

Identifying Carbon as the Source of Visible Single Photon Emission from Hexagonal Boron Nitride

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Abstract:

Single photon emitters (SPEs) in hexagonal boron nitride (hBN) have garnered significant attention over the last few years due to their superior optical properties. However, despite the vast range of experimental results and theoretical calculations, the defect structure responsible for the observed emission has remained elusive. Here, by controlling the incorporation of impurities into hBN via various bottom-up synthesis methods and directly through ion implantation we provide direct evidence that the visible SPEs are carbon related. Room temperature optically detected magnetic resonance (ODMR) is demonstrated on ensembles of these defects. We perform ion implantation experiments and confirm that only carbon implantation creates SPEs in the visible spectral range. Computational analysis of the simplest 12 carbon-containing defect species suggest the negatively charged $V_B C_N^-$ defect as a viable candidate and predict that out-of-plane deformations make the defect environmentally sensitive. Our results resolve a long-standing debate about the origin of single emitters at the visible range

56 in hBN and will be key to the deterministic engineering of these defects for quantum photonic
57 devices.

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60 Single defects in solids have become some of the most promising frontrunner hardware
61 constituents of applications in quantum information technologies and integrated quantum
62 photonics.¹ Significant effort has been devoted to isolate and deterministically engineer such
63 defects in wide bandgap materials such as diamond and silicon carbide.^{2, 3} This collective effort
64 resulted in spectacular proof of principle demonstrations ranging from quantum networks to
65 spin-photon interfaces,³ while simultaneously and steadily leading to understanding the
66 fundamental level structures of these defects.

67 Recently, hexagonal boron nitride (hBN) has emerged as a promising host material for
68 defects which display ultra-bright single photon emission (SPE)^{4, 5, 6, 7, 8}. They exhibit remarkable
69 properties: a strong response to applied strain and electric fields (Stark shifts),^{9, 10, 11} stability
70 under high pressure and elevated temperatures,^{12, 13} potential for resonant excitation above
71 cryogenic temperatures,^{14, 15, 16} and addressability via spin-selective optical transitions.^{17, 18} Yet,
72 despite the numerous experimental characterizations and in-depth theoretical attempts to model
73 their possible crystalline structure,^{6, 19, 20, 21, 22, 23, 24, 25} the nature of these defects remains
74 unknown.

75 Part of the challenge stems from standard hBN bulk crystal synthesis *via* high pressure
76 high temperature not being amenable to the deterministic control of impurity incorporation. This
77 is aggravated by the induced impurities often segregating and forming regions of inhomogeneous
78 defect concentration.²⁶ In addition, the two-dimensional, layered nature of hBN makes ion
79 implantation difficult to control. These limitations have precluded identifying the exact origin of
80 the single photon emission in the material.

81 Here, we address this problem by carrying out a detailed study surveying various hBN
82 samples grown in different laboratories by metal-organic vapor phase epitaxy (MOVPE) and
83 molecular beam epitaxy (MBE). We find compelling evidence that to observe
84 photoluminescence from SPEs the inclusion of carbon atoms in hBN is required. By
85 systematically growing samples with different carbon concentrations, we show that the carbon
86 content determines whether the photoluminescence signal originates from an ensemble of
87 emitters (high carbon concentration) or isolated defects (low carbon concentration). Defect
88 ensembles are demonstrated to display room temperature optically detected magnetic resonance
89 (ODMR). We carry out multi-species ion-implantation experiments on both MOVPE films and
90 exfoliated hBN, showing that only carbon implantation creates SPEs and that the density of
91 emitters scales directly with the implantation dose of carbon. Our results are supported by
92 rigorous modelling analysis of carbon related defects.

93 94 **Optical Properties of Carbon Doped hBN**

95 Table 1 summarizes the materials analyzed. They are epitaxial hBN samples grown by
96 different methods and under various conditions. The rationale was to understand whether the
97 single defects are intrinsic to hBN (e.g. substitutional or interstitial nitrogen or boron complexes)
98 or they involve foreign atoms (e.g. carbon). We investigated hBN samples grown by four
99 methods. 1) Metal organic vapor phase epitaxy (MOVPE) with varying flow rates of the
100 precursor triethyl boron (TEB)—a parameter known to systematically alter the levels of
101 incorporated carbon. 2) High temperature molecular beam epitaxy (MBE) on sapphire with and

102 without a source of carbon. 3) High-temperature MBE on SiC with a varying orientation of the
 103 Si face to explore the possibility of carbon incorporation occurring from the substrate. 4) Growth
 104 by the conversion of highly oriented pyrolytic graphite (HOPG) into hBN. Note, that in the
 105 current work we focus on bottom up growth of hBN as it offers an opportunity for large
 106 (centimeter) scale films of desired thickness (down to ~1 nm), as well as better control over the
 107 inclusions of impurities.
 108

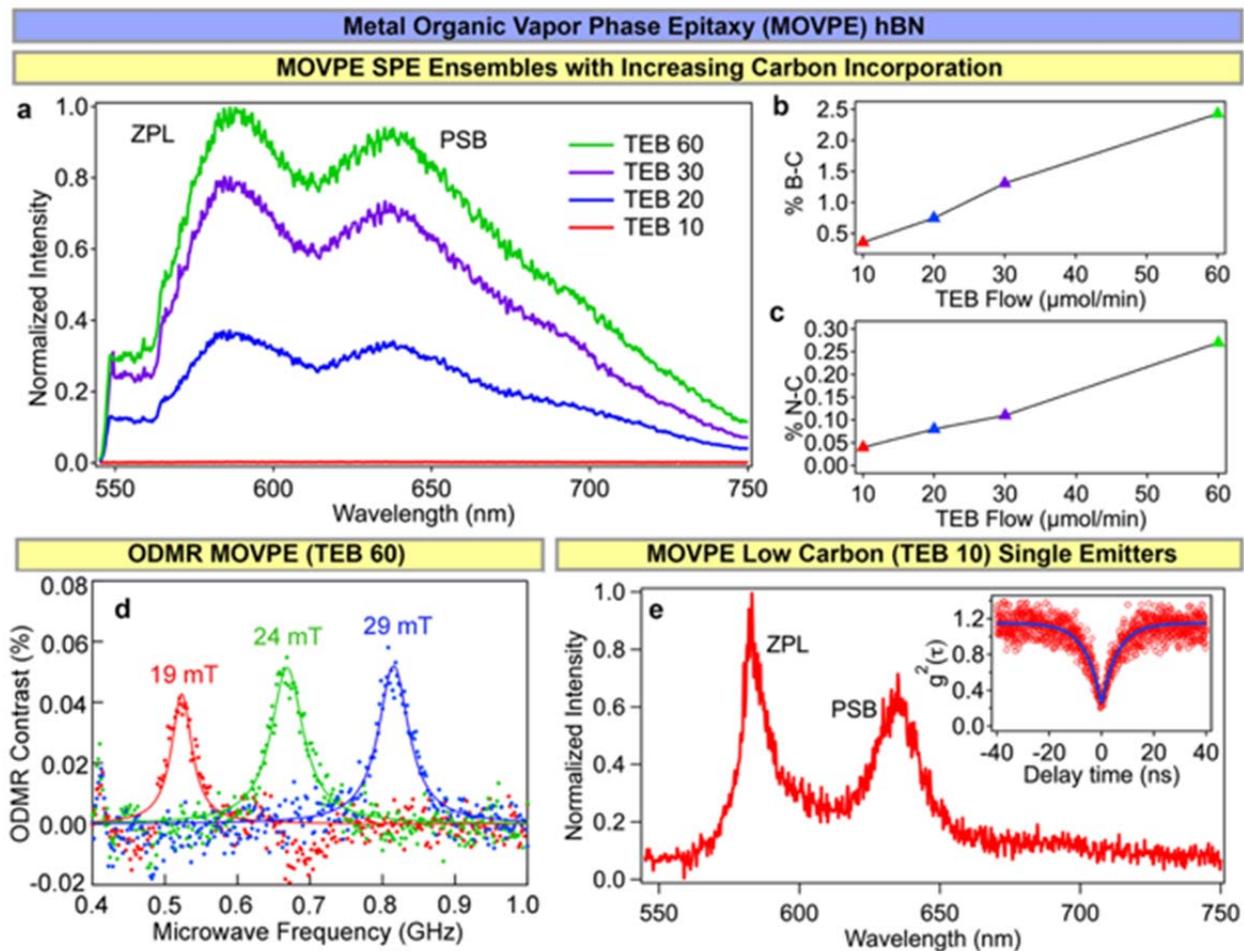
Sample	Abbreviation	Growth Method & Details	SPE Photoluminescence	Additional Info
MOVPE hBN (TEB flux 10)	MOVPE hBN (TEB 10)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 10 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Isolated SPEs, ZPLs Predominantly ~585 \pm 10 nm	~40 nm thick
MOVPE hBN (TEB flux 20)	MOVPE hBN (TEB 20)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 20 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Dense and Uniform Ensemble of SPEs with ZPL ~585 nm, PSB ~630 nm.	~40 nm thick
MOVPE hBN (TEB flux 30)	MOVPE hBN (TEB 30)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 30 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Dense and Uniform Ensemble of SPEs with ZPL ~585 nm, PSB ~630 nm.	~40 nm thick
MOVPE hBN (TEB flux 60)	MOVPE hBN (TEB 60)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 60 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Dense and Uniform Ensemble of SPEs with ZPL ~585 nm, PSB ~630 nm.	~40 nm thick
MBE hBN on Sapphire	Undoped MBE hBN on sapphire	MBE on sapphire, Boron flux from e-beam source (300W). Boron in BN crucible. Nitrogen flow 2sccm. Growth temperature 1250°C.	No SPEs Present	~20 nm thick
MBE hBN on Sapphire with Carbon Crucible	Carbon doped MBE hBN on Sapphire	MBE on sapphire, Boron flux from e-beam source (210W). Boron in carbon crucible. Nitrogen flow 2sccm. Growth temperature 1250°C.	Semi-Isolated SPEs, ZPLs Range from 570-770 nm, Density ~5-8/ μm^2	~18 nm thick
MBE hBN on Silicon Carbide (0° Si Face)	Undoped MBE hBN on SiC (0°)	SiC (Si-face, orientation-on) MBE on SiC. Boron flux from HT Knudsen source at 1875°C. Nitrogen flow 2sccm. Growth temperature 1390°C.	Very Few SPEs Density ~1 SPE in 40 μm^2	~3 nm thick
MBE hBN on Silicon Carbide (8° Si Face)	Undoped MBE hBN on SiC (8°)	SiC (Si-face, orientation 8°-off) MBE on SiC. Boron flux from HT Knudsen source at 1875°C. Nitrogen flow 2sccm. Growth temperature 1390°C.	Isolated SPEs, ZPLs Range from 575-735 nm Density ~3-5/ μm^2	~7 nm thick
HOPG \rightarrow hBN Conversion	Converted hBN	HOPG is placed in a radio frequency induction furnace at 2000°C, N_2 gas is mixed with thermalized B_2O_3 powder facilitating conversion	Dense and Uniform Ensemble of SPEs with ZPL ~580 nm, PSB ~630 nm.	Bulk

109
 110 **Table 1—Epitaxial hBN Samples with Varying Carbon Concentrations.** The 9 different hBN sample
 111 types used in the study, their growth methods, SPE characteristics, and shorthand names used for each
 112 sample type are defined. Color coding correlates with the growth methods. See methods for additional
 113 synthetic details.
 114

115 We first explore the photoluminescence (PL) from a series of hBN samples grown by
 116 MOVPE²⁷ as the triethyl boron (TEB) flow rate is increased and the ammonia flow is kept
 117 constant shown in Figure 1a. The aim of this measurement is to engineer an ensemble of hBN
 118 emitters, and to compare their properties with isolated SPEs grown using the same growth
 119 technique. A region of the TEB 10 ($\mu\text{mol}/\text{min}$) sample with the lowest percentage of carbon
 120 shows negligible fluorescence. Increasing the flow rate to TEB 20 is accompanied by the
 121 appearance of a bright fluorescence signal with two clear peaks appearing at ~585 nm and ~635
 122 nm. Further increasing the flow rate to TEB 30 and 60 provides a similarly structured PL
 123 signature, with higher fluorescence intensity, confirming that higher PL intensity directly
 124 correlates with higher TEB flux. Moderate fluctuations in the peak positions, and intensity ratio
 125 of the 585 nm and 635 nm peaks at different sample locations are consistent with emission from
 126 dense ensembles of hBN emitters. This also confirms previous findings showing that hBN
 127 emitters possess zero-phonon line (ZPL) wavelengths clustered at ~585 nm when the sample is

128 grown epitaxially.^{28, 29} The energy detuning between the ZPL of the ensemble and phonon
 129 sideband (PSB) peak is ~ 176 meV on average (Extended Data Fig. 1).^{30, 31}

130 X-ray photoelectron spectroscopy (XPS) was used to quantify the incorporation of carbon
 131 (Extended Data Fig. 2). Figure 1b(c) demonstrate a near linear correlation between C-B (C-N)
 132 bonding and increasing TEB flux, with C-B bonding being roughly an order of magnitude more
 133 prevalent than C-N bonding. Preferential formation of C-B bonds follows logically from noting
 134 the B species are introduced with three pre-existing bonds to C. PL intensity of the resulting
 135 ensemble emission likewise displays a linear correlation with carbon concentration (Extended
 136 Data Fig. 3). Based on these results, we advance that the SPE emission at ~ 580 nm in hBN is
 137 likely to originate from a carbon-related defect complex.
 138



139 **Figure 1—Photoluminescence from MOVPE hBN Samples.** *a.* MOVPE hBN grown with increasing
 140 flow rates of triethyl borane (TEB). As TEB flow increases, the fluorescence of SPE ensembles increases.
 141 *b.* Percentage of B-C bonding with increasing TEB flow evaluated by XPS. *c.* Percentage of N-C bonding
 142 with increasing TEB flow evaluated by XPS. *d.* Room temperature ODMR displayed as relative contrast,
 143 spin-dependent variation in photoluminescence ($\Delta\text{PL}/\text{PL}$), observed from the ~ 585 nm ensemble
 144 emission of MOVPE hBN (TEB 60) at applied fields of 19, 24, and 29 mT respectively. *e.*
 145 Spectrum of a representative SPE found in MOVPE hBN TEB 10. Inset displays the corresponding
 146 autocorrelation measurements from the spectrum.
 147
 148

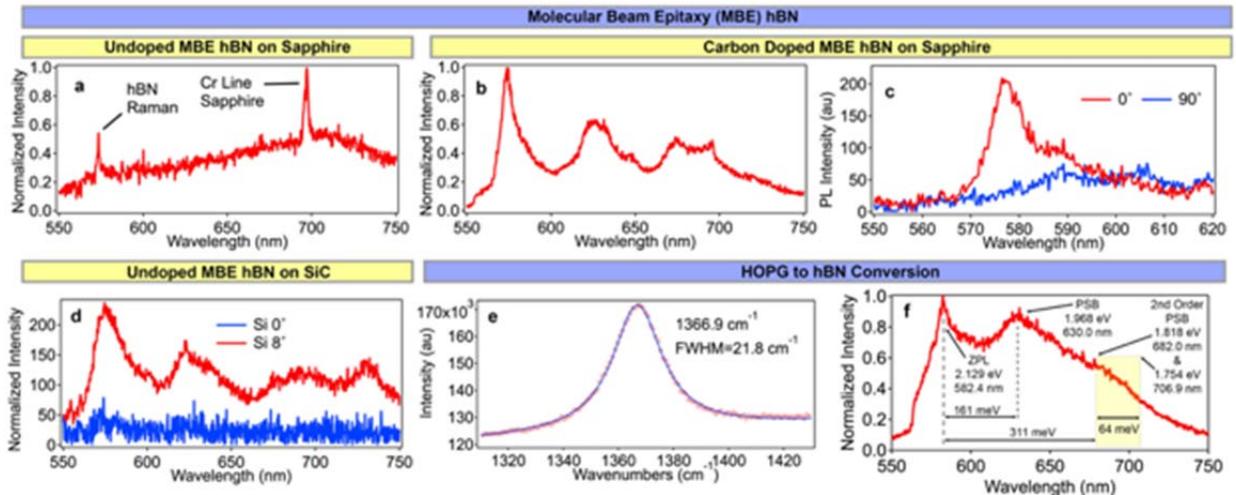
149 Figure 1d shows the ODMR spectra recorded from the TEB 60 ensemble. The highly
150 symmetric shape of the signal does not reveal a structure that would allow a clear assignment to
151 a specific intrinsic or extrinsic defect. However, it is clearly a spin-carrying defect, likely with a
152 spin state higher than $S=1/2$. By varying the static magnetic field B , we measure resonances at
153 ~ 523 , ~ 668.5 and ~ 815.4 MHz for $B = 19$, 24 and 29 mT, respectively. A value for g_e of ~ 2.09 is
154 extracted (Extended Data Fig. 4). However, we observe no splitting of the signal with the
155 magnetic field, which means that the zero-field splitting, D , should be small. In previous
156 experiments, a similar ODMR signal was observed at low temperature ($T \approx 8.5$ K),¹⁸ while our
157 measurements show that ODMR is also feasible at room temperature. We observe no narrowing
158 of the resonance upon cooling suggesting the linewidth is not governed by the coherence time
159 (Extended Data Fig. 5). The line-broadening may be due to dipole-dipole coupling, e.g. by
160 hyperfine interaction with nearby nuclei. This is consistent with the preliminary assignment that
161 the ODMR signal measured on the heavily carbon-doped sample and shown in Fig. 2d is
162 associated with a carbon-related defect.¹⁸

163 We next employ a lab-built confocal PL setup with a 532 nm excitation source, to study
164 in detail the TEB 10 sample. The level of carbon doping is such that we can isolate single
165 quantum emitters; a representative spectrum for one such emitter is shown in Figure 1d. The
166 quantum nature of the emission was confirmed by measuring the second order auto-correlation
167 function; the value of $g^{(2)}(\tau = 0) < 0.5$ (Fig. 1d inset) is conventionally attributed to a single
168 photon source with sub-Poissonian emission statistics. We measured the zero-phonon line (ZPL)
169 wavelength of 77 SPEs in the MOVPE hBN (TEB 10) sample, finding that $\sim 78\%$ of the emitters
170 are located at (585 ± 10) nm, and 95% at wavelengths < 600 nm (Extended Data Fig. 6),
171 consistent with previous studies on epitaxially grown hBN.^{28, 29} The typical line shape of these
172 emitters at room temperature is also consistent with previous studies, including the ZPL and a
173 PSB centered at ~ 177 meV from the ZPL energy. This suggests that when the carbon
174 concentration is sufficiently low, individual quantum emitters can be isolated. Their optical
175 properties and spectral distribution are consistent with those observed in samples with higher
176 carbon doping, with the difference merely being due to the density of emitters.

177 To further confirm that carbon-based defects are responsible for SPE emission from hBN
178 we analyze a series of hBN samples grown by a different method, high-temperature MBE.^{32, 33}
179 Figure 2a displays the PL spectrum observed from undoped MBE hBN grown on sapphire
180 substrate. The resulting PL signal was relatively low; no SPEs could be found despite the
181 material being of good quality as shown by a clear hBN E_{2g} Raman line. However, when the
182 elemental boron source was placed inside a carbon crucible—with otherwise identical growth
183 conditions—we observed the appearance of sharp spectral lines, shown in figure 2b. The carbon
184 crucible used for e-beam evaporation of the boron shows clear signs of sidewall etching, which
185 suggests that carbon was present in the gas phase during growth.

186 The carbon doped MBE growth resulted in a high density of emitters such that we could
187 not isolate at single sites. We instead probed the polarization dependence of particular emission
188 peaks by placing a polarizer in the collection path. Figure 2c shows one such collection, where
189 emission from a ZPL at ~ 577 nm is linearly polarized, with the PL intensity dropping to the
190 background level when the polarizer is perpendicular to the polarization direction of the probed
191 emitter.

192



193 **Figure 2—Photoluminescence from MBE and HOPG Conversion hBN Samples.** *a.* Undoped MBE
 194 hBN on sapphire displays no SPEs. *b.* Carbon doped MBE hBN on sapphire displaying a number of
 195 isolated peaks spanning the visible range. Typically, many SPEs are found within the laser excitation
 196 spot. *c.* Polarization resolved photoluminescence of a single peak in carbon doped MBE hBN on sapphire
 197 (*b*), demonstrating the polarized nature of the emission. *d.* Undoped MBE hBN on silicon carbide, with
 198 the Si face oriented at 0° (blue) and 8° off (red). While growth of the Si 0° face SiC shows no SPEs,
 199 growth on the Si 8°-off face effectively incorporates SPEs via diffusion of C from the SiC substrate. *e.*
 200 Raman spectra of the HOPG to hBN conversion sample. *f.* Converted hBN displays an SPE ensemble
 201 emission centered around ~585 nm.

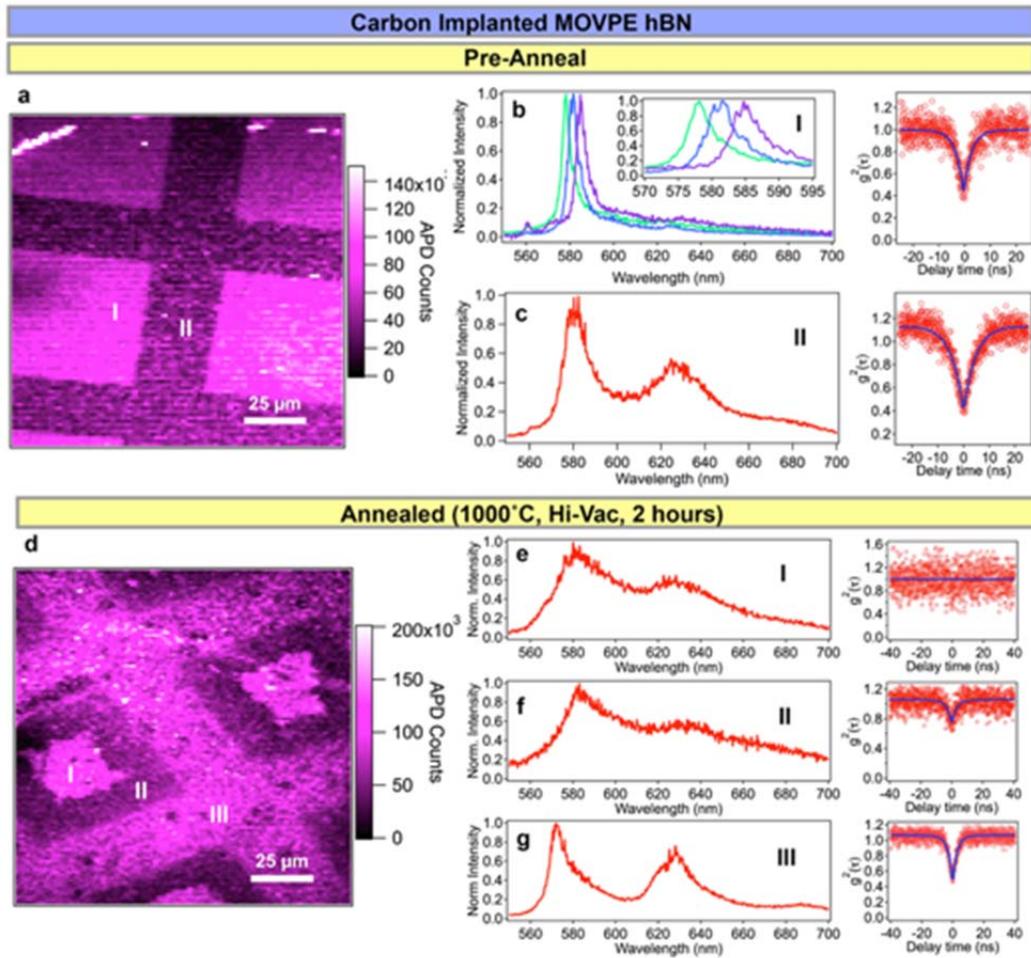
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203 We next explored MBE growth of hBN on silicon carbide (SiC), investigating different
 204 crystal orientations: specifically, with the top Si face-on (0°) and slightly off (8°). Representative
 205 spectra from both sample types (Si at 0° and at 8°) are displayed in Figure 2d. When growth was
 206 performed with the Si face at 0°, only a single SPE peak was located across a 40 μm² scan. In
 207 contrast, when the Si face is oriented at 8° we again find a high density of SPE incorporation.
 208 The incorporated SPEs display a similar ZPL distribution to the carbon doped MBE hBN on
 209 sapphire (Extended Data Fig. 6).

210

211 We attribute the incorporation of these SPEs during hBN growth on SiC to carbon
 212 diffusion from the substrate. At the growth temperature of 1390°C, some sublimation of Si from
 213 the surface of the SiC substrates is expected, with the subsequent formation of an extra carbon
 214 layer on the surface of SiC.^{32, 34} While these temperatures are sufficient to sublime Si, they are
 215 not sufficient to evaporate C from the SiC surface.³² Interestingly, C incorporation into hBN
 216 appears significantly enhanced when the Si face is oriented 8° out of plane. The observed
 217 dependence of SPE incorporation during MBE growth further supports the role of carbon in the
 origin of hBN SPEs in the visible spectral range.

218 Finally, we analyze a third technique for hBN growth, the conversion of HOPG to hBN,
 219 known to yield high quality porous hBN.³⁵ Conversion was confirmed by Raman spectroscopy
 220 (Figure 2e).³⁶ The conversion from graphite, proceeding via atomic substitutions, provides a high
 221 availability of carbon for incorporation as defects in the resulting hBN. Figure 2f displays a
 222 typical PL spectrum from the sample. We observe a bright SPE ensemble, displaying a structured
 223 emission profile with ZPL and PSB peaks displaying similar transition energies as observed for
 224 high carbon MOVPE ensembles.



225 **Figure 3—MOVPE hBN (TEB 10) Samples Implanted with Carbon.** Implantations were done at a dose
 226 of 10^{13} ions/cm² and an energy of 10 keV, using a TEM grid with $50 \mu\text{m}^2$ square apertures as a mask. **a.**
 227 Confocal scan of carbon implanted sample, where square areas marked (I) were implanted, and those
 228 marked (II) were masked. **b.** Spectra from implanted areas (I) display narrow ZPLs with almost no PSB
 229 and are attributed to emitters created via implantation. A representative $g^{(2)}(\tau)$ is shown to the right. **c.**
 230 Spectra and $g^{(2)}(\tau)$ from the masked area (II) display borderer ZPLs, and prominent PSBs. **d.** Confocal
 231 scan of the carbon implanted sample, post annealing, where areas marked (I) and (II) were implanted,
 232 while area (III) was masked. **e.** A representative spectra and $g^{(2)}(\tau)$ from area (I), showing an ensemble of
 233 hBN emitters, and a corresponding $g^{(2)}(\tau)$ measurement showing no dip as expected for ensemble
 234 emission. **f.** A representative spectra and $g^{(2)}(\tau)$ from area (II) showing evidence of quantum emission but
 235 with significant spectral contributions from nearby SPEs resulting in a $g^{(2)}(\tau)$ value of ~ 0.75 . **g.** A
 236 representative spectra and $g^{(2)}(\tau)$ from the masked area (III) post annealing showing a well-resolved SPE
 237 and PSB and a $g^{(2)}(\tau)$ confirming a single emission center.

238 ION IMPLANTATION

239 We now turn our attention to using ion implantation for defect creation, in an attempt to
240 confirm the role of carbon. We performed a series of implantation experiments (dose: 10^{13}
241 ions/cm², energy 10 keV) with carbon as well as silicon and oxygen used as controls to rule out
242 the possibility for the photoemission to be due to native vacancy defects. The implantation
243 experiments were performed on MOVPE hBN (TEB 10) films to compare the relevant results to
244 those for the samples synthesized while increasing carbon content during growth.

245 Figure 3a shows the confocal scan of the TEB 10 sample after carbon implantation, but
246 prior to annealing, where a TEM grid with $50\ \mu\text{m}^2$ square apertures was used as a mask. The
247 implanted region is labelled I, while the masked region is labelled II. Figure 3b displays spectra
248 collected from emitters within the implanted region (I), and a representative $g^{(2)}(\tau = 0) < 0.5$,
249 confirming the quantum nature of the emission from these centers. Figure 3c displays a
250 representative emitter from the masked region (II), showing the typical line shape of the ZPL and
251 the PSB peaks found in TEB 10 films, with the corresponding $g^{(2)}(\tau = 0)$ shown to the right.

252 Inside the C-implanted region, most emitters ($\sim 80\%$) display narrow ZPL peaks ($\sim 5\ \text{nm}$
253 FWHM) and extremely weak PSBs, compared to the typical ZPL/PSB found in these TEB 10
254 films (Extended Data Fig. 7). The remaining $\sim 20\%$ of SPEs within the implanted region display
255 similar line shapes and phonon coupling to those for the emitter in figure 3c and are attributed to
256 preexisting SPEs in the region. Our results indicate that the sharp emission lines belong to SPEs
257 created via implantation of C ions. The reasons for the observed narrow line shape and the
258 minimal phonon coupling are explored further *via* computational modelling below.

259 The samples were then annealed in high vacuum ($1000\ \text{°C}$, $<10^{-6}$ Torr, 2 hours), and the
260 same set of measurements was performed. As shown in figure 3d, the implanted regions are still
261 visible, they however show variations in PL intensity. This effect is likely due to ion scattering
262 around the mask edges and vacancy diffusion—which have been observed for implantation in
263 diamond.³⁷ The PL spectra from three different areas are shown in figure 3e–f, and correspond to
264 (I) the implanted region of high PL intensity, (II) the implanted region of lower PL intensity, and
265 (III) the masked region of the film.

266 Figure 3e displays a representative spectrum from inside region I, where we found broad
267 emission similar to those observed in the high TEB flux growths. This emission is confirmed to
268 be due to an ensemble of SPEs as the corresponding $g^{(2)}(\tau)$ measurements show no anti-bunching
269 despite the associated ZPL/PSB structure. A similar spectral signature is observed consistently
270 throughout region (I), again implying the creation of an ensemble of C-based SPEs. Figure 3f
271 displays a representative spectrum from the implanted region II, where we again observe
272 luminescence with a similar line shape. The overall ensemble signal remains homogeneous in
273 this region, although appears less dense and bright, and the $g^{(2)}(\tau)$ measurement shows a value of
274 ~ 0.75 , confirming the presence of fewer emitters within a confocal spot. Note that in both
275 implanted areas (I and II) we no longer find the narrow emission lines with low phonon coupling
276 found prior to annealing. Finally, Figure 3g displays a representative spectrum from region III
277 (masked area), showing a typical ZPL and PSB profile with a $g^{(2)}(0) < 0.5$. Control experiments
278 implanting silicon and oxygen with otherwise identical conditions were also performed, but the
279 emitters, either singles or ensembles were not observed (Extended Data Fig. 8).

280 To further study SPE formation via ion implantation we performed dose dependent
281 experiments with carbon fluences over the range 1×10^{11} – 10^{14} ions/cm², while oxygen and silicon
282 implantation at 1×10^{13} ions/cm² served as a control. Both MOVPE (TEB 10) hBN and exfoliated

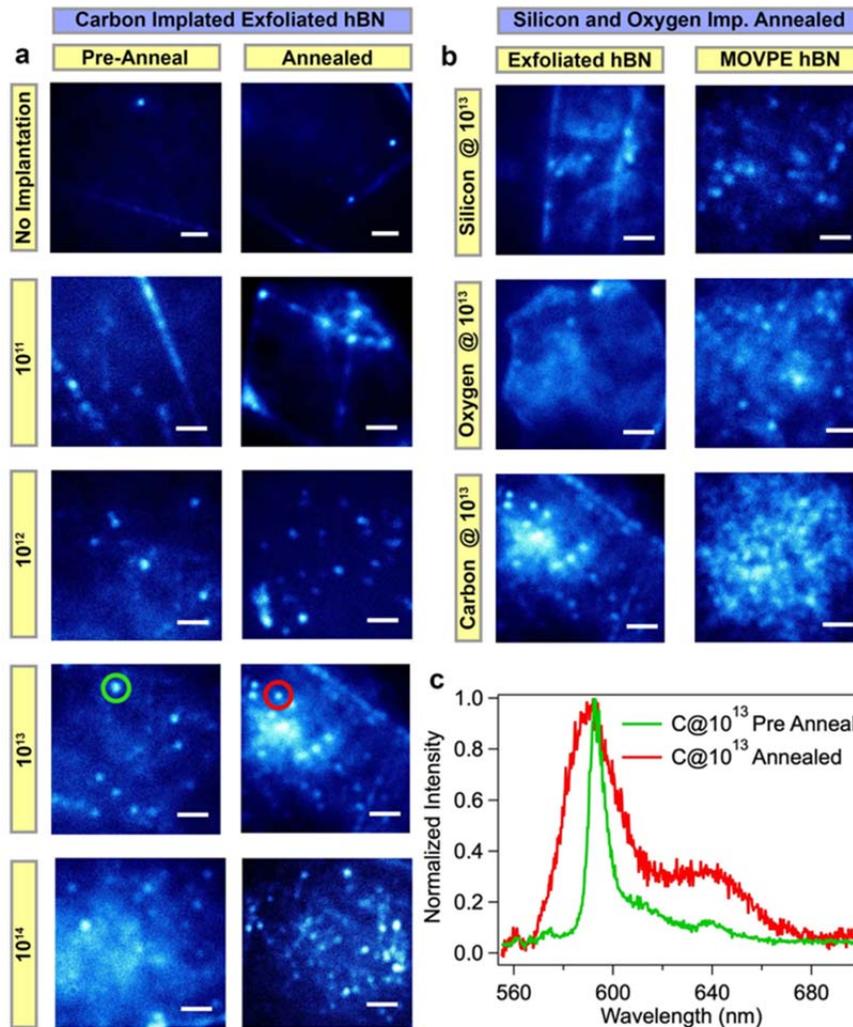
283 pristine hBN flakes (HQ Graphene) were used. The samples were analyzed via wide field
284 imaging, allowing for the direct visualization of the resulting SPE density.

285 Figure 4a shows representative images from the exfoliated hBN flakes before and after
286 annealing. The results demonstrate unambiguously that emitter creation scales with the dose of
287 carbon implantation in both cases, which directly confirms the creation of SPEs. Only a few
288 emitters are formed pre-annealing, even at higher doses, but a direct correlation between SPE
289 formation and implantation fluence is clearly evident post-annealing.

290 Figure 4b shows a direct comparison for carbon, oxygen and silicon ion implantations at
291 a dose of 1×10^{13} ions/cm². For the MOVPE samples implanted with oxygen and silicon we
292 observe a similar SPE density to pristine TEB 10, while carbon implantation significantly
293 increases the density. This is because all ions create vacancies which is indicative of them being
294 involved along carbon in the defect structure. In the exfoliated samples, only carbon implantation
295 results in the direct formation of single emitters at a high density.

296 Figure 4c shows two spectra recorded from the localized emission spots in the carbon
297 implanted exfoliated samples, before and after annealing. Green and red circles in figure 4a mark
298 the position of the recorded spectra in each case. Additional wide-field imaging and spectral
299 characterization for exfoliated and MOVPE hBN are displayed in Extended Data Fig. 9&10.

300 In light of the implantation results, we briefly consider a potential ancillary role of
301 carbon. This could occur through the stabilization or charge state modification of alternative
302 defects, as well as modification of the material Fermi level. Critically, our implantation results
303 allow us to rule out these possibilities. The creation of SPEs prior to annealing with C
304 implantation only (i.e. not with Si and O implantation), despite clear evidence of increased
305 vacancy creation excludes the secondary role of carbon as that of simply *activating* native
306 vacancy complexes. Furthermore, complex native defects (e. g. $V_N N_B$) or non-carbon heteroatom
307 impurities involving O and Si are similarly inconsistent with our results. Note also that the dose
308 dependent implantation experiments conclusively demonstrate that the density of created SPEs
309 scales with the fluence of C ions in high purity hBN materials.



311 **Figure 4—Wide field Imaging of Ion Implanted MOVPE and Exfoliated hBN.** Scale bars in each case
 312 are 2 μm . **a.** Exfoliated hBN samples for a series of carbon implanted samples with increasing fluences
 313 from 10^{11} - 10^{14} ions/ cm^2 . The samples were analyzed before and after annealing in high vacuum ($1000\text{ }^\circ\text{C}$,
 314 $<10^{-6}$ Torr, 2 hours). Isolated bright spots (corresponding to SPEs) increase with the dose of carbon
 315 implantation. **b.** MOVPE (TEB 10) and exfoliated hBN samples implanted with carbon oxygen and silicon
 316 implanted samples at a fluence of 10^{13} ions/ cm^2 . For both material types SPE density is not increased by
 317 O and Si implantation but increases upon C implantation. **c.** Spectra from carbon implanted exfoliated
 318 hBN before and after annealing. Red and green circles in panel a identify the position in which the
 319 spectrum was recorded.

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ELECTRONIC STRUCTURE CALCULATIONS

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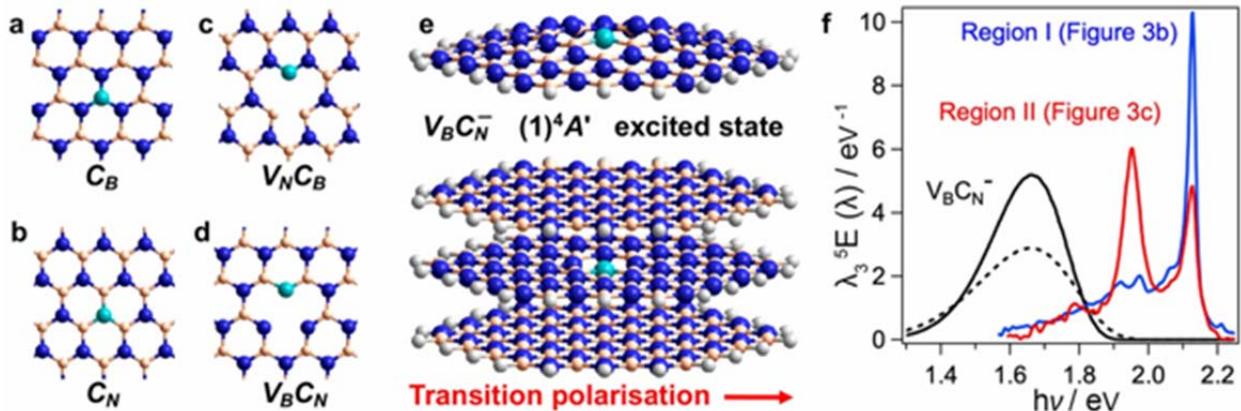
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To gain further insight into the structure of the carbon defect, we searched for defect transitions from which the observed photoemission could originate. To do so, time-dependent density-functional theory³⁸ (TD-DFT) calculations were performed using the CAM-B3LYP³⁹ density functional (see SI for extensive details). These are supported by calculations using the HSE06 density functional⁴⁰ and the advanced equation-of-motion coupled cluster singles and doubles (EOM-CCSD)⁴¹ methods. Four main defect candidates were considered: C_B , C_N , $\text{V}_\text{N}\text{C}_\text{B}$, and $\text{V}_\text{B}\text{C}_\text{N}$ (Figure 5a-d) in their neutral, negative (-1), and positive (+1) charged states. Two spin

329 manifolds were considered for each (either singlet and triplet or else doublet and quartet), as well
 330 as at least ten excited states of each type. Calculations were performed using 3-ring, 5-ring, and
 331 10-ring model compounds containing 1 or 3 hBN layers, to account for the effects of the host
 332 matrix on the defect. Figure 5e displays the 3-ring, 1-layer and 3-layer, model for $V_B C_N^-$.
 333 Calculations on 10-ring systems were performed using a mixed quantum-mechanics/molecular-
 334 mechanics (QM/MM) scheme, utilizing an AMBER⁴² potential fitted to mimic CAM-B3LYP
 335 results on 5-ring h-BN.

336 Given the large number of possible defect candidates considered, we proceeded by
 337 eliminating unsuitable ones by benchmarking our calculations to known experimental properties.
 338 We focused on three well established experimental features of the SPEs, a ZPL energy transition
 339 of ~ 2.1 eV,^{28, 29} a fast excited state lifetime of $\sim 2-6$ ns,⁷ and a high quantum efficiency.⁴³
 340 Accordingly, computational results were filtered to reproduce first, a CAM-B3LYP-calculated
 341 lowest-energy transition of 1.6 – 2.6 eV (based on the expected *worst-case* computational error,
 342 calibrated for this method to be ± 0.5 eV),²² and second, an oscillator strength exceeding 0.1,
 343 compatible with the observed short photoluminescence lifetime and high quantum yield. Few
 344 defects have lowest transition energies in this range, and most transitions are predicted to have
 345 oscillator strengths one hundredth of this or much less. Based on these considerations, only two
 346 candidates remain of interest amongst the options considered: the $(1)^4B_1 \rightarrow (1)^4A_2$ transition in
 347 $V_B C_N^-$, and the $(2)^3B_1 \rightarrow (1)^3B_1$ transition in $V_N C_B$. Of these, $V_N C_B$ is immediately eliminated
 348 as its spectral bandshape and most other properties are highly inconsistent with observed
 349 features; hence we focus on $V_B C_N^-$.

350



351

352 **Figure 5—Computational Modelling.** Properties were determined for defects in their neutral and ± 1
 353 charged states. Indicative high-symmetry defect structures are shown in (a)-(d) (N- blue, B- peach, C-
 354 cyan): (a) for C_B^+ , C_B^- , C_B ; (b) for C_N^+ , C_N^- , C_N ; (c) for $V_N C_B^-$, $V_N C_B^+$, $V_N C_B$; and (d) for $V_B C_N^-$, $V_B C_N^+$, $V_B C_N$.
 355 It is concluded that the only feasible emission source is the $(1)^4B_1 \rightarrow (1)^4A_2$ transition in $V_B C_N^-$, with
 356 fully optimized 3-ring 1-layer and 3-ring 3-layer structures shown in (e), along with the allowed in-plane-
 357 perpendicular electric polarization vector. In (f), its predicted band shape (black dashed: basic CAM-
 358 B3LYP 3-ring 1-layer model, black solid: QM/MM EOM-CCSD 10-ring 3-layer out-of-plane distorted
 359 model) is compared to observed ones from Region I (blue, Fig. 3b C-Implanted) and Region II (red, Fig.
 360 3c masked). The observed spectra are shown after correction for instrument response functions and
 361 converted from raw emission $E(\lambda)$ to bandshape $\lambda^5 E(\lambda)$ plotted versus energy $h\nu = hc/\lambda$, displaying
 362 broadening to a resolution of 0.01 eV. The predicted spectra are both too low in energy and too broad
 363 than the experimental ones, but the assignment is within computational uncertainty.

364

365 The ground state of $V_B C_N^-$ is predicted to be $(1)^4A_2$, with unpaired electrons in $a_1(\sigma)$,
366 $b_1(\pi)$ and $b_2(\sigma)$ orbitals. Four low-energy excited states are predicted, of which the lowest-
367 energy one would need to be $(1)^4B_1$. One-layer models predict that this state undergoes out-of-
368 plane distortion which lowers the energy. The distortion however can be either removed or
369 enhanced once multi-layer models are considered. This transition has dominant $a_1(\sigma) \rightarrow b_2(\sigma)$
370 character, polarised in-plane and perpendicular to the defect's C_{2v} axis (see Figure 5e), with an
371 oscillator strength exceeding 0.1. Figure 5f compares calculated emission bandshapes $E(\nu)/\nu^5$
372 (obtained as the raw emission scaled by wavelength to the 5th power) with calculated ones. The
373 $(1)^4B_1 \rightarrow (1)^4A_2$ emission is predicted to be slightly lower in energy and much broader. The
374 calculated width is environment dependent (Figure 5f) and dominated by how the calculations
375 perceive torsional changes at the defect associated with light emission that generate low-
376 frequency phonons. The observed spectra in Region I are indicative of such effects, but their
377 magnitude is reduced to one third. The observed spectra in Region II are very different, primarily
378 manifesting the effects of activation of BN-stretch phonons instead. It could be that the
379 perceived sensitivity of $V_B C_N^-$ photoemission to local environment can account for the stark
380 contrast in the observed spectra (Figure 5f).

381 The most significant shortcoming of the proposal of this defect as the dominant hBN SPE
382 would be that intense absorption is predicted in only one polarization, whereas experiments
383 suggest that higher-energy absorptions exist with alternate polarization.^{7, 9} However, of the 24
384 defect manifolds considered herein, it is the only one to remain of interest. More complex
385 carbon-cluster defects, including for instance C_2C_N and C_2C_V have been considered as
386 alternatives^{44,45}.

387
388 In summary, we have presented rigorous experimental results to confirm the central role
389 of carbon in hBN quantum emitters in the visible spectral range. We compared samples grown
390 by MOVPE, MBE, and HOPG conversion. All methods exhibited a direct correlation between
391 the introduction of carbon as a precursor/substance and the formation of SPEs. Furthermore,
392 MOVPE growth enabled us to deterministically control carbon incorporation and vary the
393 density of the quantum emitters from singles to ensembles and observe room temperature
394 ODMR. We have also generated SPEs using direct ion implantation of carbon and showed that
395 their density scales with the implantation dose. Employing a TD-DFT method, we proposed the
396 negatively charged $V_B C_N^-$ as a suitable transition to explain the observed results. Our results will
397 accelerate the deployment of visible quantum emitters in hBN into quantum photonic devices
398 and will advance potential strategies for the controlled engineering of quantum emitters in van
399 der Waals crystals.

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420

421

422 **Author Contributions**

423 N.M. and I.A. designed the experiments. N.M., J.R.R., C.B., and I.A. wrote the manuscript with
424 contributions from all co-authors. N.M. performed experimental measurements and data analysis.
425 J.R.R. and M.J.F. performed the computational calculations. Ion implantation and MOVPE
426 growth was performed by D.C., C.J. and H.H.T. MBE growth was carried out by T.S.C., C.J.M.,
427 P.H.B., and S.V.N. HOPG to hBN Conversion samples were fabricated by H.L., and A.Z.. A.G.
428 and V.D. performed ODMR experiments. I.A., C. B. and M.T. supervised the project. All
429 authors discussed the results and contributed to the manuscript.

430

431 **Competing interests**

432 The authors declare no competing interests.

433

434 **Data Availability**

435 Most experimental and theoretical data for this work is provided. Confocal maps and wide field
436 images are available from the corresponding author upon request due to their size.

437

438 **Methods**

439 *Metal Organic Vapor Phase Epitaxy.* hBN layers were grown on commercially available 2”
440 sapphire substrates using metal organic vapor phase epitaxy (MOVPE), as described in.²⁷
441 Triethyl boron (TEB) and ammonia were used as the boron and nitrogen precursors, respectively,
442 while hydrogen was the carrier gas. The precursors were introduced into the reactor as short
443 alternating pulses, in order to minimize parasitic reactions between TEB and ammonia. hBN
444 growth was carried out at a reduced pressure of 85 mBar and the growth temperature was set to
445 1350°C. In the present study, the TEB flux was varied from 10 μmol/min to 60 μmol/min to
446 study the effect on carbon incorporation on sub-bandgap luminescence from the hBN films. For
447 ion implantation, PL and SPE measurements, cm-sized hBN films were transferred from
448 sapphire on to SiO₂/Si substrates, using water-assisted self-delamination.²⁷ Thickness of the hBN
449 films was also measured using atomic force microscopy, as shown in the supplementary
450 information. X-ray photoelectron spectroscopy was used for determining the impurity levels in
451 the as-grown MOVPE-hBN films, as shown in the supplementary information. A gentle etching
452 using Ar beam was performed in-situ to remove adventitious carbon and impurities from the
453 surface; all spectra were collected from the bulk of hBN films.

454

455 *Molecular beam epitaxy.* BN epilayers were grown using a custom-designed Veeco GENxplor
456 MBE system capable of achieving growth temperatures as high as 1850 °C under ultra-high

457 vacuum conditions, on rotating substrates with diameters of up to 3 inches. Details of the MBE
458 growth have been previously published.³² In all our studies, we relied on thermocouple readings
459 to measure the growth temperature of the substrate. For all samples discussed in the current
460 paper the growth temperature was in the range 1250–1390 °C. We used a high-temperature
461 Knudsen effusion cell (Veeco) or electron beam evaporator (Dr. Eberl MBE-Komponenten
462 GmbH) for evaporation of boron. High-purity (5 N) elemental boron contains the natural mixture
463 of ¹¹B and ¹⁰B isotopes. To contain boron in the e-beam evaporator we used boron nitride and
464 vitreous carbon crucibles. We used a conventional Veeco RF plasma source to provide the active
465 nitrogen flux. The hBN epilayers were grown using a fixed RF power of 550 W and a nitrogen
466 (N₂) flow rate of 2 sccm. We used 10 × 10 mm² (0001) sapphire and on- and 8°-off oriented Si-
467 face SiC substrates. Variable angle spectroscopic ellipsometry (VASE) provided the thickness of
468 the hBN layers.

469
470 *HOPG to hBN Conversion.* The conversion takes place in a graphite crucible. A HOPG crystal
471 is placed in the center of the crucible on a separate graphite holder. Small holes in the stage
472 holding the HOPG allow vapors from the boron-oxide powder, placed at the bottom of the
473 crucible, to flow to the HOPG crystal. A radio frequency induction furnace is then heated to
474 2000 °C, and N₂ gas is introduced as the nitrogen precursor. A central tube mixing the nitrogen
475 gas with the boron-oxide vapor pre-mixes the precursors prior to arriving at the HOPG crystal.
476 Further details can be found here.³⁵

477
478 *Ion Implantation.* Ion implantation was carried out on 40 nm-thick MOVPE-hBN films, grown
479 using a TEB flux of 10 μmol/min. For this, the hBN films were first transferred on to SiO₂/Si
480 substrates. A copper grid with a square mesh (GCu300, ProSciTech) was used as the
481 implantation mask. Carbon, silicon and oxygen were separately implanted into the hBN films.
482 During implantation, the ion energy and fluence were 10 keV and 10¹³ ion/cm², respectively.

483
484 *Confocal Microscopy.* The optical measurements were carried out using a confocal microscope
485 equipped with a 532 nm excitation source. The collected signal was sent either to a spectrometer
486 or to an avalanche photodiode for photon statistics measurements. The $g^{(2)}(\tau)$ measurements were
487 analyzed and fitted without background correction unless specified otherwise. More details on
488 the setup can be found in Ref²⁸

489
490 *ODMR.* The ODMR spectra were measured with a confocal microscope setup. A 100× objective
491 (Olympus MPLN100X) was used to focus a 532-nm laser (LaserQuantum opus 532) onto the
492 sample and collect the PL signal. The PL signal is collected back through a 650-nm short-pass
493 dichroic mirror for separation from scattered laser light. Additionally, a 532nm and 550nm long-
494 pass filter were used before the PL was detected by a silicon avalanche photodiode (Thorlabs
495 APD440A) to filter out the laser light. The microwave field was applied through a signal
496 generator-plus-amplifier system (Stanford Research Systems SG384 + VectaWave VBA1000-18
497 Amplifier); the sample was placed on a 0.5-mm-wide copper stripline. In order to detect the
498 ODMR signal (i.e. the relative ΔPL/PL contrast) by lock-in technique (Signal Recovery 7230),
499 the microwaves were driven with an on-off modulation. The resonant condition was changed
500 with the external magnetic field by mounting a permanent magnet below the sample.

501

502 *Raman Spectroscopy.* Raman spectroscopy measurements were carried out on an In-Via confocal
503 Raman (Renishaw) system using a 633-nm excitation source. Calibration of the Spectrometer
504 was carried out using a Si substrate to 520 cm^{-1} . The peaks were then fitted to a Lorentzian line
505 profile, from which the corresponding peak center position and full width at half maximum
506 (FWHM) were extracted. Samples were analyzed after transfer to SiO_2 .

507
508 *Atomic force microscopy (AFM).* The thickness of the hBN films transferred on to SiO_2/Si
509 substrates was measured using tapping mode AFM (ScanAsyst-Air, MultiMode 8, Bruker). The
510 AFM scan was performed at the film boundary to facilitate thickness measurement across the
511 step-edge, as shown in supplementary information Figure S8.

512
513 *Computational.* Many innovative approaches are used in order to model defects with large 3D
514 spatial deformations, as described in detail in Supplementary Information. The core elements are
515 the use of Gaussian-16* to perform TD-DFT calculations within a QM/MM model utilizing
516 CAM-B3LYP and an AMBER h-BN force field fitted to mimic CAM-B3LYP. Spectra are
517 simulated with the Huang-Rhys model based on analytically obtained second-derivatives for
518 both ground and excited states.

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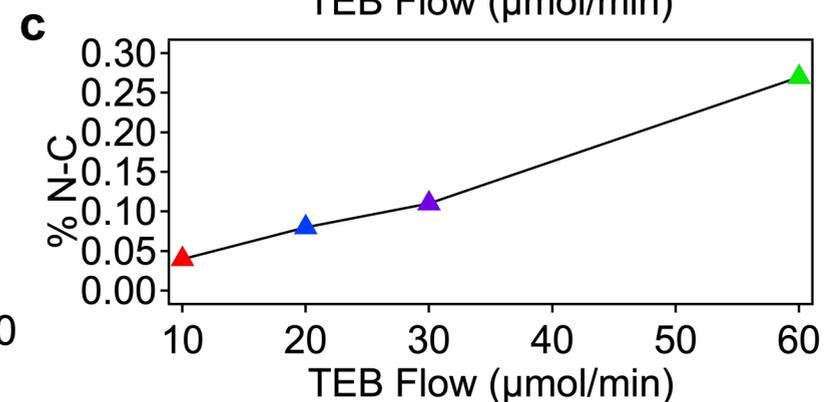
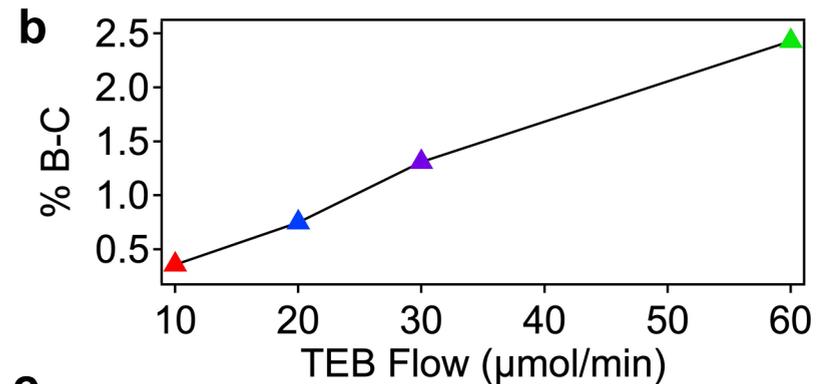
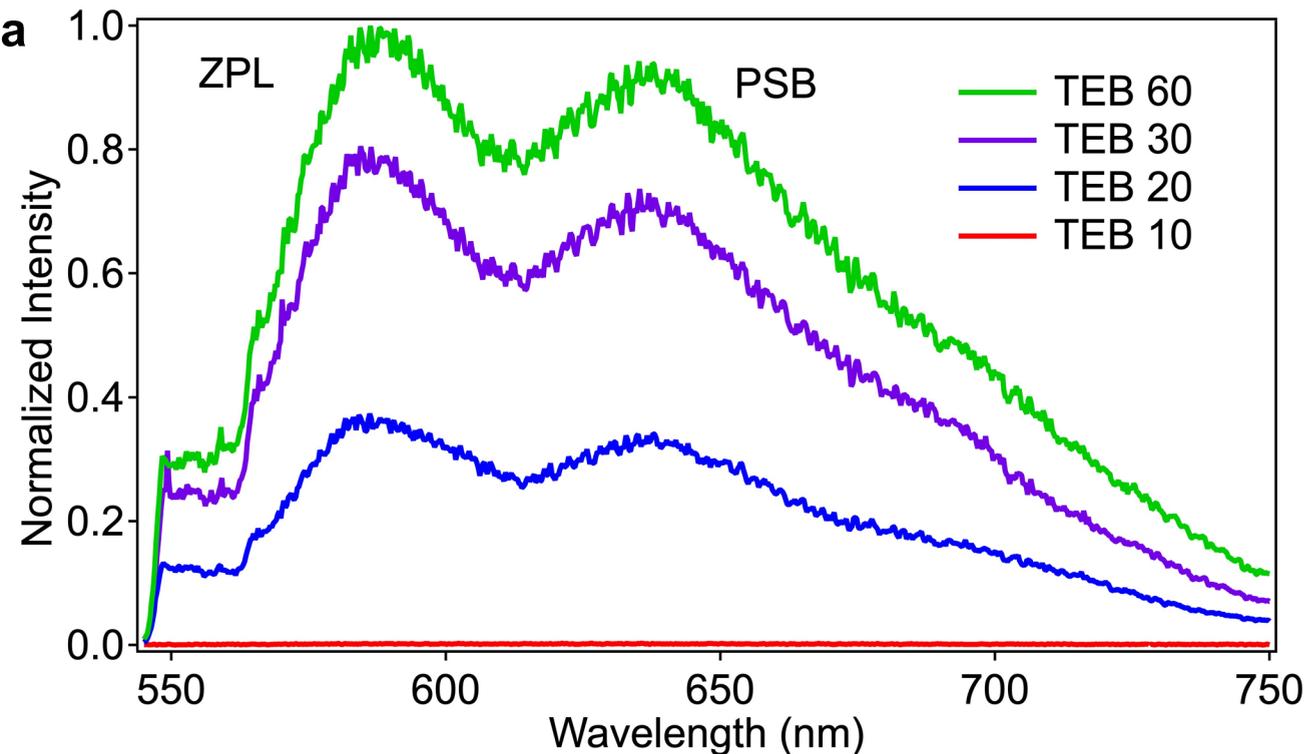
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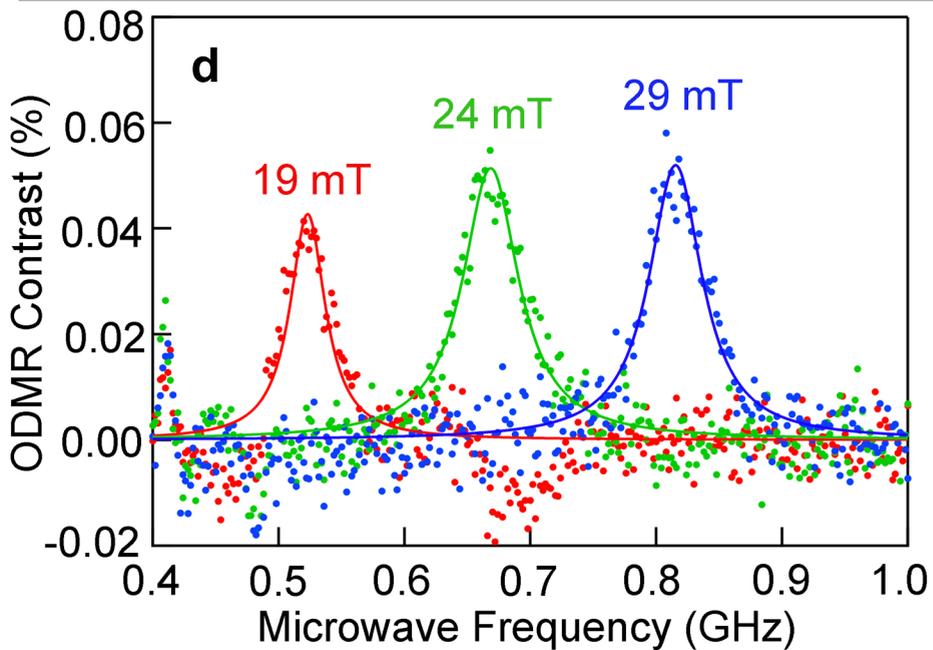
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Metal Organic Vapor Phase Epitaxy (MOVPE) hBN

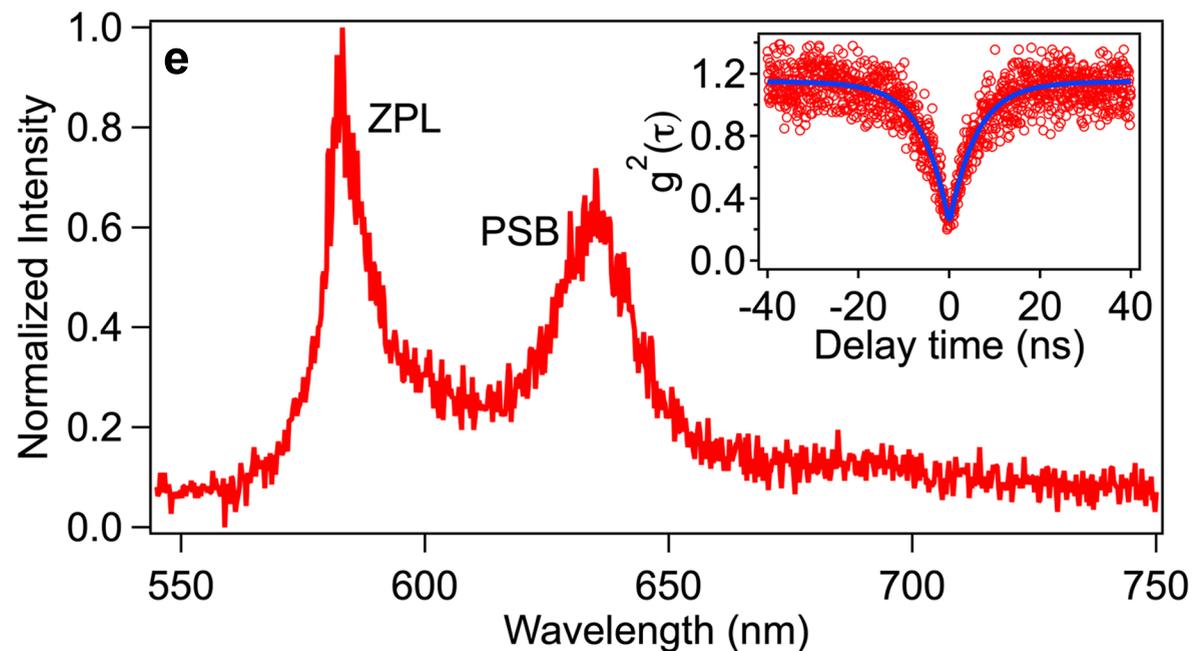
MOVPE SPE Ensembles with Increasing Carbon Incorporation



ODMR MOVPE (TEB 60)

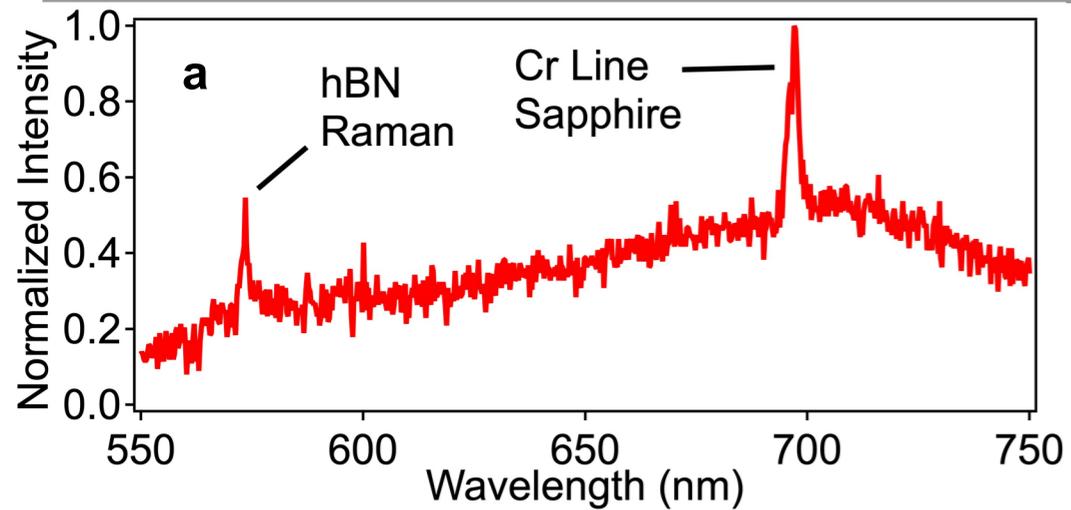


MOVPE Low Carbon (TEB 10) Single Emitters

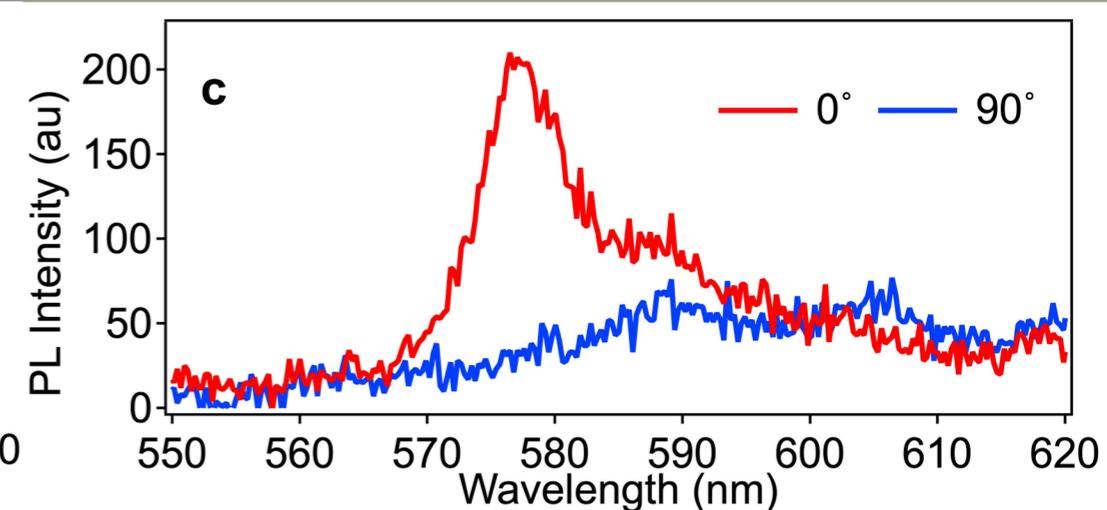
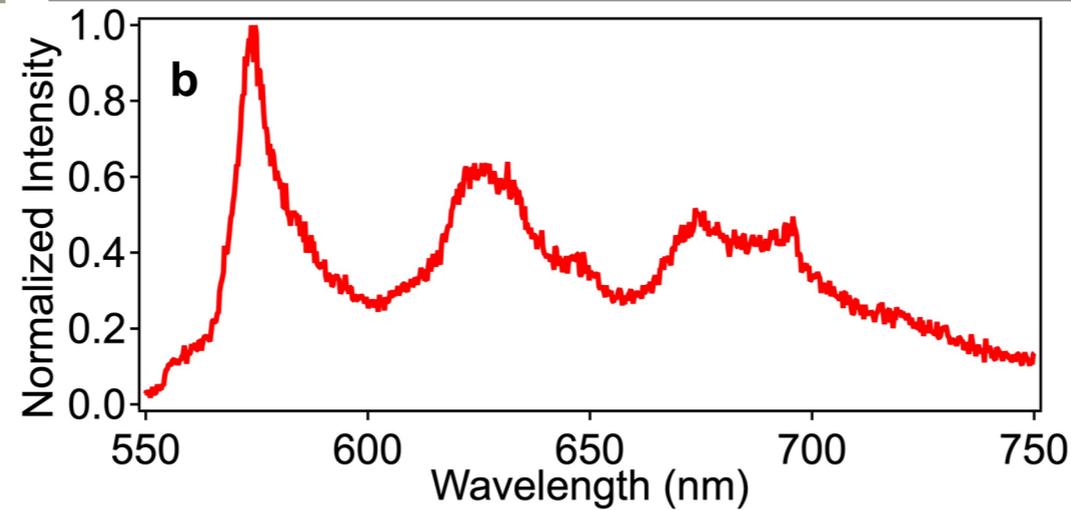


Molecular Beam Epitaxy (MBE) hBN

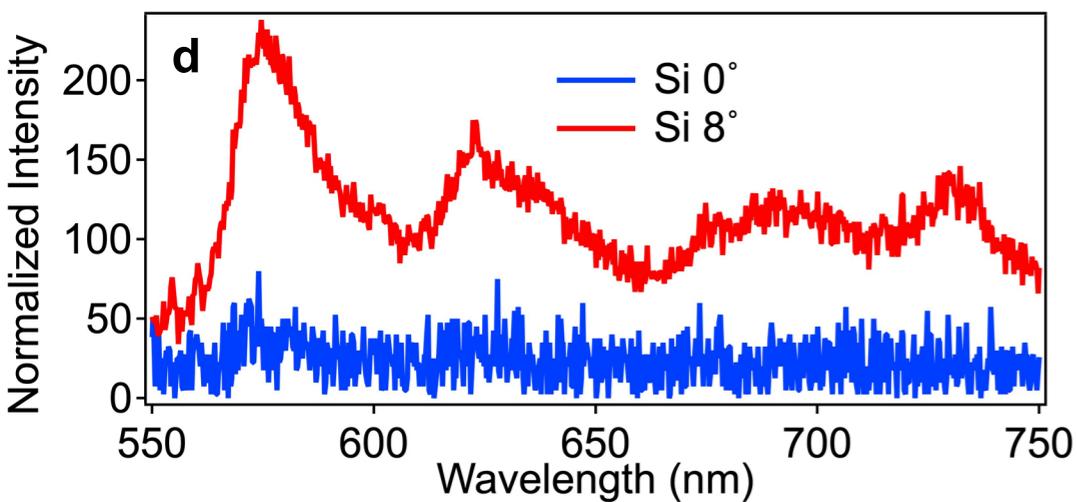
Undoped MBE hBN on Sapphire



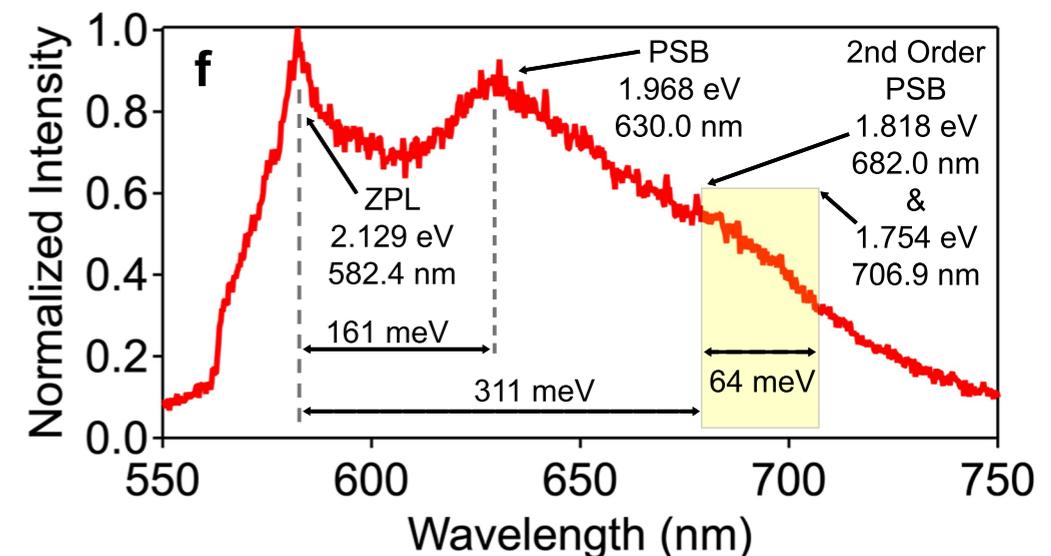
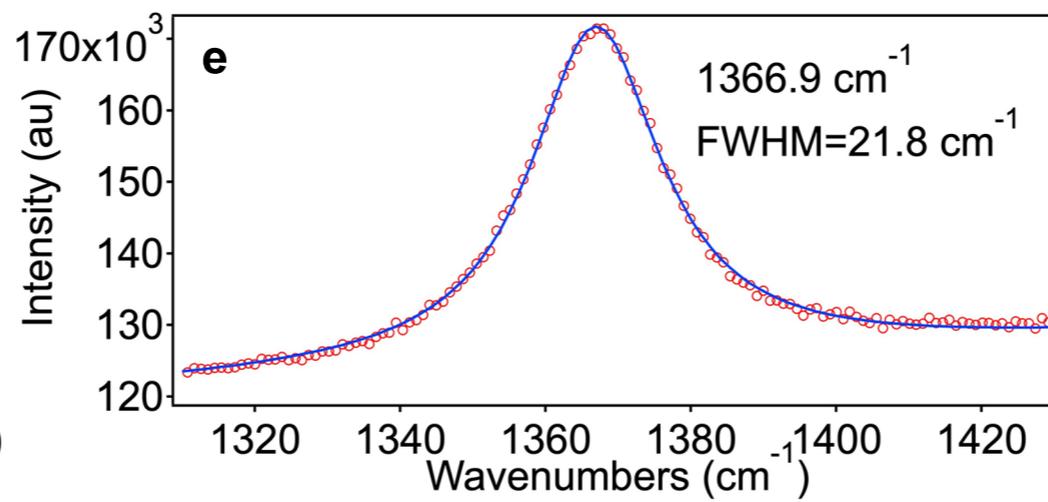
Carbon Doped MBE hBN on Sapphire



Undoped MBE hBN on SiC



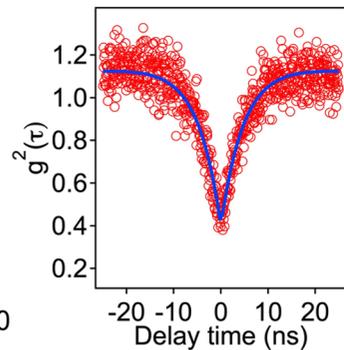
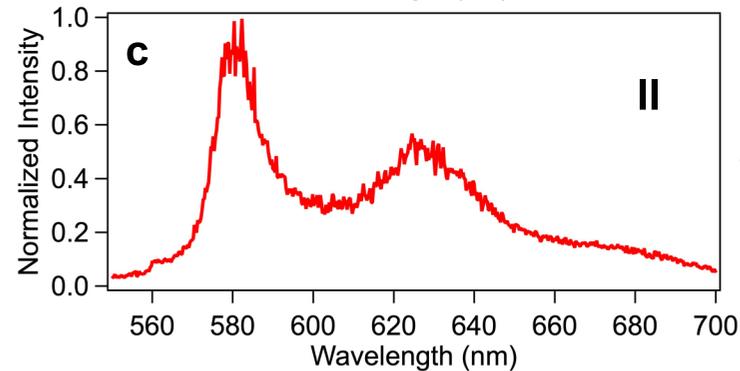
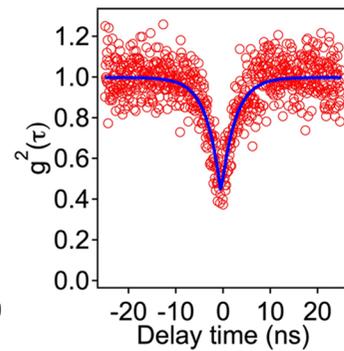
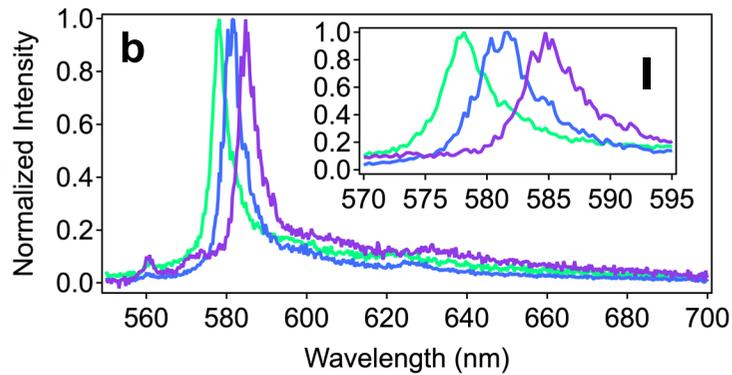
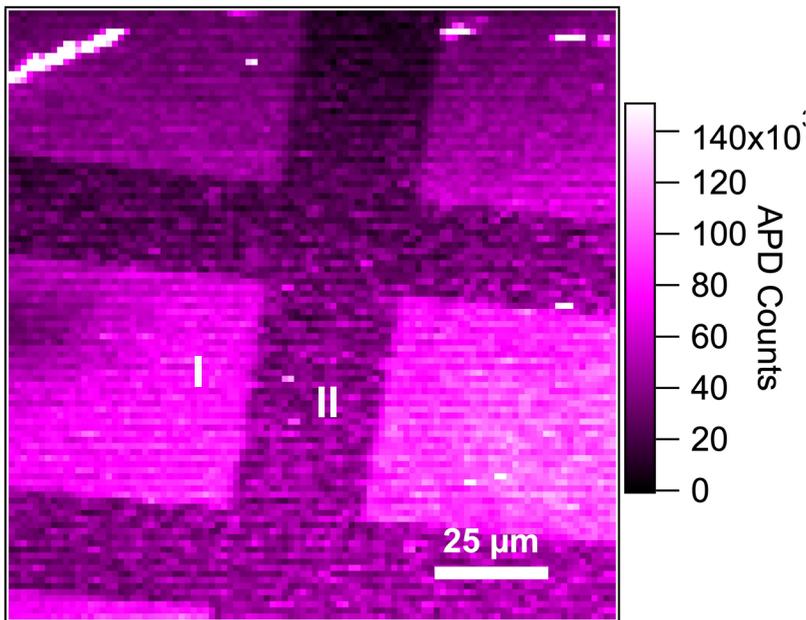
HOPG to hBN Conversion



Carbon Implanted MOVPE hBN

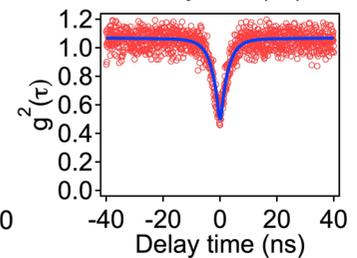
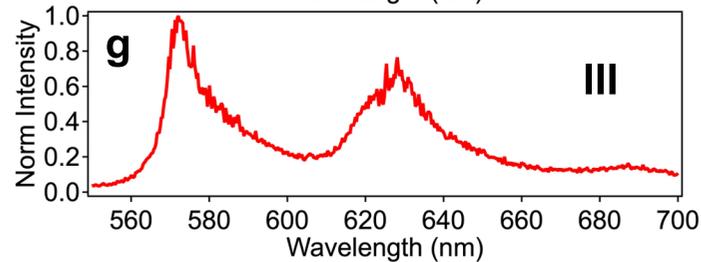
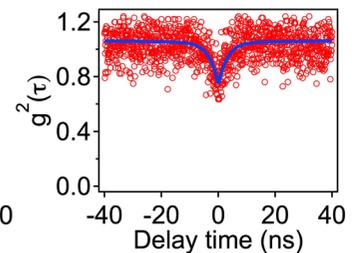
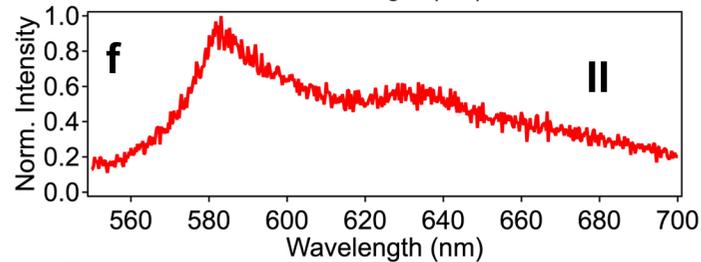
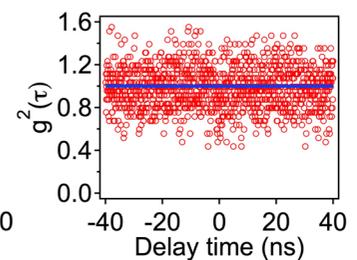
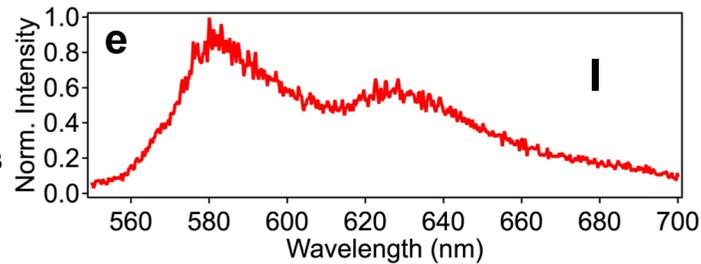
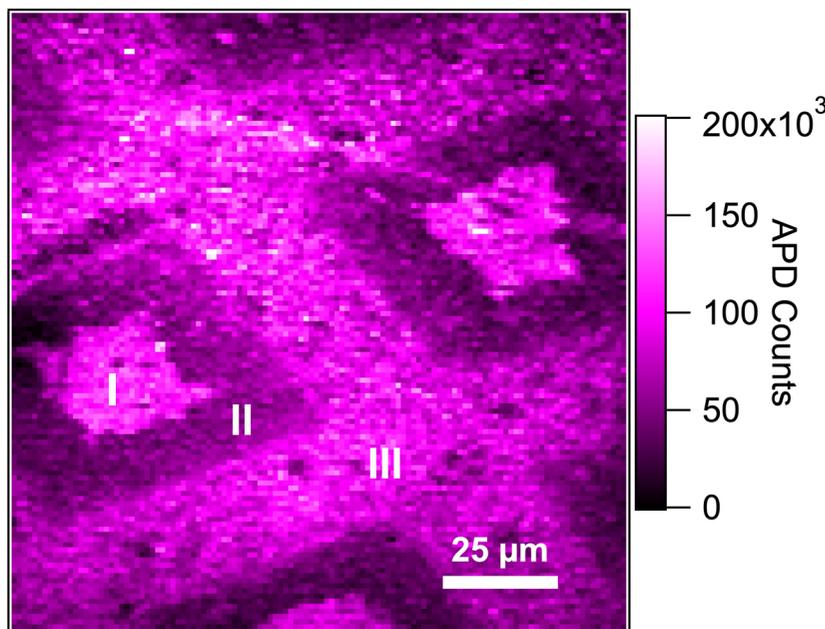
Pre-Anneal

a



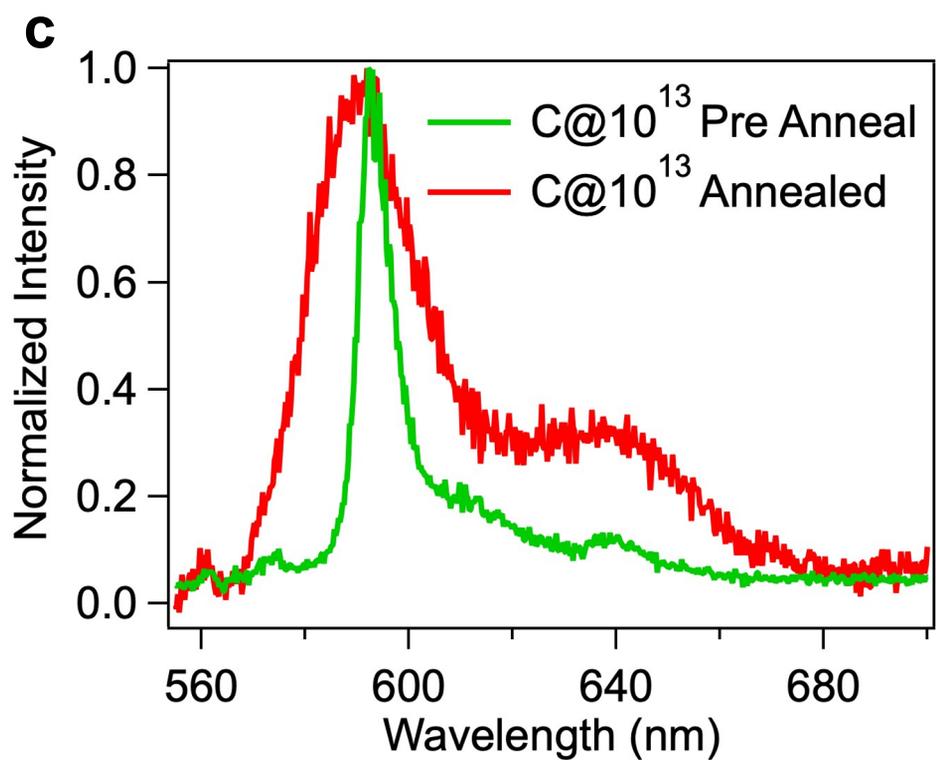
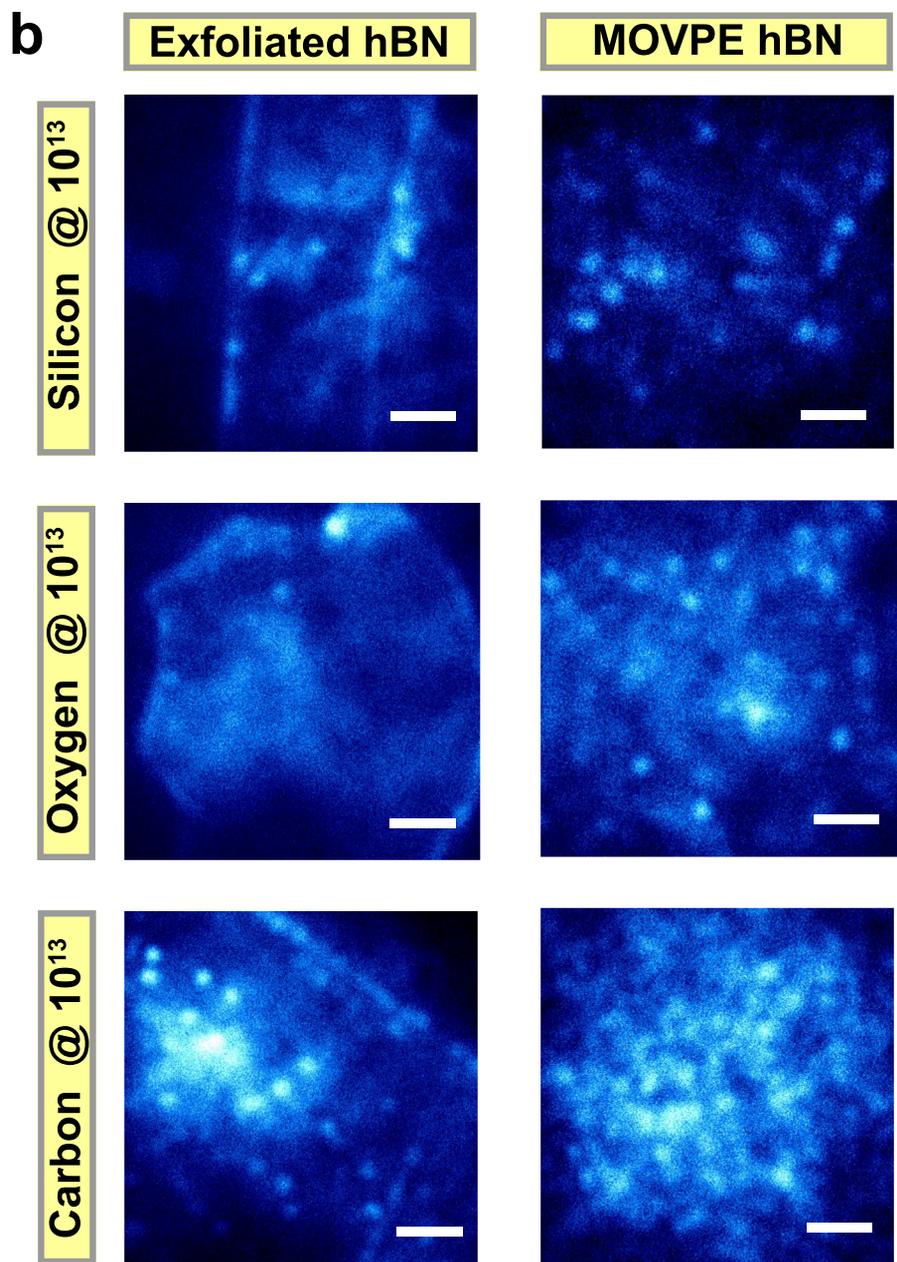
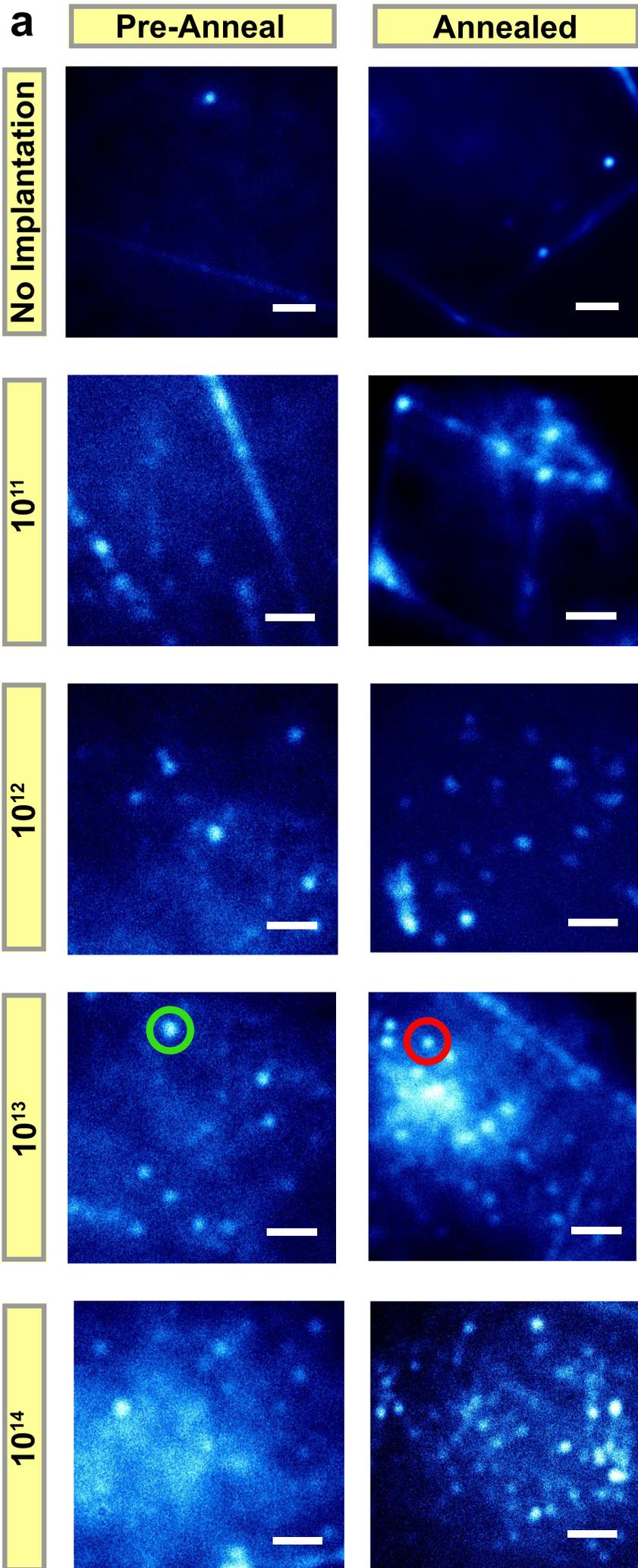
Annealed (1000°C, Hi-Vac, 2 hours)

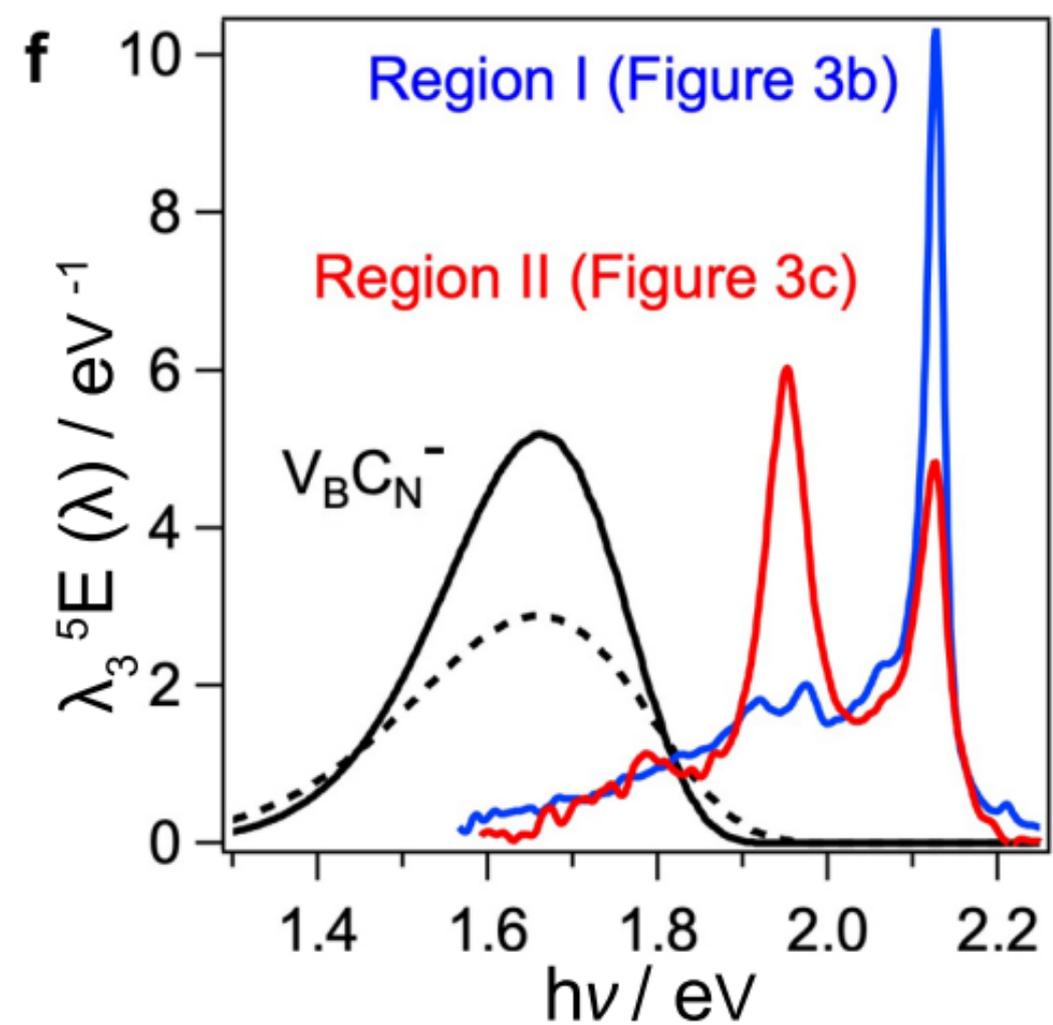
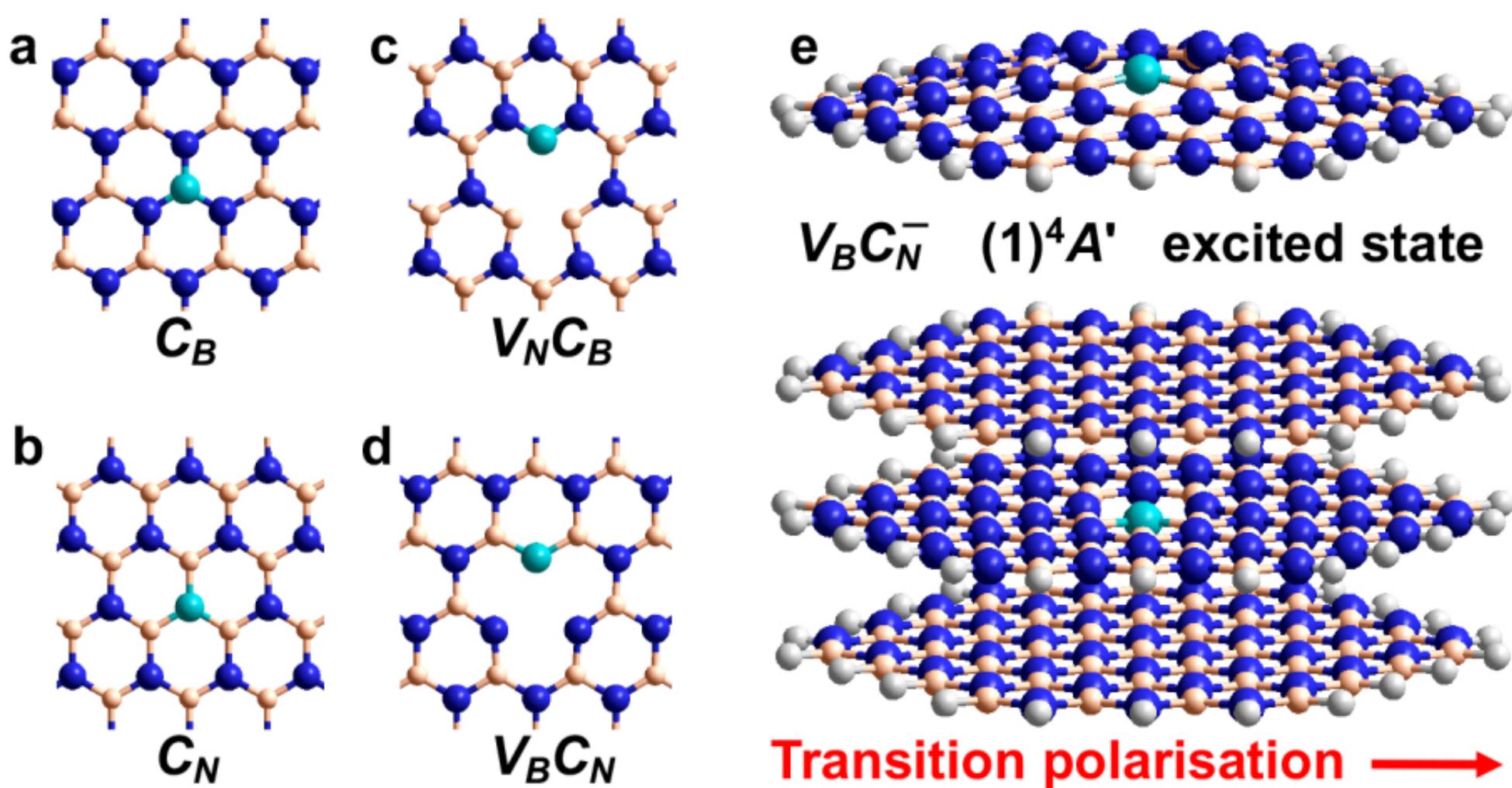
d



Carbon Implanted Exfoliated hBN

Silicon and Oxygen Imp. Annealed





Sample	Abbreviation	Growth Method & Details	SPE Photoluminescence	Additional Info
MOVPE hBN (TEB flux 10)	MOVPE hBN (TEB 10)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 10 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Isolated SPEs, ZPLs Predominantly $\sim 585 \pm 10$ nm	~ 40 nm thick
MOVPE hBN (TEB flux 20)	MOVPE hBN (TEB 20)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 20 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Dense and Uniform Ensemble of SPEs with ZPL ~ 585 nm, PSB ~ 630 nm.	~ 40 nm thick
MOVPE hBN (TEB flux 30)	MOVPE hBN (TEB 30)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 30 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Dense and Uniform Ensemble of SPEs with ZPL ~ 585 nm, PSB ~ 630 nm.	~ 40 nm thick
MOVPE hBN (TEB flux 60)	MOVPE hBN (TEB 60)	MOVPE on Sapphire, Precursors (triethyl borane & ammonia) TEB flow 60 $\mu\text{mol}/\text{min}$, H_2 carrier gas, 1350°C	Dense and Uniform Ensemble of SPEs with ZPL ~ 585 nm, PSB ~ 630 nm.	~ 40 nm thick
MBE hBN on Sapphire	Undoped MBE hBN on sapphire	MBE on sapphire, Boron flux from e-beam source (300W). Boron in BN crucible. Nitrogen flow 2sccm. Growth temperature 1250°C.	No SPEs Present	~ 20 nm thick
MBE hBN on Sapphire with Carbon Crucible	Carbon doped MBE hBN on Sapphire	MBE on sapphire, Boron flux from e-beam source (210W). Boron in carbon crucible. Nitrogen flow 2sccm. Growth temperature 1250°C.	Semi-Isolated SPEs, ZPLs Range from 570-770 nm, Density $\sim 5-8/\mu\text{m}^2$	~ 18 nm thick
MBE hBN on Silicon Carbide (0° Si Face)	Undoped MBE hBN on SiC (0°)	SiC (Si-face, orientation-on) MBE on SiC. Boron flux from HT Knudsen source at 1875°C. Nitrogen flow 2sccm. Growth temperature 1390°C.	Very Few SPEs Density ~ 1 SPE in $40\mu\text{m}^2$	~ 3 nm thick
MBE hBN on Silicon Carbide (8° Si Face)	Undoped MBE hBN on SiC (8°)	SiC (Si-face, orientation 8°-off) MBE on SiC. Boron flux from HT Knudsen source at 1875°C. Nitrogen flow 2sccm. Growth temperature 1390°C.	Isolated SPEs, ZPLs Range from 575-735 nm Density $\sim 3-5/\mu\text{m}^2$	~ 7 nm thick
HOPG \rightarrow hBN Conversion	Converted hBN	HOPG is placed in a radio frequency induction furnace at 2000°C, N_2 gas is mixed with thermalized B_2O_3 powder facilitating conversion	Dense and Uniform Ensemble of SPEs with ZPL ~ 580 nm, PSB ~ 630 nm.	Bulk