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Revealing polytypism in 2D boron nitride with UV photoluminescence



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Boron nitride exhibits various crystal structures. The subgroup of layered boron nitrides includes several polytypes such as hexagonal (hBN), Bernal (bBN), and rhombohedral (rBN) BN. The latter two are non-centrosymmetric, potentially leading to piezoelectric or ferroelectric properties. A key challenge related to the polytypism of sp^2 -bonded BN is distinguishing between these polytypes. We demonstrate that the optical response of the 4.1-eV defect can be used to differentiate hBN from rBN. Photoluminescence and cathodoluminescence measurements on samples grown by metalorganic vapor phase epitaxy (MOVPE) show a zero-phonon line at 4.096 eV for hBN and 4.143 eV for rBN. Our calculations confirm that the photoluminescence originates from a carbon dimer, $C_B C_N$ (C_2), which is sensitive to the local environments of different polytypes. We demonstrate that different polytypic compositions of hBN and rBN can be achieved by MOVPE, which could pave the way for future applications in large-area van der Waals heterostructures.

Boron nitride can crystallize in different phases including cubic and wurtzite phases that have sp^3 -hybridized bonds and hexagonal or rhombohedral phases that are constructed by flat layers of atoms of sp^2 bonds, with a large separation between two layers joined by van der Waals bonds. However, at ambient conditions the sp^2 configurations are the stable phases^{1–4}. Boron nitride in the sp^2 -bonded hexagonal phase (hBN) is a very popular 2D material with insulating properties and is commonly used in various types of van der Waals heterostructures^{5,6}. Color centers in boron nitride can serve as bright UV and visible single photon emitters^{7,8}. Hexagonal boron nitride has an indirect bandgap, but shows very bright luminescence with nearly 100% efficiency^{9–12}. Although hBN has a high resistivity and it is still unclear whether effective doping can be achieved, there is still hope for light-emitting devices, since electroluminescence of pristine BN was recently demonstrated in van der Waals heterostructures⁶.

The hBN polytype exhibits an AA' stacking sequence and is characterized by an indirect bandgap^{13–16}. However, the existence of other polytypes, such as Bernal BN (bBN) with AB stacking (where the second layer B is shifted along the m -axis in relation to layer A) and rhombohedral BN (rBN) with ABC stacking (with an additionally shifted C layer) was recently experimentally demonstrated^{16–18}. The stacking sequence of atomic layers for different polytypes is plotted in Fig. 1. All of these forms have

different band structures, as predicted theoretically and observed experimentally via the near bandgap optical emission^{3,13,14,19–21}.

Layered boron nitride crystallizes in honeycomb layers stacked one onto another. The layers have hexagonal symmetry. The unit cells are plotted in Fig. 1a–c. The main crystallographic planes are the c -plane (plane normal to the layer surface), a -plane and m -plane. Figure 1d–f shows these planes. Their Miller and Miller–Bravais indices are: c : (001) and (0001), a : (110) and (1 $\bar{1}$ 20), and m : ($\bar{1}$ 10) and ($\bar{1}$ 100). In Fig. 1d, it is visible that the hBN polytype (AA' stacking) has hexagonal structure that preserves inversion symmetry. The rBN polytype (ABC stacking order) shown in Fig. 1e shows parallel lines of B–N atoms pairs, what can lead to electric polarization. In this work, we demonstrate that defect-related optical emission in the UV-B spectral range is sensitive to the changes in the stacking sequence of atomic layers, suggesting that mid-gap photoluminescence can be used to identify the sp^2 -BN polytype as previously suggested for bBN²². Specifically, we focus on the 4.1 eV color center emission, which has been extensively studied in the literature^{10,23–27}. There is an ongoing debate regarding its origin, with various interpretations proposed: nitrogen vacancy²⁸, carbon ring²⁹, Stone–Wales defect³⁰ or a carbon dimer (C_2) at boron and nitrogen sites, $C_B C_N$ ^{27,31–34}, which according to our calculations appear to be the most probable interpretation. Here, we

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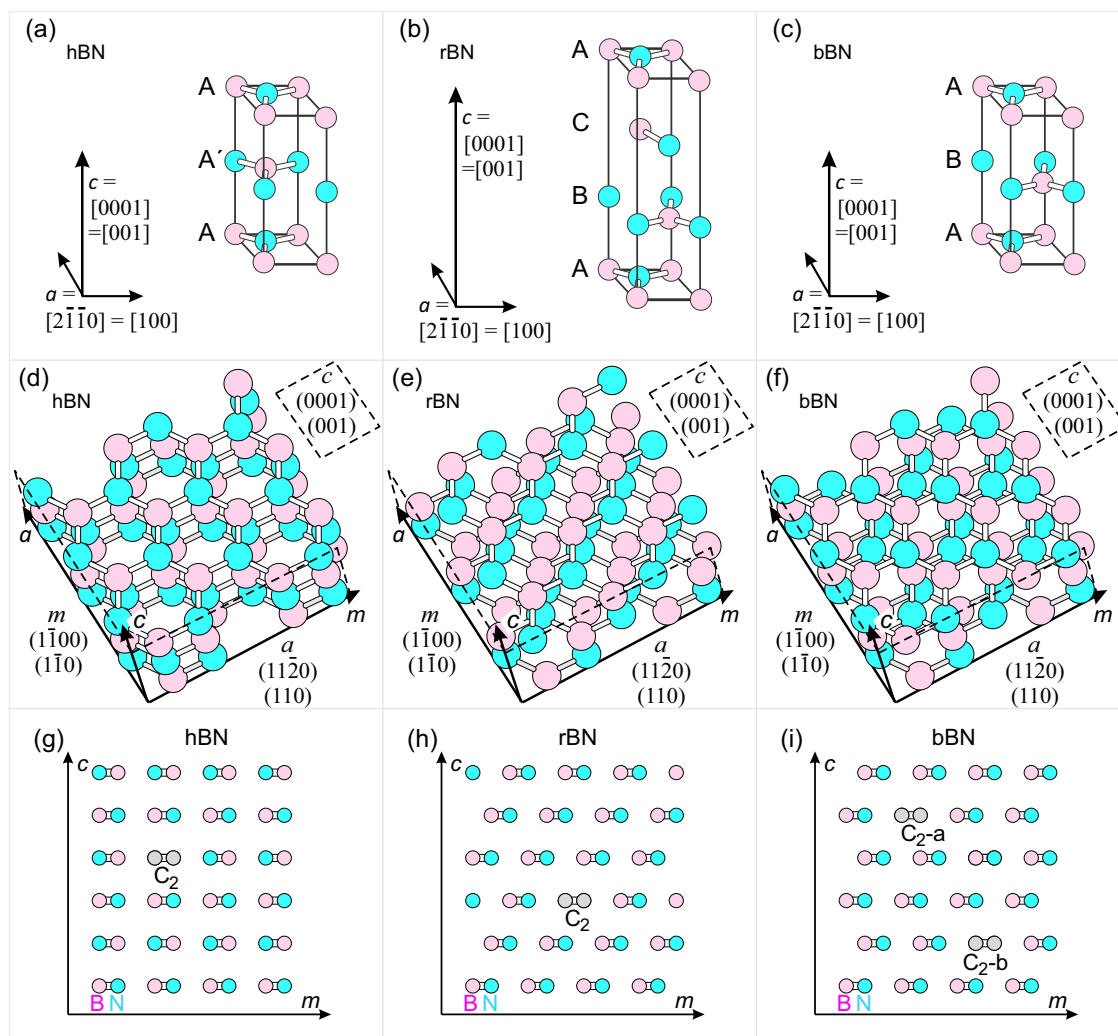


Fig. 1 | Different stacking orders of sp^2 -BN layers resulting in different polytypes. Upper row: the unit cells: (a) hBN, (b) rBN and (c) bBN. In the middle: quasi 3D cubes of BN crystals delimited by a , c and m planes: (d) hBN, (e) rBN, and (f) bBN. View along the c axis. Layers of BN can be distinguished by color of bonds: the top

layer has white bonds, middle – grey, bottom – dark grey. In the bottom row: the arrangement of atoms surrounding carbon dimers C_2 ($C_B C_N$) in a plane: (g) hBN, (h) rBN, and (i) bBN.

illustrate the concept of polytype identification using the carbon dimer $C_B C_N$ as an example. In sp^2 -hybridized boron nitride, the B–N covalent bonds lay in the a -plane: (110) , so a pair of carbon atoms that replaces boron and nitrogen atoms ($C_B C_N$) are positioned in the a -plane. Therefore, the most convenient way to analyze arrangement of atoms is in the a -plane cross-section view as depicted in Fig. 1g–i. Hexagonal boron nitride is formed by AA' stacking, where the A' layer is rotated by 60° what can be observed in Fig. 1a, d. Rhombohedral and Bernal boron nitride is formed by consecutive layers shifted along the direction of B–N bonds (see Fig. 1b, c, h, i). Depending on the polytype, the surrounding of the incorporated carbon dimer changes. From the electronegativity of the atoms, it follows that the boron atom is charged positively while the nitrogen atom is charged negatively, so the B–N pair is an electric dipole. In rBN all such dipoles around the $C_B C_N$ pair are in the same direction, while in hBN the direction varies and dipoles compensate each other. The bBN polytype with zigzag-like dipole stacking provides two options for $C_N C_B$ incorporation that are marked in Fig. 1i as C_2-a and C_2-b . In the case of the C_2-a dimer position, one C atom has two close boron neighbors in the upper and lower layer and the another C atom has no close neighbors. In the case of the C_2-b dimer, only one C atom is directly surrounded by two nitrogen atoms. These difference between the two positions may be the origin of two different emission lines^{22,34}. Variations in defect emission energy due to changes in the local

environment have been also reported for SiC. In SiC, differences in defect energy levels for hexagonal and cubic position are attributed to the local environment of the defects³⁵. For example, in 4H-SiC and 6H-SiC, donor energy levels differ significantly due to the influence of local symmetry^{36–39}.

Such small differences in the crystal structure of the material lead to significant changes in its properties. Different ordering induces changes in the band structure and causes a redshift of the energy gap value for rBN relative to hBN or a blueshift for bBN³. Additionally, the relative shifts and twists of subsequent atomic layers lead to a change in the symmetry group, which consequently induces piezoelectric, pyroelectric or ferroelectric effects⁴⁰. Moreover, since rBN crystals have no inversion symmetry, they can display even-order nonlinear optical phenomena like the frequency doubling effect (second-harmonic generation)⁴¹. The ability to identify or produce the appropriate polytype opens up completely new possibilities for applications in two-dimensional heterostructures.

Due to the similar lattice constants, an unambiguous identification of polytypes for high-quality epitaxial layers or exfoliated flakes is particularly difficult when using conventional X-ray diffraction (XRD). On the other hand, the weak van der Waals interaction between atomic layers causes nearly no difference between polytypes in the energy of the most pronounced E_{2g}^{high} (Raman active) or E_{1u} (IR active) phonon modes, so Raman

spectroscopy and other techniques that focus only on these phonons are not distinctive.

As we demonstrate below, the variations in the environment of the carbon dimer C_{B-N} notably impact the energy of the characteristic photoluminescence lines associated with this particular defect emission at 4.1 eV. Consequently, the polytype can be readily and unequivocally identified. Carbon-related defects are particularly useful for such identification, as carbon readily incorporates into BN^{27,42,43}. Consequently, it is one of the most prevalent impurity in this material including in state-of-the-art, high-crystalline-quality bulk crystals⁴⁴.

Results and discussion

One of the most common techniques for the structural characterization of crystals is XRD. However, in contrast to powder-like samples for thin crystals and films there are serious limitations regarding observed peaks during the experiment. The only peaks observed in the $2\theta/\omega$ scan are those for (00 l) Miller indices, and the other peaks cannot be observed because atomic planes are aligned parallel to the thick substrate. Since the distance between sp^2 -BN atomic layers in different stacking orders is practically the same ($d = 0.333$ nm)¹⁸, it is hard to experimentally distinguish between AA', AB and ABC stacking sequence by observation of (002) and (003) peaks around $2\theta \approx 27^\circ$ ^{18,20}. The main differences can be found for the peaks around $2\theta \approx 40^\circ$ – 45° . In hBN, in this angular range peaks related to (100) and (101) planes are expected, while in rBN, reflections from (101) and (102) planes should be present^{18,20}. In the case of bBN, the angular positions of the peaks within this range are indistinguishable from those of hBN. The primary distinction between these two polytypes lies in the intensity ratio of the peaks at 41.63° and 43.91° . To access those peaks, the atomic planes in sp^2 -BN have to be rotated relative to the substrate or the film has to be free-standing without substrate underneath. Therefore, to obtain a sample by metal-organic vapor phase epitaxy (MOVPE) which allows to easily distinguish polytypes by XRD, we grew a sample under conditions which support rapid growth of misoriented BN flakes. The morphology of this sample, presented in the Supplementary Fig. 1, indicates the presence of flakes misaligned at large angles with respect to the substrate. The random distribution of flake orientations allows us to treat the sample similar to a powder, providing access to diffraction conditions for (100), (101) and (102) atomic planes. As a reference for hBN we used commercially available bulk crystals. To meet the diffraction conditions for bulk hBN we conducted measurements for a free-standing crystal. To enable such measurements, we specifically bent the hBN crystal so that one part adheres to the substrate, while the other protrudes vertically from the substrate.

In Fig. 2, we present the XRD results for the MOVPE-grown BN sample with randomly oriented flakes and commercially available bulk hBN. As can be seen in Fig. 2a, for the MOVPE-grown sample only rBN-related (101) and (102) peaks were detected with no clear evidence of hBN. A broad asymmetric background signal originates most likely from some unconnected single atomic layers giving signal from the (100) plane. Since the size of the X-ray beam is about 3×10 mm, the obtained signal is averaged over almost the whole sample. This leads to the conclusion that the sample is composed predominantly of rBN. In contrast to the MOVPE-grown sample, the $2\theta/\omega$ scan presented for bulk hBN crystal (Fig. 2b) reveals two peaks at positions corresponding to (100) and (101) planes in hBN with no evidence of rBN inclusions. Throughout the further analysis, we use these two samples as a reference for rBN and hBN.

UV-photoluminescence

Pure boron nitride emits light near its band edge in the UV-C range at about 6 eV, which is experimentally very challenging to measure¹⁸. However, in many samples also a defect-related mid-bandgap luminescence in the UV-B range is observed^{7,10,23,24,26,27,45}. Very characteristic and intensively studied is the color center emission at about 4.1 eV that is composed of a zero-phonon line with series of phonon replicas lines, which is often interpreted as a carbon dimer (C_2), for which carbon occupies the closest-neighbor boron and nitrogen sites, C_{B-N} ^{21,27,31–33}.

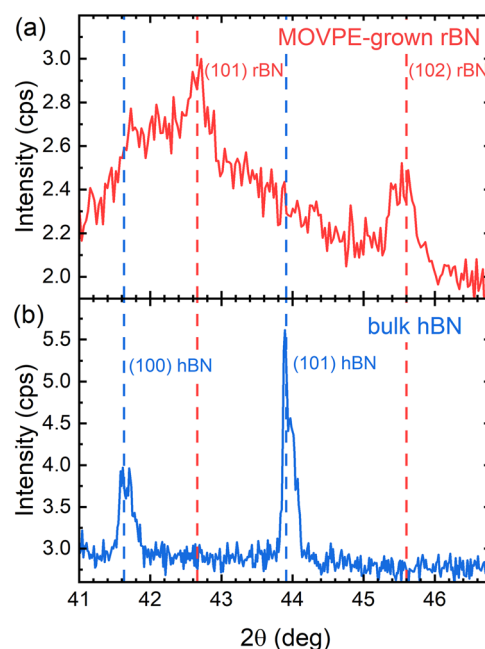


Fig. 2 | Identification of the reference samples polytype by X-ray diffraction. The X-ray diffraction $2\theta/\omega$ scans for (a) MOVPE-grown rBN and (b) free-standing, commercially available hBN bulk crystal measured as a reference. Blue and red dashed lines refer to the angular positions of hBN- and rBN-related XRD peaks, respectively.

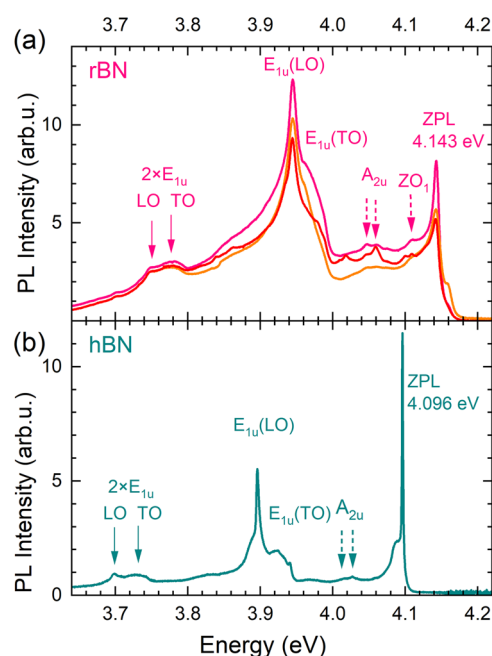


Fig. 3 | UV-B photoluminescence spectra collected for the reference samples. Photoluminescence spectra characteristic for (a) three MOVPE-grown samples containing rBN and (b) reference bulk hBN sample. Zero-phonon lines (ZPL) and selected phonon replicas characteristic for rBN and hBN are marked.

In fact, the photoluminescence (PL) spectra in the UV-B range observed for our samples exhibit strong zero-phonon lines (ZPL) with associated phonon replicas. In Fig. 3a we present the spectra of MOVPE-grown rBN reference sample, i.e. the one for which clearly evident (101) and (102) XRD peaks were observed (Fig. 2a), and two samples of similar spectra. The ZPL for rBN is observed at 4.143 eV (299.2 nm) which is blueshifted by $\Delta E_{ZPL} = 47$ meV in respect to hBN ZPL at 4.096 eV

(302.6 nm) presented in Fig. 3b. Both ZPLs are followed by similar shift of dominant phonon mode at ~ 200 meV. This shift is most probably a result of the different local surrounding of a defect in rBN and hBN (see Fig. 1). It is worth to note that in the case of bBN, two ZPLs were already reported at 4.14 eV and 4.16 eV²². The coincidence of the 4.14 eV line in bBN with the ZPL in rBN is not unexpected. As depicted in Fig. 1, the defect surroundings in rBN and bBN exhibit similarities. In both cases the carbon dimer is surrounded by only two atoms in adjacent atomic layers (one boron and one nitrogen for rBN and two boron (C_2 -a) or two nitrogen (C_2 -b) for bBN) while for hBN the carbon dimer neighbors with four atoms (two boron and two nitrogen). In some of our MOVPE-grown samples, a small peak at 4.16 eV is also observed, which suggests the presence of bBN inclusions in our epitaxial layers. Usually this contribution is very small, therefore, it does not influence our further interpretations.

The ZPLs for both types of samples are quite narrow. In the case of the reference sample (hBN), the ZPL is symmetric and the observed full width at half maximum (FWHM) is 4 meV (0.3 nm). After including instrumental broadening an about two times lower FWHM value can be estimated. In the case of the 299.2-nm line (assumed as rBN), the ZPL is asymmetric, broadened at the low-energy side, probably by Stokes phonon replicas. At the high energy side, it has a steep slope related to a Gaussian curve with the FWHM of 8 meV (0.7 nm) for the best, thick samples. Such a narrow width suggests a well-ordered crystal structure.

At the low energy side, the ZPLs are broadened most likely by interactions with acoustic phonons, which is also supported by our first principles calculations (see Supplementary Information for details Section II). The observed symmetric broadening is likely attributed to structural inhomogeneities within the sample, particularly due to turbostratic twisting of the atomic layers. These twists, along with grain boundaries and the resulting crystal dislocations, induce inhomogeneous strain, which may manifest as symmetric line broadening.

As presented in the Supplementary Information Section III, the lifetime of PL lines is of the order of 1 ns, therefore the homogenous broadening is negligible (of the order of a few μ eV). Since the broadening is much lower than the energy shift between ZPLs in the two materials ($\Delta E_{ZPL} = 47$ meV), the ΔE_{ZPL} must be due to a regular, well-defined change of the defect structure or ordering of the crystal such as a change of the polytype. The interaction between the covalently bonded atoms involves energies of many eV and the density functional theory calculation presented in ref. 31 shows that a modification of the defect structure (adding or removing neighboring atoms) changes the electronic states of defects significantly. Taking this into account, the ΔE_{ZPL} shift is much smaller in comparison to the energy expected for changes of covalent bonds of the defect. However, the order of magnitude of the ΔE_{ZPL} shift observed experimentally is right when considering the influence of translations between subsequent atomic layers in different polytypes, as evidenced by density functional theory (DFT) calculations³⁴.

It can be noticed that the PL background observed for MOVPE-grown samples is higher than for bulk BN. We believe that the broad background signal is most likely originating from a disorientation of atomic planes. Such a broad emission was reported in ref. 27 as D330 band.

The PL spectra for reference hBN and rBN presented in Fig. 3 exhibit a rich structure of phonon replicas. The most intensive replicas are related to the optically active E_{1u} mode. For the E_{1u} mode the atoms vibrate only in the c -plane (001), which is parallel to the sp^2 -BN layer^{5,46}. We do not expect that a difference in stacking would significantly influence such phonons. In fact, the E_{1u} (LO) replica observed in Fig. 3 has nearly the same energy 198 meV and 200 meV in rBN and hBN, respectively. Similar observations are noted for E_{1u} (TO) and two- E_{1u} (LO)-phonon replicas.

However, the situation changes for the A_{2u} mode, which represents vibrations perpendicular to the c -plane^{19,46,47}. Therefore, the alteration in stacking order is anticipated to significantly impact these modes, thus we experimentally observe shifts in their energies. The peaks in the A_{2u} region, indicated by dashed arrows, can be associated with phonons of energies 82 meV and 96 meV in rBN and 70 and 80 meV in hBN.

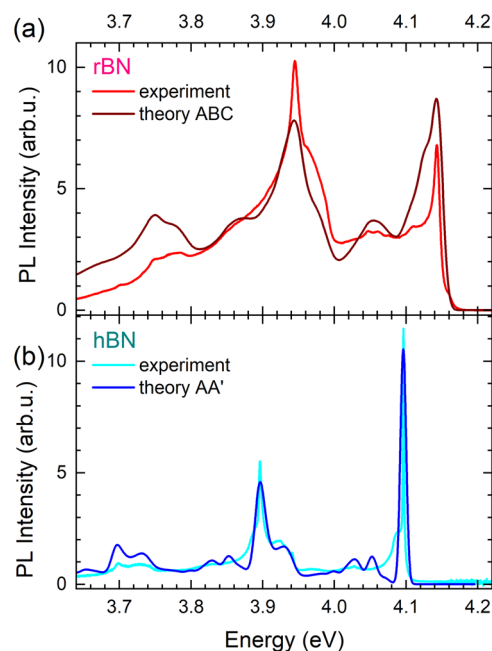


Fig. 4 | Calculated emission spectra of C_6C_8N defect in sp^2 -BN. Comparison of calculated emission spectra (dark lines) with experimental PL spectra (light lines) for (a) rBN and (b) hBN.

Time resolved luminescence shows that the lifetimes are of the order of 1 ns. For the hBN reference sample from Fig. 3b, the measured lifetimes are $\tau = (0.95 \pm 0.05)$ ns for both ZPL and E_{1u} (LO) phonon replica, as expected. In the case of MOVPE-grown samples a variation of lifetimes ranging from 0.7 to 0.9 ns was observed for the narrow-line samples with a pure 4.14-eV line (rBN). These values are quite similar to the PL lifetime of the hBN sample. Generally, even for samples with a mixed polytypic composition, which show spectral lines both at 4.14-eV (rBN) and 4.10-eV (hBN), lifetimes are above 0.5 ns. These samples are described in the next chapter “Application of UV luminescence analysis” and the obtained PL lifetimes were in the range 0.5–0.7 ns. In other semiconductors, a large number of defects usually causes fast nonradiative recombination^{48,49}. The fact that we do not observe large differences in PL emission lifetimes between the reference high-quality bulk hBN and different MOCVD-grown samples can be understood by small overlapping of wave functions of the color centers and other defects. Both the thermal escape and tunneling are suppressed by high barriers, so the color centers are not substantially sensitive to the presence of other defects. Similar lifetimes were also reported in literature^{10,27}.

To identify the defect responsible for the observed photoluminescence, we compared experimental results with theoretical calculations concerning emission within this spectral range³⁴. Our analysis pointed towards the carbon dimer C_6C_8N as the most promising candidate. Subsequently, we performed spin-polarized DFT calculations to determine the emission spectra of C_6C_8N defects in sp^2 -BN with various stacking orders. To this end, we developed a new multiconfiguration Δ SCF method that mimics the spin-adapted wave functions in the optical excited state force calculations (see Supplementary Information Section II). We applied it to a periodic model to simulate an infinite number of layers. The obtained emission lines were modeled taking into account an “effective” broadening effect, by assigning Gaussian functions to each active mode. The broadening may be due to a specific modification in a stacking pattern, such as turbostratic twisting. The resulting spectra for the C_6C_8N defect show a very good agreement with our experiments for both rBN and hBN, as presented in Fig. 4. The ZPL of the carbon dimer emission energy was obtained equal to 4.21 eV and 4.09 in rBN and hBN, respectively. This accuracy is excellent especially considering that the standard Δ SCF method typically underestimates the ZPL energies

of $C_B C_N$ by $\sim 0.5 \text{ eV}^{32}$. While a correction term has been applied to the excitation energy to address this discrepancy^{29,32}, it has not been applied to the forces. We found it crucial to accurately calculate the forces as well in order to closely match the experimental spectra of $C_B C_N$ in rBN, as demonstrated in Supplementary Fig. 2.

The interesting comparison between the calculated photoluminescence spectra lies in the phonon replicas. The main difference in the carbon dimer spectra for hBN and rBN can be observed in the range related to the phonons of A_{2u} symmetry which are out-of-plane phonon modes, as well as in the low-energy acoustic phonon range (see Supplementary Fig. 3). As expected, the contribution of the A_{2u} phonon in hBN is not observed, given that the $C_B C_N$ carbon defect incorporates within the sp^2 -plane. However, a contribution of the A_{2u} phonon in rBN, attributed to the out-of-plane distortion, was experimentally identified at 92.6 eV. This three-layer feature is also briefly mentioned in ref. 5. Another notable difference between hBN and rBN is the emergence of low-energy out-of-plane phonons at $\sim 20 \text{ meV}$. This effect is directly observable in our experiment as an asymmetric broadening of ZPL. Interestingly, no substantial spectral broadening has been observed for the defect emission in bBN²². This is due the C_{2v} symmetry of $C_B C_N$ defect in hBN and bBN, which prohibits the coupling of its A_1 electronic wavefunctions to A_2 phonons. In contrast, in rBN where the defect exhibits C_{1h} symmetry, this constrain is lifted, leading to spectral broadening as an indication of the absence of C_{2v} symmetry, or in other words, an asymmetric arrangement of neighboring layers. The cumulative effect of the out-of-plane phonons in rBN is manifested as an out-of-plane distortion in the excited state of $\sim 3^\circ$. Moreover, as outlined in this paragraph and depicted in Fig. 4, the experimental spectra of sp^2 -BN are in great agreement with the theoretically calculated spectra of the $C_B C_N$ defect. Hence, we attribute the observed spectra to the $C_B C_N$ defect. This interpretation, previously proposed, aligns with the omnipresence of carbon in MOVPE technology, where triethylboron, containing six carbon atoms per molecule is commonly employed. This factor contribute to luminescence across different spectral ranges^{8,27,50}. Additionally, a carbon dimer, the smallest possible carbon cluster, is intrinsically found in triethylboron, the boron precursor used during growth.

Application of UV luminescence analysis

As presented before, using MOVPE it is possible to grow rBN layers consisting of randomly oriented flakes as evidenced for the reference MOVPE-grown rBN sample (see Supplementary Fig. 1). However, for most of the applications flat, high-quality sp^2 -BN is required. This raises the question, whether it is possible to control polytypic composition of high-quality material by adjusting MOVPE growth conditions. To answer this question, we grew a series of samples using slightly different conditions, and we choose a set of three characteristic samples (S_1 , S_2 , S_3). More details about the growth process can be found in Experimental methods and characterization results (scanning electron microscopy, X-ray diffraction, Fourier-transform Infrared spectroscopy, photoluminescence) in Supplementary Information Section IV.

In Fig. 5, we present typical high-resolution transmission electron microscopy (HRTEM) images for samples S_1 , S_2 , and S_3 . Images of a larger area are presented in the Supplementary Information Section V. It is evident that all three polytypes are present in our samples. However, an analysis of multiple images for each sample suggests variations in polytypic composition among them. Sample S_1 (Fig. 5a) exhibits the highest contribution from rBN, with other polytypes being in the minority. Conversely, sample S_3 (Fig. 5c) displays the most significant amount of hBN, although other polytypes also contribute significantly. Sample S_2 demonstrates the least polytypic homogeneity, with all polytypes easily discernible.

Since HRTEM only provides an insight into the local crystal structure, we also performed top-view cathodoluminescence (CL) hyperspectral imaging along randomly chosen $5 \mu\text{m}$ -long lines with a spot size of 3 nm

and step size of 100 nm . As can be seen in Fig. 5d–f, luminescence is detected only in some segments of the line suggesting that the optical response of the material is indeed defect-related and that the defects are not equally distributed. Furthermore, intensity variations of the ZPL can be observed as well as changes of the ratio between the spectral components of rBN and hBN. A clear contribution originating from bBN at 4.16 eV could not be detected due to a low signal-to-noise ratio. To make the analysis more quantitative we deconvoluted the spectra into five components: rBN-related spectrum, hBN-related spectrum, and three broad Gaussian curves: at the maxima of the ZPL and at two of the strongest phonon replicas. Such background components can be physical explained as a twist of subsequent atomic layers which leads to the broadening of spectral lines as presented in ref. 34. By fitting the intensity of all five components, we could extract the contribution of rBN and hBN for each collected spectrum. This result can be found in the right panels of Fig. 5d–f and in the form of a video in the Supplementary Information. It is noteworthy that the intensity ratio of spectral components does not necessarily reflect the polytypic composition ratio, as the optical response and efficiency of defect creation may vary among different polytypes. The details of the fitting procedure can be found in the Supplementary Information Section VI. While the S_1 spectrum is dominated by rBN component (Fig. 5d), CL spectrum of the sample S_2 comprises a mixture of components associated with both rBN and hBN (Fig. 5e). The most intense hBN-related component we observed in sample S_3 , for which the widest areas of hBN were found in HRTEM.

To determine the average polytypic composition in each sample, we conducted macro-photoluminescence experiments with a spot size of $\sim 50 \mu\text{m}$. Consistent with CL findings, we observe varying intensity ratios of ZPLs at 4.14 eV and 4.10 eV, indicating differences in polytypic composition among the samples. As anticipated from TEM and CL analyses, sample S_1 exhibits a prominent peak at 4.14 eV with characteristic phonon replicas (Fig. 5g) suggesting that the sample is indeed dominantly rBN. In the PL spectra of samples S_2 and S_3 (Fig. 5h, i), distinct and well-resolved ZPLs are observed at both energies: 4.14 eV and 4.10 eV. The changing intensity ratio of these peaks suggests a varying composition with a higher fraction of hBN in sample S_3 . Furthermore, collecting macro-PL spectra over a wide spatial area allowed us to detect for all the samples (Fig. 5g–i) a very subtle signal at 4.16 eV associated with bBN, consistent with the presence of bBN observed in HRTEM images.

By comparing these three samples, we demonstrate that it is possible to obtain a different composition ratio between hBN and rBN by using wafer-scale MOVPE growth technology. However, the major factor that determines a specific polytype formation remains an open question. Several hypotheses have been proposed, including the influence of carbon contamination from metalorganic precursors and substrate pre-treatment, which yields specific atomic step edges^{51,52}. Our results suggest that the ramping time to high temperatures may also be important. However, to disentangle all the possible factors more experimental work is needed, for which the presented method of polytype identification will be of great importance. Although more work is needed to demonstrate the precise control over the growth of a desired polytype in flat, epitaxial sp^2 -BN layers, the presented results suggest that this goal may be achievable by MOVPE growth of sp^2 -BN on sapphire, which could open up the way for scalable growth of different BN polytypes using a well-established, industrial growth method.

In summary, we have demonstrated that different sp^2 -BN polytypes can be grown by MOVPE and we present a facile way to distinguish between these polytypes. We have shown that the characteristic, impurity-related UV photoluminescence with a ZPL at about 4.1 eV is influenced by the structural polytype of the material. The observed lines are quite narrow and shift significantly with a change of stacking order. We observed emission energies for ZPLs at 4.096 eV and 4.143 eV, which, according to XRD results, can be ascribed to defect emission in hBN and rBN, respectively. The energy difference of $\Delta E_{\text{ZPL}} = 47 \text{ meV}$ is much larger than the line widths (FWHM about 8 meV), which allows us to clearly distinguish between sp^2 -BN polytypes. Cathodoluminescence measurements with sub-micrometer

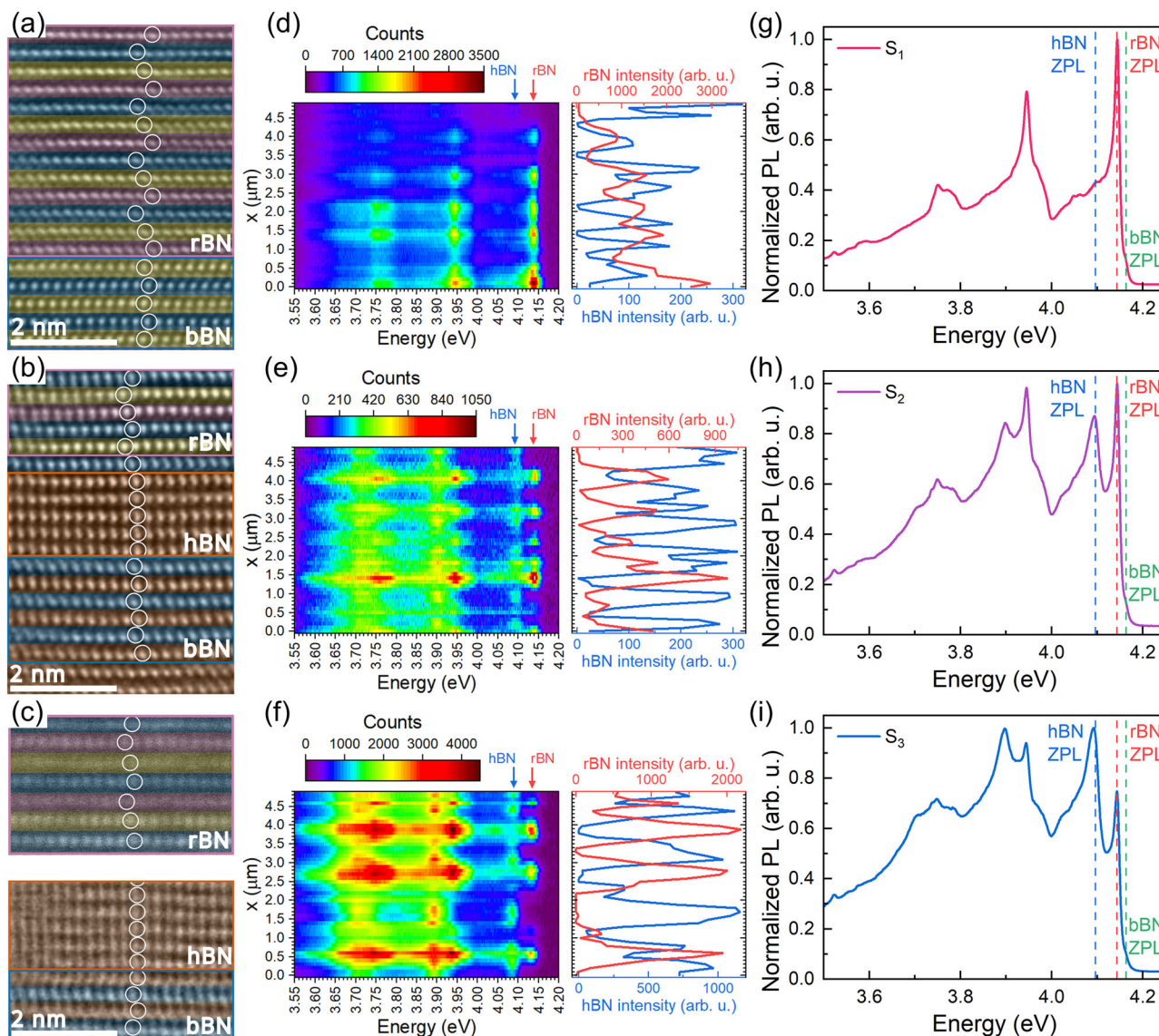


Fig. 5 | Polytype identification of MOVPE-grown samples S_1 , S_2 , S_3 conducted with different experimental techniques. Exemplary transmission electron microscopy (TEM) pictures for the samples (a) S_1 , (b) S_2 , (c) S_3 . The overlaid colors depict atomic layers which are aligned similarly. The white rings are guide to the eyes. Hyperspectral line-scans of cathodoluminescence collected along a 5 μm -long line on the samples (d) S_1 , (e) S_2 , (f) S_3 . Curves in the panel on the right side of the map

indicate the intensity of the spectral components which correspond to rBN (red) and hBN (blue). **g–i** Macro-photoluminescence spectra measured at 8 K for epitaxial samples with different polytypic composition. Blue and red arrows in (d–f) indicate the position of zero-phonon lines for hBN and rBN, respectively. Dashed lines in (g–i) indicate the position of zero-phonon lines for hBN (blue), rBN (red) and bBN (green).

resolution facilitate a deconvolution of the overall spectra to estimate the local ratio of hBN/rBN - related peaks for samples consisting of a mixture of polytypes. To support our experimental findings, we have performed first principles DFT calculations that show that all characteristic features of the spectra can be reproduced when considering a C_BC_N (C_2 -dimer) defect embedded in different sp^2 -BN polytypes. Although we utilized the C_BC_N defect emission to sense the stacking sequence of sp^2 -BN, it is likely that other defects are also sensitive to polytypism.

While in the case of bulk sp^2 -BN crystal growth, the most commonly obtained polytype is hBN, for epitaxial growth, it is possible to obtain both hBN and rBN. We demonstrate that by MOVPE one can grow high-quality, flat BN layers with different polytypic composition, as evidenced by HRTEM, cathodoluminescence and macro photoluminescence, which are techniques that cover a large range of length scales. Therefore, our results not only present a facile way to distinguish between different sp^2 -BN polytypes, but also constitutes a first step towards the deterministic control over the growth of sp^2 -BN polytypes on the wafer scale.

Experimental methods

Samples

The boron nitride layers on sapphire substrates were grown using an Aixtron CCS 3 $\times$ 2" MOVPE system designed for the growth of nitride compounds. The reference epitaxial rBN samples were grown on 70 nm-thick AlN template at $T = 1025\text{--}1100^\circ\text{C}$ using Continuous Flow Growth (CFG) mode^{53,54}. The temperature was controlled by ARGUS optical pyrometer. High-quality samples were grown using Two-stage Epitaxy growth protocol on 2-inch sapphire substrates with 0.6° towards m -plane misorientation angle^{55,56}. CFG buffer layer was grown for 10 min at 1300°C for each sample. After this step, the temperature was ramped up to 1400°C where the Flow Modulation Epitaxy took place. The ramping temperature time varied between samples: S_1 – 15 min, S_2 – 8 min, S_3 – 5 min. The temperature ramping was the only growth parameter which was varied, which also shows that even minor adjustments in the growth process can influence the polytypic composition of the final material, underscoring the need for further research to achieve precise control over the MOVPE growth of

specific polytypes. The reference bulk hBN sample was provided by HQ Graphene company. None of the samples in this study underwent special treatment to increase carbon defect concentrations. In MOVPE, carbon atoms are inherently present during growth (e.g., ethyl groups in TEB), leading to the formation of carbon-related defects in the crystal structure.

X-ray diffraction

XRD $2\theta/\omega$ scans were measured with a Panalitical X'Pert setup with standard CuK α X-ray source. The beam was formed by the symmetrical Bragg–Brentano optics. To obtain rocking curves of (101) and (102) reflections for the reference MOVPE-grown rBN the offset of 7° in respect to diffraction conditions for sapphire substrate was established to avoid strong signal from crystalline substrate and observe diffraction on misoriented rBN crystallites. To observe diffraction on hBN bulk flake it was specifically bent so that one part adheres to Si/SiO $_2$ substrate, while the other protrudes vertically from the substrate.

First principles simulations

The first principles calculations were carried out within the Vienna ab initio simulation package code^{57,58}, using a plane wave basis and projector augmented wave potentials^{59,60}. The defects were embedded in a 9×9 bilayer supercell model to avoid the interactions of defect with its periodic images. The Γ -point approximation was used for Brillouin-zone sampling. We used the DFT-D3 method of Grimme⁶¹ for dispersion correction of the vdW interaction. The hybrid density functional of Heyd, Scuseria, and Ernzerhof⁶² was used to optimize the geometries and electronic properties with modified mixing parameter $\alpha = 0.32$ of Fock exchange. The cutoff energy of plane-wave is 450 eV and all ions were allowed to relax until the Hellman–Feynman forces were less than $0.01 \text{ eV}\text{\AA}^{-1}$. The excited states were calculated with a new multiconfiguration Δ SCF method, presented in Supplementary Information Section II.

Transmission electron microscopy

The electron transparent samples for cross-section imaging were prepared using focused gallium ion beam in a FEI Helios NanoLab 600 system (FIB). HRTEM investigations were performed using an image corrected Titan Cubed 80–300 microscope operating at 300 kV.

Photoluminescence

For photoluminescence (PL) spectroscopy, the samples were excited with light generated as third harmonic (in the range 4.2–5.1 eV) of a Ti:Sapphire laser. Two BBO crystals were used to obtain the short-wavelength light. A Schwarzschild mirror objective was used for micro-PL spectroscopy. The spectra were recorded with an Acton 300-mm spectrometer (grating of 1800 g/mm) and a Hamamatsu CCD camera. The experimental resolution, determined as FWHM of mercury lines, was 0.15 nm (about 2 meV). The time-resolved PL (TRPL) was measured using a Hamamatsu streak camera with quartz optics (transmission up to 200 nm). To obtain a better signal-to-noise ratio macro photoluminescence spectra were acquired from high-quality samples using the 4th harmonic of a continuous wave mode-locked Ti:Sapphire laser (196 nm, spot size 50 μm) at 8 K. Spectra were recorded with a Czerny–Turner monochromator ($f = 300 \text{ mm}$) featuring a 1800 grooves/mm grating and a back-illuminated CCD camera (Andor Newton 920).

Cathodoluminescence

To study local optical properties Hitachi SU-70 scanning electron microscope equipped with Gatan MonoCL3 cathodoluminescence (CL) spectrometer was used. To avoid samples electron charging, samples were delaminated from sapphire substrate and transferred onto p -doped Si/SiO $_2$ substrate⁶³. After layer transfer no wrinkles characteristic for as-grown samples were present. CL line-scans collected using hyperspectral mode with the CCD camera were used to record the local energy changes of the spectral features in a selected area on the sample surface. Series of spectra were collected along the

specified 5 μm long lines with the step of about 100 nm and collecting time per pixel – 40 s. All the collected spectra were measured using accelerating voltage of 5 kV, the beam current of 3 nA (the parameters were optimized for the best intensity to spatial resolution) at temperature of 5 K and with use of diffraction grating with 1200 l/mm optimized at 300 nm.

Data availability

The authors declare that the data supporting the findings are available at: <https://doi.org/10.18150/FNNWXN>.

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Author contributions

J.I., K.P.K., A.G., J.B., A.W. conceived of the presented idea. S.L., A.P., A.G. developed the theoretical formalism and performed calculations. J.I., K.P.K., M.T., A.K.D., P.T., I.R., M.B., M.W., S.K., A.R., B.J.K. carried out the experiments. J.I., K.P.K., M.T., P.T., I.R. analyzed the experimental data. J.I., K.P.K., P.T., I.R., S.L., A.P. visualized obtained data. J.I., A.K.D. grew the samples. J.I., K.P.K., S.L., A.P. prepared original draft. G.K., A.G., J.B., A.W. reviewed and edited manuscript. J.I. administrated the project. J.I., P.T., A.P., A.G., J.B., A.W. were responsible for funding acquisition. All authors discussed the results and contributed to the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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