Hexagonal boron nitride: a review on selfstanding crystals synthesis towards 2D nanosheets

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Abstract
Hexagonal boron nitride (hBN) is emerging as essential for 2D material-based technologies. New optoelectronic applications require high crystal quality hBN with low defect density and contamination. While vapor-phase processes like chemical vapor deposition can produce large-area hBN thin films, self-standing hexagonal boron nitride crystals provide exfoliated nanosheets of very high quality. The synthesis of these self-standing hBN crystals prior to the exfoliation process is the focus of this review. Theses syntheses are described with emphasis on crystal size, purity, and defects. These considerations are based on various recently developed physical studies, including optical characterizations such as luminescence measurements highlighting the crystallinity and structural defects of hBN crystals.

1. Introduction
The development of van der Waals heterostructures and novel electro-photonic applications have highlighted the outstanding properties of 2D hexagonal Boron Nitride (hBN). The first isolation of its few-atomic-layer thick form in 2008 by mechanical exfoliation [1] gave the 2D materials family its only insulating material to date. Exfoliated hBN still show the properties of bulk hBN, a large bandgap and bright luminescence in the deep UV [2], an excellent chemical inertness and oxidation resistance [3, 4], a high mechanical robustness along with low density and high thermal conductivity [5]. From its nanoscale nature, exfoliated hBN inherits low dimensional quantum confinement providing specific electronic and optical properties. Its high surface to volume ratio also enhances its mechanical and chemical characteristics. Its atomically flat surface, free of dangling bonds limits hBN interactions with adjacent materials and makes hBN a perfect passivation layer for encapsulation [6] and as thermal interface for van der Waals heterostructures [7]. As a substrate, hBN highly enhances the electric properties of graphene and other 2D materials [8, 9]. It was reported as a perfect candidate for supporting 1D carbon nanotubes as well [10].

hBN monolayer also presents unique properties as active layer. They show a piezoelectric response [11], behave as hyperbolic materials for nanophotonics [12] exhibiting single photon emission (SPE) at room temperature and spin-photon coupling for quantum technologies. For reviews on these subjects, see [13–15]. Functionalized hBN has also received attention for energy conversion and storage (for a recent review, see [16]). These attractive properties already gave rise to several sensor devices integrating hBN as key feature such as UV emitter and detector [17, 18], uncooled terahertz photodetectors [19, 20], or neutron detector [21, 22]. Electronic devices, from tunneling field effect transistors [23, 24] to resistive switching memory [25] were reported as well. In general, the chemical purity of single crystalline hBN is a key-issue. Indeed, any defect in the crystal lattice or contaminant will locally deform the hBN atomically flat surface and modify its bandstructure. However, these defects could be controlled and engineered for specific application such as SPE [26], they are most often unwanted [27] and synthesis methods focus on reducing their occurrence.
Table 1. Solvothermal synthesis process details.

| Group       | Reference | Temperature °C | Dwell time h | Precursors/solvents                      |
|-------------|-----------|----------------|--------------|-----------------------------------------|
| Hao et al   | [46]      | 200–500        | 48–72        | BBr + Li3N/Benzene                      |
| Chen et al  | [47]      | 350            | 12–72        | BBr + NaN3/Benzene                      |
| Gu et al    | [48]      | 700            | 6 h          | NaBF4 + NaNH2/LiBr + Na                 |
| Yano et al  | [49]      | 800            | 24 h         | B+NaN3/Na                               |

Several routes have been developed for hBN syntheses. For economic considerations, commercial hBN is traditionally produced by combustion synthesis [28]. Microplasma dissociation [29] and numerous chemical vapor deposition (CVD) processes were proposed (for a review, see [30]). Vapor deposition processes produce wafer-scale polycrystalline hBN. The grain size is generally up to several tens of micrometers with a triangular shape. Vapor deposited films grow on specific materials (mostly metals) and need to be transferred on the target substrate for industrial process integration. Wafer-scale single crystal hBN synthesis has recently been achieved on copper substrate (see [31, 32] for atomistic-modelling). To date, none of these techniques led to the high crystalline quality and purity of freestanding hBN crystals. Freestanding hBN optical properties stand out from any other hBN sources [33, 34] and are still unrivaled for electronic transport and van der Waals heterostructures applications [19, 35]. Yet, crystal size reaching over the millimeter-scale remain a challenge. Their quality and homogeneity are still being investigated and potential for improvement does exist. For device integration, those freestanding hBN crystals need to be exfoliated into nanosheets. This matter is not in the scope of the current paper but a recent review is dedicated to exfoliation and device integration of hBN [36].

This paper will only focus on the syntheses of freestanding hBN crystals. First, low temperature hBN synthesis are briefly described. Then, growth of freestanding hBN single crystals by high pressure high temperature (HPHT) [27], atmospheric pressure high temperature (APHT) [37] and polymer derived ceramic (PDC) [38] methods are reviewed. The processes are studied in terms of size, purity and crystal quality of final hBN. Mostly based on recent luminescence and other optical characterization studies, these results are a basis for further process understanding and optimization.

2. Low temperature growth processes

Boron nitride has been used in the industry for more than a century. Among numerous applications, it can be found as lubricant, reinforcement in composites or texture agent for cosmetics. For these applications, price is the key parameter and low temperature synthesis are preferred. Crystal size and quality are not considered. Some new fields, such as hBN inks for printable devices [39], may require hBN nanoparticles. They can be obtained by liquid phase exfoliation from bulk hBN followed by sonication or by synthesis at low temperature. The low temperature synthesis methods are portrayed in the next paragraphs.

2.1. Combustion synthesis

Combustion synthesis gave the first forms of boron nitride as early as 1842 [40]. Nowadays, it is the most important source of commercial hBN powder thanks to a high yield and a fast reaction. As such, little information is given on the process but earlier litterature can provide some insight [28, 41, 42]. Combustion synthesis is based on the nitridation of boron oxide [43, 44]. Traditionally, boric acid (B2O3) was mixed with urea (CH4N2O) and heated between 500 °C and 1000 °C but urea can now be replaced by N2 gas [45]. Pyrolytic hBN exhibits broad XRD peaks demonstrating low crystal quality and presence of turbostratic boron nitride. The crystallite size ranges from 100 nm to 1 µm. The hBN powder referred to as commercial hBN in the following sections is produced by combustion synthesis.

2.2. Solvothermal synthesis

Solvothermal synthesis benefits from low temperature and ease of preparation to produce large quantity of low-priced micrometer to nanometer-sized hBN particles (as small as 1 nm [46]). Two precursors of BN are mixed with a liquid solvent and heated at moderate temperatures (generally below 500 °C) in an autoclave. Table 1 gathers some details and references on these processes. Solvothermal hBN exhibits broad XRD peaks demonstrating poor crystal quality [47]. Turbostratic boron nitride is often reported along with hBN.
3. High temperature growth techniques

3.1. Description of the different processes

The current reference of selfstanding hexagonal boron nitride is provided by T. Taniguchi and K. Watanabe at NIMS (National Institute for Material Science in Tsukuba, Japan). Growing interest in hBN led two other research groups to explore the synthesis of large area hBN single crystals, namely KSU (Kansas State University in Kansas, USA) and LMI-Mateis (Laboratoire des Multimatériaux et Interfaces and Mateis laboratory, in Lyon, France). Each group has developed or optimized its own method. Figure 1 gives an overview of different samples from these three groups. The process conditions cover a wide range of temperature, pressure and duration (figure 2). Boron nitride has a very high melting temperature (over 3000 °C [50]), which is lowered when BN is mixed with a solvent. Therefore, all reported methods of hBN freestanding crystal synthesis are based on the use of a solvent also referred to as catalyst or crystallization promoter.

3.1.1. Solvent selection for high temperature processes

Wentorf, who first reported the synthesis of cubic BN, claimed that alkali and alkali-earth metals were the best catalysts for cubic BN synthesis and among them, the lower the atomic weight, the better [53]. This work paved the way for cBN and later hBN single crystals synthesis. It also sparked the interest in alkali and alkali-earth solvents, which have been predominantly used since for hBN synthesis. Reportedly, barium nitride (Ba₃N₂) [27, 54, 55], lithium nitride (Li₃N) [38, 56–59], lithium bromide (LiBr) [48], sodium [49] and magnesium [60]. Alkali and alkali-earth solvents have low melting temperature, below 1000 °C that
ensures high diffusivity through the high temperature treatments. Thanks to their efficiency, low solvent/BN atomic ratios are needed (of less or of the order of 1:1 [56, 60, 61]).

Nakano et al showed experimentally that lithium and calcium compounds were indeed good solvents [62] before their successors Watanabe et al began using barium nitride as their regular solvent [51, 54, 63]. Barium nitride is sometimes mixed with Li$_3$BN$_2$ for cBN [64, 65] as well as hBN [27, 54, 61] synthesis. The efficiency of alkali and alkali-earth solvents is sometimes granted to the formation and later decomposition of alkali–BN intermediate compound such as, Li$_3$BN$_2$ [38, 56] Ba$_3$B$_2$N$_4$ [54] and MgBN$_3$, MgBN$_2$ [60] or Mg$_2$B$_2$N$_4$ [64, 66]. The formation of Li$_3$BN$_2$ has been observed and well documented [67–69]. The compounds involving magnesium and barium, however, are more controversial. Anyway, the overall mechanism involving an intermediate compound remains an unresolved matter. The high sensitivity of such solvents to oxidation makes them unsuitable for preparation in ambient environment and they should be handled carefully in a moisture free environment to prevent contamination of the final hBN. Indeed, regardless of the solvent, its contamination (by foreign C and O atoms) seem to end up in the final hBN crystals [51, 55]. The high solubility of BN in alkali and alkali-earth solvents leads to crystallization of hBN in the solvent matrix. After cooling, dissolution of the solvent matrix is necessary to free the crystals. Dissolution is traditionally carried out using hot Aqua Regia [54, 70, 71].

The metallic alloys' ability to dissolve BN is much lower than alkali compounds'. Hence, much more metal solvent is needed in regard to alkali solvent. Typically, a weight ratio of 20:1 is considered [72, 73]. An advantage of these solvents is that a metal could be chosen for its propensity to effectively entrap C and O contaminants. Molybdenum was reported as a possible C-getter [61]. Ishii and Sato reported the first metal solvent hBN synthesis in 1982 with molten silicium [74]. The obtained flakes were of acceptable size (up to 2 mm) but of variable crystalline quality and purity (pale yellow color instead of clear transparent), and metal solvents were put aside. Metal alloy solvents have high melting temperature, over 1100 °C [75, 76]. Yet, their chemical stability makes them more practical solvents than alkali systems, and this fact lead Watanabe et al to perform a first HPHT process using pure nickel as solvent [71] providing only tens of microns wide hBN crystals. This experiment brought the idea of an atmospheric pressure hBN synthesis using Ni and Ni–Mo solvents [61]. Taniguchi et al showed that the higher the boron and nitrogen solubility in the alloy, the bigger the hBN crystals produced. Yet, nitrogen solubility is low in most metals and no Metal–BN complex formation occurs. Molybdenum was first used for its propensity to dissolve nitrogen [61, 77], and chromium was later reported to be a better solvent for N atoms [72]. Since then, chromium has been used as the nitrogen solvent agent in every metallic alloy solvents reported: Ni–Cr [37, 73, 78, 79], Co–Cr [77], Fe–Cr [52, 80, 81]. Iron was chosen in replacement of nickel for its lower cost [52] and gave similar hBN.

### 3.1.2. High pressure high temperature synthesis

HPHT process needs high mechanical pressure provided by a hydraulic press [82], a closed Mo or BN crucible with BN source and a solvent. Reportedly alkali based lithium nitride [83] or alkali-earth barium nitride [54], magnesium [60] or even nickel [71] were used as solvent. Pressure ranges from 2.5 GPa [60] to 5.5 GPa [54] and the BN phase diagram has been studied up to 10 GPa using this technique [50]. Indeed, numerous early HPHT studies aiming at drawing the BN phase or P–T diagram have been carried out with and without solvent [50, 66, 83–85]. In particular, an early comprehensive analysis of the reaction path at HPHT by TGA/DSC coupled with in situ synchrotron XRD gave an insight of the possible growth mechanisms of BN phases in the BN/Li$_3$N system at HPHT [86]. Yet, hBN quality and properties was seldom reported. Until Watanabe et al founding article pointing out its luminescence properties [27], hBN was discarded as a waste [82].

HPHT method is also referred to as temperature gradient method. The temperature gradient in the HPHT chamber is inherent to the press geometry and difficult to control. This gradient is often mentioned by Taniguchi et al but is never quantified, neither are the exact temperature and duration of the process (table 2). For Zhigadlo, the temperature difference is estimated at 70 °C between the top and bottom ends of the crucible at 1450 °C [87]. In the NIMS’ press, the BN source dissolves at the bottom end of the crucible and crystallizes at his top end thanks to the temperature decrease [63] (figure 3 in the case of cBN synthesis).

#### Table 2. HPHT process parameters.

| Group      | Reference | Max temperature °C | High temperature process duration h | Pressure GPa | Solvent   |
|------------|-----------|--------------------|-------------------------------------|--------------|-----------|
| NIMS       | [27, 54, 55] | 1500–1750          | 20–80                               | 4–5.5        | BaBN      |
| NIMS       | [71]      | 1300–1900          | 0.3                                 | 4.5–6        | Ni        |
| Zhigadlo   | [60]      | 1950               | 0.5–2                               | 2.5          | Mg        |

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Figure 3. Growth cell chamber: (a) grown cBN crystal, (b) solvent, (c) undissolved hBN source transformed into cBN, (d) Mo sample chamber. Reprinted from [64], Copyright (2001), with permission from Elsevier.

| Group     | Reference | Max temperature °C | High temperature process duration h | Solvent       |
|-----------|-----------|---------------------|-------------------------------------|---------------|
| NIMS      | [74]      | 1850                | 2                                   | Si            |
| NIMS      | [61]      | 1430                | 70                                  | Ni, Ni–Mo     |
| NIMS      | [72]      | 1430                | 70                                  | Ni, Ni–Cr     |
| KSU       | [37]      | 1500                | 100–175                             | Ni–Cr         |
| KSU       | [78]      | 1500                | 100                                 | Ni–Cr         |
| KSU       | [52]      | 1550                | 75                                  | Fe–Cr         |
| KSU       | [79]      | 1550                | 75                                  | Ni–Cr         |
| KSU       | [80]      | 1550                | 50                                  | Fe–Cr         |
| KSU       | [81]      | 1550                | 62                                  | Fe–Cr         |
| SEU-FEI   | [88]      | 1450                | 75                                  | Ni–Cr         |

Long soaking time (>20 h for Taniguchi et al) and a careful choice of the soak temperature (between 1500 °C and 1750 °C with BaBN solvent) allows BN long range diffusion through the barium boron nitride layer [27]. In Zhigadlo’s system, B and BN powders are closely mixed with Mg and only short range diffusion occurs allowing for a shorter process (4 h overall process duration) [60]. The whole HPHT assembly with solvent + BN system in a Mo or BN sealed crucible makes it free from external contamination such as furnace or gas contamination. However, the contamination is then dependent on the preparation process which becomes critical when using alkali or alkali-earth solvents [54].

3.1.3. Atmospheric pressure high temperature synthesis

Metal solvent hBN growth under APHT is performed in a horizontal tube furnace under gas flow, allowing the use of N₂ gas as the nitrogen source. The APHT process, originally developed by Kubota et al [72] was improved by Hoffman et al with Ni–Cr solvent [37] and Fe–Cr later [52, 80] (table 3). Boron and nitrogen sources are traditionally BN powder or crucible. However, pure boron powder can also be used as boron source and more specifically monoisotopic B powder leading to isotopically enriched and monoisotopic hBN [78–80] with specific properties [35, 89]. Metal solvent under atmospheric pressure method needs high temperature dwell time as long as 48 h to ensure the dissolution of B and N atoms and saturation of the alloy. Ni–Cr is the best and most widely employed metal solvent reported so far. Optimized synthesis with Ni–Cr has a soaking step of 24 h at 1500 °C [37, 88]. Then, as the temperature is slowly lowered to the temperature of crystallization (for Ni–Cr and Fe–Cr, between 1550 °C and 1400 °C [52, 79, 80]), the BN supersaturation increases in the liquid metal solvent. This supersaturation drives the crystallization of hBN. The metallic alloy is originally placed upon the BN source, therefore, long range diffusion takes place for the hBN recrystallization on top of the metal solvent. The crystallisation occurs at temperatures above the eutectic point of the alloys so that the crystals may grow on top of a liquid phase. The liquid ensures a high diffusivity and will further solidify and deform. Strains can be induced into the hBN upon solidification [73] but the crystals are then easily retrieved directly from the ingot surface. The open system is prone to contamination from gas flow or furnace elements. Attention should be payed to the formation of a passivating layer on top
of the liquid that could hinder the formation of the crystals or prevent it totally in the cases of Ti or Si solvent [90].

3.1.4. Polymer derived ceramics for hBN

PDC route uses a reactive molecular precursor containing B and N atoms along with other elements instead of BN or pure B powder with nitrogen based gas (see table 4). The precursor has a chemical activity and tends to degrade to form BN at low temperature. The precursor behaves as a metastable BN phase that will recrystallize into hBN during the heating phase, as confirmed by in-situ XRD and TGA/DSC [93] and similar to the mechanisms reported in [91]. Reported hBN precursors are ammonia borane (H$_3$NBH$_3$) [91, 94] and a borazine derivative [38, 56–59]. Borazine stands out as it shares its hexagonal structure with target hBN (figure 4) and borazine has indeed been widely used for CVD hBN film generation [95–97]. Liquid borazine is very volatile at room temperature, hence, for crystal growth, its polymeric form is preferred and is obtained as a white powder after a polymerization process [98]. The formation of hBN by polymeric precursors is greatly enhanced using alkaline based solvent such as Li$_3$N [56, 57], promoting the mobility of the species once melted [86]. Solvent and precursors are previously mixed so that no long range diffusion occurs. The technique is fast (crystals >1 mm reported in processes as fast as 8 h [38]). The thermal treatment can be achieved by different methods, spark plasma sintering (SPS) [56, 92], pressure controlled furnace (PCF) [38], gas pressure sintering (GPS) or by heating at the atmospheric pressure [91]. At atmospheric pressure, the strong release of gaseous species during the thermal process tends to form a hBN foam [91]. A pressure of 90 MPa [56] or 180 MPa [38] is able to densify the product. PCF and atmospheric heating processes are open systems and therefore, without the proper precautions, may lead to ambient contamination. PDC route is a fast and versatile route, but greatest care about contamination sources should be taken throughout the process. In addition to alkali solvents, the precursors used are generally very sensitive to contamination as well. Polyborazylene is reactive and highly sensitive to moisture and air [99].

3.2. Crystal size and optimization

Temperatures as low as 700 °C ([48]) have been reported for hBN synthesis. Nevertheless, a temperature over 1500 °C seems to be necessary for growing single crystals with lateral size larger than 1 mm (see figure 5, lowest reported growth temperature for millimeter-scale crystals [37, 80]). Often found in hBN-related bibliography, the word flake refers to polycrystalline freestanding hBN crystal as presented in figure 1. Reported flakes of several millimeters generally contain single crystals over 1 mm and are summarized for the main groups in table 5.

Considering the crystal lateral size, an optimal temperature is reported either with PDC [56] or metal flux method [37]. Edgar et al reported that the thickness and shape of the crystals vary with the soak

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**Table 4. PDC process parameters.**

| Group   | Reference | Temperature $^\circ$C | Pressure MPa | Dwell time h | Precursor/solvent          | Furnace type |
|---------|-----------|------------------------|--------------|--------------|-----------------------------|--------------|
| Wang et al [91] | 1300 | Atm | 0 | Ammonia borane/O | Tube furnace |
| LMI [92] | 1800 | 90 | 1 | Polyborazylene/Li$_3$N | SPS |
| LMI [56] | 1800 | 90 | 6 | Polyborazylene/Li$_3$N | SPS |
| LMI [38] | 1800 | 180 | 8 | Polyborazylene/Li$_3$N | PCF |
| LMI [59] | 2000 | 9.5 | 5 | Polyborazylene/Li$_3$N | GPS |

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**Figure 4.** Borazine polymerization. Reproduced with permission from [93].
Figure 5. Flake size vs process temperature from various papers and research groups.

Table 5. Reported flake size from different growth methods and groups.

| Group     | Reference       | Growth method | Solvent type        | Max. lateral flake size |
|-----------|-----------------|---------------|---------------------|-------------------------|
| NIMS      | [27, 54, 55]    | HPHT          | Alkali              | >500 µm                 |
| Zhigadlo  | [60]            | HPHT          | Alkali-earth        | 2.5 mm                  |
| KSU       | [37, 52, 79–81] | APHT          | Metal               | 1–7 mm                  |
| SEU-FEI   | [88]            | APHT          | Metal + C           | >500 µm                 |
| LMI       | [38]            | PDC-PCF       | Alkali              | >1 mm                   |

temperature. At 1500 °C, crystals are hexagonal and thick with low lateral size, whereas at 1700 °C, hBN crystals are mostly triangular, thinner and with larger lateral size. For this process, maximal crystal thickness was obtained with soak times of 24–48 h. With HPHT, a minimum temperature of 1700 °C is necessary for growing well crystallized hBN with Mg solvent [60]. As shown in figure 6(A), Zhang et al reported that adding carbon in the metal solvent produces larger hBN flakes and set the optimized weight percentage at 1.8 %wt. Indeed, EDS mapping shows that in presence of carbon, N atoms are more present in the Ni-rich phase with no difference with the Cr-rich phase. The authors also claim that carbon atoms act as a reducing agent for BOx species that hinder the nitrogen diffusion. Hence, carbon addition enhances the diffusion of the nitrogen toward the solvent and its subsequent dissolution. Higher nitrogen concentration in the solvent would then lead to larger hBN, as originally discussed by Kubota et al [61].

The only reported hBN crystals with lateral size exceeding the millimeter in less than 12 h were grown using alkali [38], alkali-earth [60] or Si solvent [74] and short range diffusion. The crystal size distribution is very wide and ranges from 50 to 1000 µm² at 1800 °C in PDC coupled with SPS [56] and from 300 to 4000 µm² at 1450 °C in APHT [88] (figure 6). Those size distributions were obtained with respectively 8 h and 75 h of thermal process and share a similar profile. They suggest a random nucleation over a wide range of temperatures. The control of nucleation is critical. To monitor it, a wide range of cooling rates were explored in APHT, from 0.5 °C h⁻¹ to 10 °C h⁻¹ [37, 79]. The lowest cooling rates seem to yield the largest crystal but the slow cooling is limited by the need for a short overall process duration. In an attempt to control nucleation, liquid phase epitaxy with BaBN solvent in HPHT apparatus have been reported but gave only little hBN crystal <10 µm [61]. It is a possible way to minimize nucleation and favor large hBN crystals that can be explored in the future. Seeded growth has already been efficiently used for the growth of cBN in the HPHT apparatus with Li₃BN₂ solvent [100] (figure 7), but never for hBN [37]. Similarly, no study of the pressure influence on crystal characteristics have yet been reported.

The influence of the process parameters were individually explored in order to produce the largest hBN crystals. Now, a global understanding will be essential for improving the different processes. It is also important to note that the very definition of size is an issue. There is no consensus on how to measure it. Some authors provided the statistical size distribution over a random sample [56, 88], but most often only the order of magnitude or a scale over the image of the biggest flake obtained is given. Nevertheless, the lack of uniformity in the measurements does not mitigate the significant progress that was made increasing hBN crystal size both for APHT and PDC methods following on from HPHT with more potential for scaling.
Each team is able to monitor its process with its own understanding and definition of size. The largest single crystals can be selected for applications requiring it and potential for further optimization does exist. To conclude, despite the notable differences between the types of processes in terms of temperature, pressure or solvent’s nature, common tendencies and mechanisms are observed. Optimization of the flake size for scalable device integration needs to be considered along with the reduction of defect and contaminant densities which are primordial for the final device performance.

4. Defect and impurities

Several studies report hBN flakes lateral size of several millimeters, however pure and defect-free single crystals remain smaller. Reducing the density of contaminant is crucial for electronic and opto-electronic applications as it hinders hBN properties. Moreover, 2D defects are a weakness of the hBN crystal and will favor a mechanical failure upon exfoliation leading to smaller resulting exfoliated nanosheets. Hence, being able to control and reduce the density of defects not only will improve the hBN functional properties, but also its ease of exfoliation and integration. This section will focus on available data which are mainly optical characterizations to propose principles for monitoring contamination and crystal defect in order to enable further process optimization.
Figure 8. Raman and CL measurements at 10 K of various hBN samples. Cathodoluminescence intensity scale is specific to each sample. The CL part between 200 and 230 nm has been extended x50 and x7 for the LMI and commercial hBN from Saint-Gobain samples respectively, for easier representation. Reproduced from [33]. © IOP Publishing Ltd. All rights reserved.

4.1. Optical characterization methods for hBN
Raman spectroscopy is a non-destructive and fast characterization technique for hBN. Two modes are accessible, the interlayer shear mode and in-plane mode at respectively 52.5 and 1366 cm\(^{-1}\). The hexagonal structure of hBN makes the in-plane mode much stronger than the interlayer one. The full width at half maximum (FWHM) of a Raman peak depends on the quality of the crystal structure and the stronger peak at 1366 cm\(^{-1}\) is often considered alone. A narrow peak is representative of highly ordered, defect and contamination free hBN. The FWHM is able to efficiently distinguish CVD-grown hBN of the best quality (between 15 and 50 cm\(^{-1}\)) from freestanding hBN crystals but it is unable to effectively differentiate the crystal quality or density of defects and impurities among high quality freestanding hBN crystals (between 7 and 9 cm\(^{-1}\), for non monoisotopic hBN) [33].

Although still debated [34], growing interest for cathodoluminescence (CL) and photoluminescence (PL) is setting up new standards for hBN characterization. Excitation from UV light in PL or electron beam in CL creates excitons in hBN. A photon is emitted upon exciton recombination and its energy directly depends on the local bandstructure. Any defect or impurity introduces specific levels in the bandgap leading to an identifiable luminescence signature. Hence, non-destructive luminescence measurements are expected to monitor efficiently both contamination and structural defects in hBN [34, 101, 102] even at room temperature [73]. Precise probing could then give precious insight on local crystal structure. Note that the presence of defects or impurities not only adds low energy peaks in the luminescence spectra but also tends to reduce the intrinsic luminescence signal of pure hBN bandgap at 215 nm/5.5 eV [33] (figure 8).

4.2. Carbon and oxygen contamination and vacancies
Raman and CL measurements of HPHT (NIMS), PDC-SPS (LMI) and two commercial hBN (from Saint-Gobain and HQ Graphene) samples are presented in figure 8. The four samples are highly crystalline as attested by the Raman FWHM between 7.3 and 8.2 cm\(^{-1}\). All their CL spectra show the intrinsic luminescence at 215 nm with intensity decreasing as the FWHM value increases. The structure between 220 and 240 nm is attributed to crystalline defects and are observed for the four samples. Two narrow peaks at 320 nm and 350 nm appear for the PDC-SPS (LMI) sample and are also found in the NIMS sample while much lower in the latter (the high energy one is noted by \(\alpha\)). They are attributed respectively to C [55, 102] and O atoms [103]. These contributions also appear around 4 eV in the room temperature PL measurements of APHT crystals [73]. Commercial BN (from Saint-Gobain and HQ Graphene) CL spectra show a weak intrinsic signal and a broad peak centered at around 4.3 eV/290 nm, signature of high impurity density and
deep defect levels (figure 8). Strong carbon segregation can appear in CVD-grown hBN [104] and is also observed in PDC [91] or by Taniguchi et al who reported the formation of C-rich domains on their HPHT crystals [51, 55] with distinct CL responses (figure 9).

C and O solvent contamination is found in the final hBN [51, 55]. However, whether metal or alkali solvent were used, and regardless of the growth method, no solvent atom has yet been observed in the grown crystals. The BN source is a potential vector of contamination in each method and its purity should be closely watched for. BN crucibles which have been widely used for hBN synthesis [21, 38, 52, 60, 105] are now questioned and replaced by alumina crucible when allowed by the process. Commercial BN powder is also a source of impurities and high temperature pre-treatments to purify the BN powder and crucibles have been reported (up to 2100 °C [54, 93]). HPHT hBN from Taniguchi et al has much less C and O contamination than any other reported hBN [33]: the HPHT apparatus couples a tightly closed system ensuring low external pollution with high pressure preventing defect formation. Sample preparation and furnace environment are the main sources of contamination. Thermally and high current activated carbon diffusion was reported in PDC coupled with SPS furnace [56] and this matter is now well-known for SPS [106–108]. The presence of oxygen and surface oxidation effects on optical properties have also been shown to be critical [103]. Hence, great care should be taken about the sample preparation and furnace cleaning. In addition, hydrogen gas can be mixed with argon or nitrogen flow [52] and is naturally present in PDC route [38, 56], to act as a C and O getter.

A first principle calculation showed that the formation of a N self-interstitial has low formation energy and that it can explain the high concentration of N vacancies [109] first mentioned by Sato et al [74] and linked to carbon impurities [110]. Conversely, based on computational studies, Weston et al showed that native point defects are highly unlikely to form in perfectly pure hBN but claim that self-interstitials are thermodynamically favored by C and O contamination in substitutional sites [111]. Moreover, Weston et al predict that point defects’ low migration barrier makes them highly mobile and would favor their coalescence. Hence, unexpected contamination may strongly increase the density of point defect and explain the formation of the C-rich domains.

Impurities are the expected source of SPE (emission wavelength at 650 nm) [26]. SPE has been observed in freestanding crystals from any source with various densities. The exact nature of single photon emitters in hBN is still debated but it is clear that they are related to either B or N vacancies and to C or O substitution (see [112] for a review). Recently, based on a broad investigation of grown hBN films, Mendelson et al claimed that C atoms are the only source of SPE in the visible range and calculated a potential defect structure [113]. Their model implies a double vacancy contribution with substitutional carbon \( V_B C_N \) and denies any role of oxygen. A precise optical investigation of those centers in HPHT C-doped crystals lead to equivalent
conclusions [114]. Additionally, measurements on exfoliated hBN from single crystals show single photon emitter concentration higher on 2D defects [26] and wrinkles due to curvature [115, 116]. Interactions between point defects were investigated using density functional theory. Vacancies are likely to induce strong N–N bonds and molecular bridges between adjacent layers. These bonds would then be a channel for further structural defects formation and diffusion [117]. Also, localised defects close to each other lead to enhanced electron tunnelling and hinder the insulating behavior of hBN [118]. Therefore, reducing the contamination density, and specifically carbon impurities, would help lowering the concentration of crystal defects in hBN. It would also limit the propensity of C to segregate and, hence, would improve its functional properties.

4.3. Striaes and 2D defects

Commercial BN source is full of structural defects [33] and Edgar et al claim that those defects can end up in the final recrystallized hBN [80]. Hence, pure B powder could produce hBN devoid from that contribution. Processes involving long range diffusion would also be less likely to incorporate such defects. The long dissolution step (>20 h for Taniguchi et al and >12 h for Edgar et al) promotes the growth of hBN from isolated B and N atoms. PDC is naturally exempt of these defects, but others could possibly appear. Hydrogen release upon thermal treatment can create porosities and defects in the initial polymeric structure might still be present after sintering. Edgar et al reported that the XRD peak narrow when increasing the soak temperature, which indicates that the higher the temperature, the better the crystal quality [37]. As for the crystal size, high temperature and thermal gradient are key parameters for controlling growth and defect formation.

Optical microscope reveals long and straight lines in the hBN flakes (figure 10), often drawing triangular domains. Those lines could be dislocations or crystal stacking faults and were referred to as ‘striaes’ by Taniguchi et al [61]. The structure of CVD grown hBN grain boundaries were investigated and described by vacancies and dislocations contributions [119]. Nevertheless, the ‘striaes’ observed in freestanding hBN crystals do not show the luminescence signature of structural defect such as dislocations or vacancies [51, 61]. They exhibit stronger intrinsic PL signal at 215 nm than bulk hBN which was attributed to internal light scattering and no additional contribution at 250 nm and above was observed [61]. These results support the idea that the striaes are not grain boundaries but rather buried 2D defects of yet unknown nature. Inversely, Edgar et al treat them as grain boundaries and carried an etch pit density measurement. They observed two types of pits [73]. The dislocation density equals $5 \times 10^6$ cm$^2$ on single crystals and is higher alongside the grain boundaries.

The theoretical study of the defects in grain boundaries showed that defects could be favoured by high local strain, and more specifically by long range curvature perpendicular to the hexagonal structure [119]. Long range curvature can appear in the metal solvent method upon alloy solidification and local strain when there is a large difference in thermal expansions between hBN and the solvent matrix [73].

Very recently, spatially resolved PL was performed on APHT hBN. Its high purity was confirmed by the absence of any signal around 4.1 eV, characteristic of C or O contamination. Yet, when considering intrinsic PL signal around 5.8 eV (215 nm), high spatial inhomogeneity was measured [34]. This inhomogeneity was attributed to non-radiative recombination centers but their physical nature has not yet been identified.

Therefore, although hBN crystal defects and their relation to luminescence are not yet fully understood, luminescence measurements have demonstrated their versatility. The improvement of optical
characterization techniques open the way to their understanding and will enable further optimization of the growth process of freestanding hBN crystals.

5. Conclusion and perspectives

2D materials and their heterostructures appear very promising for optoelectronic applications. Whether it is used as a substrate or as an active layer, high quality 2D hexagonal boron nitride presents high hopes. Vapor-phase processes like CVD can achieve large-scale coverage, but exfoliated nanosheets from self-supporting hexagonal boron nitride crystals are still preferred for demanding applications. Indeed, the purity and crystal quality of the self-standing hBN produced at high temperature are still unmatched. For all methods presented here, it is proven that solvent selection is extremely important and that an optimal process temperature is expected and should produce the largest crystals. Indeed, fine control of process parameters and sample preparation is needed to control nucleation. Precise control should potentially enable seeded growth towards optimal hBN synthesis. For opto-electronic applications, crystal defects and contamination are also to be precisely monitored. Actually, crystal defects not only hinder hBN properties, but also its ease of exfoliation. The development of optical characterizations, with photo and catho luminescence among others, and their physical interpretation are on their way to enable further optimization of the process in order to reduce both crystal defects and contamination.

Data availability statement

No new data were created or analysed in this study.

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