor Deposition. *Small***19**, 2301086 (2023).
- 380 29. Kobayashi, Y. *et al.* Hexagonal boron nitride grown by MOVPE. *J Cryst Growth* **310**, 5048–
381 5052 (2008).
- 382 30. Chou, H. *et al.* Dependence of h-BN Film Thickness as Grown on Nickel Single-Crystal
383 Substrates of Different Orientations. *ACS Appl Mater Interfaces* **10**, 44862–44870 (2018).
- 384 31. Lee, Y. H. *et al.* Growth selectivity of hexagonal-boron nitride layers on Ni with various crystal
385 orientations. *RSC Adv***2**, 111–115 (2012).
- 386 32. Henry, A. *et al.* Early stages of growth and crystal structure evolution of boron nitride thin
387 films. *Jpn J Appl Phys***55**, 05FD06 (2016).
- 388 33. Mendelson, N. *et al.* Identifying carbon as the source of visible single-photon emission from
389 hexagonal boron nitride. *Nat Mater***20**, 321–328 (2021).
- 390 34. Sharma, S. *et al.* The Influence of Carbon on Polytype and Growth Stability of Epitaxial
391 Hexagonal Boron Nitride Films. *Adv Mater Interfaces* **11**, 2400091 (2024).
- 392 35. Ayari, T. *et al.* Novel Scalable Transfer Approach for Discrete III-Nitride Devices Using Wafer-
393 Scale Patterned h-BN/Sapphire Substrate for Pick-and-Place Applications. *Adv Mater Technol*
394 **4**, 1900164 (2019).
- 395 36. Sundaram, S. *et al.* MOVPE of GaN-based mixed dimensional heterostructures on wafer-scale
396 layered 2D hexagonal boron nitride - A key enabler of III-nitride flexible optoelectronics. *APL*
397 *Mater***9**, 061101 (2021).
- 398 37. Sundaram, S. *et al.* Wafer-scale MOVPE growth and characterization of highly ordered h-BN
399 on patterned sapphire substrates. *J Cryst Growth* **509**, (2019).

- 400 38. Wu, X. *et al.* Weak antilocalization in epitaxial graphene: Evidence for chiral electrons. *Phys*
401 *Rev Lett* **98**, 136801 (2007).
- 402 39. Beenakker, C. W. J. *et al.* Quantum Transport in Semiconductor Nanostructures. in *Solid State*
403 *Physics - Advances in Research and Applications* vol. **44** 1–228 (1991).
- 404 40. Van der Pauw, L. J. A method of measuring the resistivity and Hall effect of disks of arbitrary
405 shape. *Philips Technical Review* vol. 20 Preprint at (1958).
- 406 41. Novoselov, K. S. *et al.* Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**,
407 197–200 (2005).
- 408 42. Zhang, Y. *et al.* Experimental observation of the quantum Hall effect and Berry's phase in
409 graphene. *Nature* **438**, 201–204 (2005).
- 410 43. Datta, S. *et al.* *Electronic Transport in Mesoscopic Systems. Cambridge Studies in*
411 *Semiconductor Physics and Microelectronic Engineering* (Cambridge University Press, 1995).
- 412 44. Shivaraman, S. *et al.* Raman spectroscopy and electrical transport studies of free-standing
413 epitaxial graphene: Evidence of an AB-stacked bilayer. *Phys Rev B Condens Matter Mater Phys*
414 **87**, 195425 (2013).
- 415 45. Riedl, C. *et al.* Quasi-free-standing epitaxial graphene on SiC obtained by hydrogen
416 intercalation. *Phys Rev Lett* **103**, 246804 (2009).
- 417 46. Ristein, J. *et al.* Origin of doping in quasi-free-standing graphene on silicon carbide. *Phys Rev*
418 *Lett* **108**, 246104 (2012).
- 419

Supporting information

HIGH-QUALITY HEXAGONAL BORON NITRIDE SELECTIVELY GROWN ON PATTERNED EPIGRAPHENE BY MOVPE

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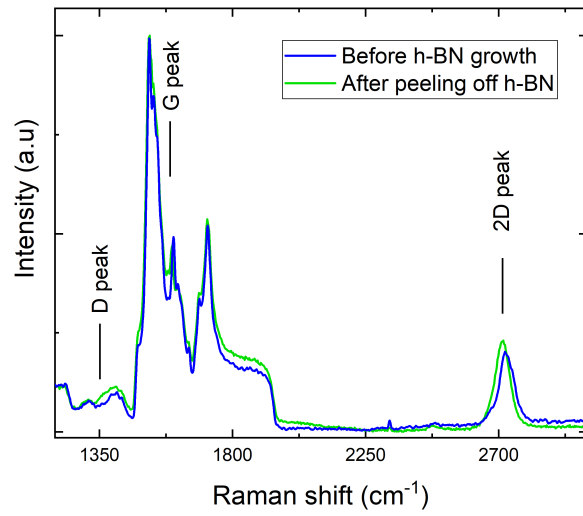


Figure S1. Raman spectra of epigraphene before the growth of h-BN (blue trace) and after the removal of the h-BN layers (green trace), showing no significant D peak intensity, indicating no detectable damage to the epigraphene.

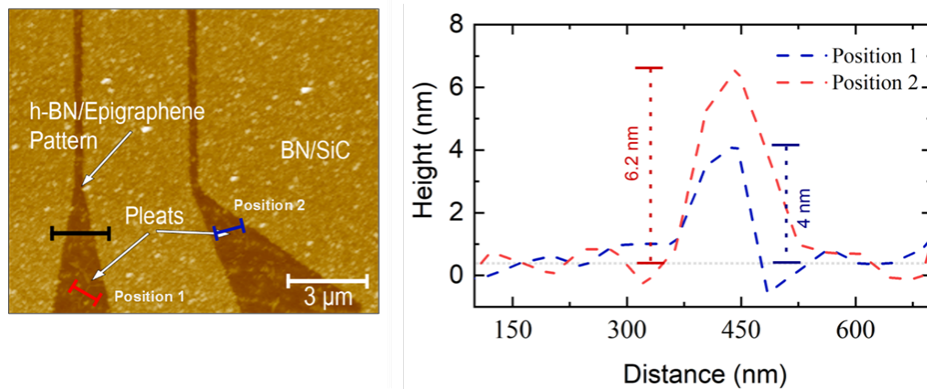


Figure S2. AFM height profiles across the pleats at two different positions.

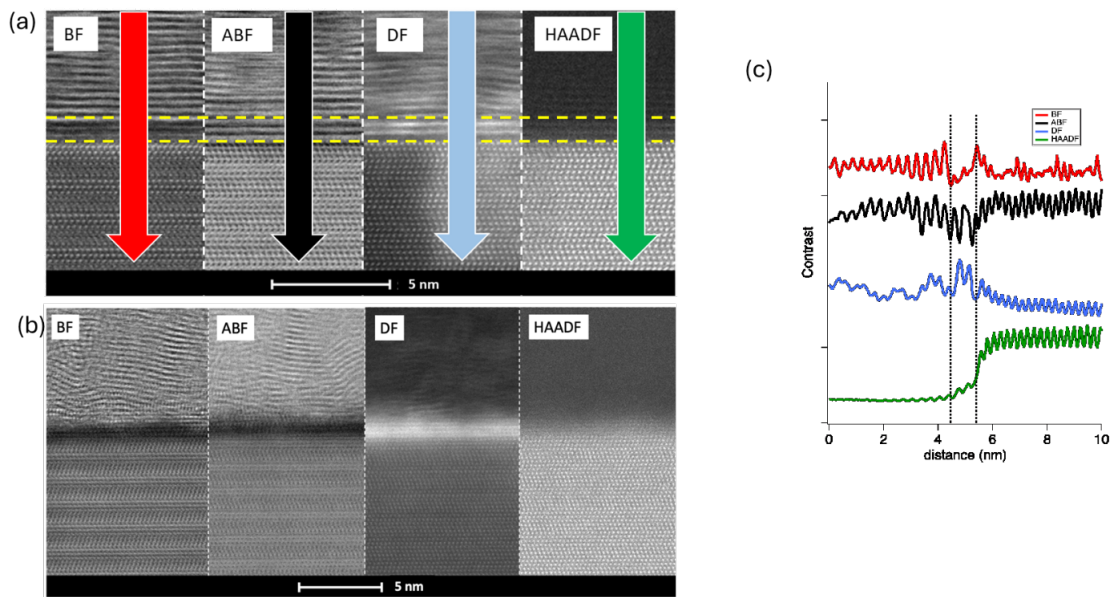


Figure S3: Montage of HRSTEM images of the (a) h-BN/EG and (b) turbostratic BN/SiC with the different contrasts acquired at the same time in the Titan G2. BF, ABF and DF images show the influence of the interface signal on the contrast. Indeed, in (b) the first layers above the SiC appears darker or brighter depending on the detector. (c) Intensity profile along the interface of h-BN/EG/SiC revealing the contrast variation with respect to the detector.

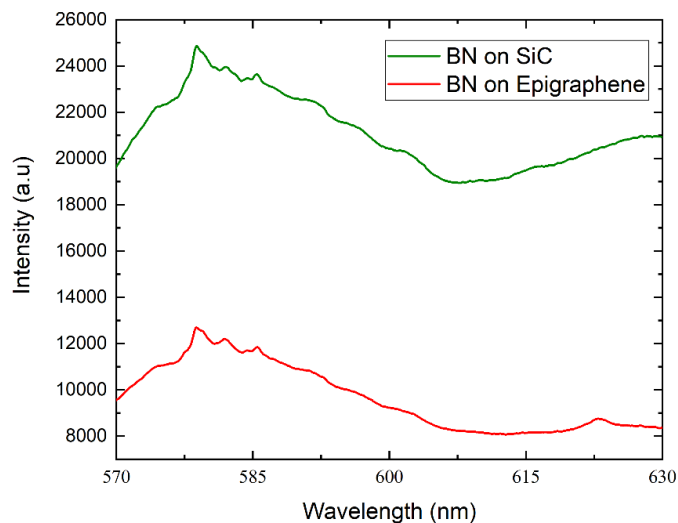


Figure S4. Emission spectra recorded for a 20 nm h-BN/epigraphene pattern and 20 nm BN/SiC under identical conditions, showing a difference in fluorescence intensity (approximately twofold).

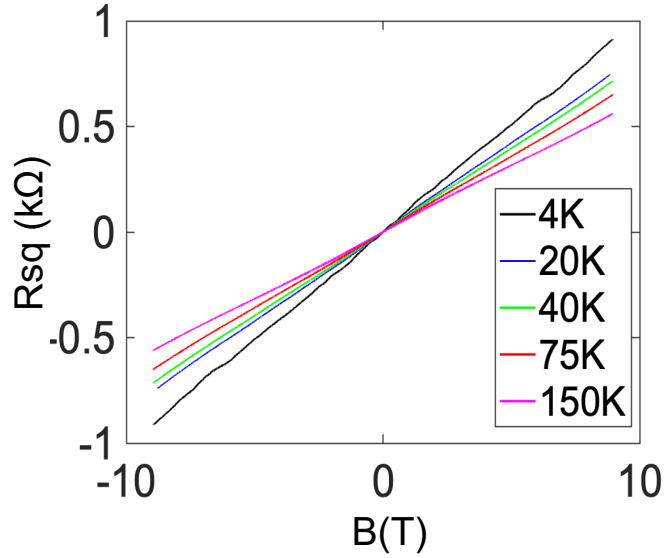


Figure S5. Symmetrized Hall effect for sample 1 ($6\ \mu\text{m} \times 15\ \mu\text{m}$ Hall bar). The Hall resistance is linear in field as expected for large charge densities. Small deviations from linearity (Shubnikov-de-Haas) are observed at low temperature and high field.

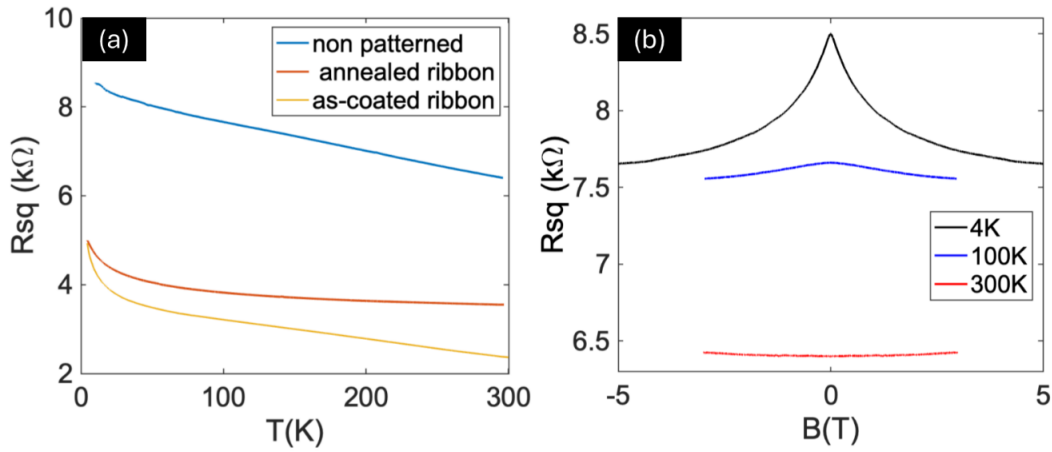


Figure S6. Sample 2: non-patterned graphene coated with 30 nm BN on a $3.5 \times 4.5\ \text{mm}^2$ SiC chip. Eight contacts are silver paste-bonded at the periphery of the chip. The resistance and Hall effect are measured by the Van der Pauw method¹ by changing the current injection leads and voltage probes. (a) Temperature dependence of the square resistance for the plain chip compared with the two patterned Hall bars (sample 1 non annealed, and sample 2 annealed) and (b) magnetoresistance.

REFERENCES

- (1) van der Pauw, L. J. A Method of Measuring the Resistivity and Hall Effect of Disks of Arbitrary Shape. *Philips Technical Review*. 1958.