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Quantum Emitters in MOVPE-Grown Layered Boron Nitride

Dissertation presented

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Abstract

Boron nitride (BN) is an sp^2 -hybridized two-dimensional (2D) material with a wide bandgap (~ 6 eV). Its crystal lattice hosts color centers that emit across a wide spectral range, from the near-infrared (NIR) to the ultraviolet (UV). These defects can be utilized in modern quantum technologies. In particular, negatively charged boron vacancies (V_B^-) function as ultra-sensitive quantum sensors of magnetic field, temperature, and pressure, whereas visible-range-emitting point defects serve as single-photon emitters (SPEs) for applications in secure quantum communication.

Most research on quantum emitters in BN relies on small flakes, with an area of several tens of μm^2 , exfoliated from bulk crystals. While this approach is useful for studying the fundamental properties of color centers, it cannot be used in practical applications due to limited scalability and reproducibility. This problem may be addressed using metal-organic vapor phase epitaxy (MOVPE), which enables the growth of large-area BN layers on few-inch substrates.

This work focuses on the fabrication, characterization, and engineering of quantum emitters in BN obtained by MOVPE. Importantly, color centers form already during the material growth, and no post-growth fabrication is necessary to obtain them. The scope of the research discussed covers both the formation of defects during growth and their subsequent modification.

First, the results of the optical characterization of point defects in high-quality BN layers are discussed. The studied material hosts numerous color centers emitting in the green spectral range, acting as SPEs even at room temperature. Statistical analysis indicates the presence of at least three types of defects emitting in this spectral range, which may differ in atomic structure or symmetry of local environment. The investigated emitters are strongly coupled to out-of-plane phonons, as revealed by temperature-dependent measurements. The next part encompasses optimization of growth conditions for the generation of quantum emitters. Among many parameters that determine the properties of BN, layer thickness and TEB flow rate, which govern the amount of carbon available during the growth, were analyzed. The results show that a higher thickness of the BN layer leads to higher emitter stability. On the other hand, an excessively high TEB flow rate applied during growth leads to a decrease in emission purity. In addition, it

is found that, with all other growth parameters kept constant, the concentration of green emitters is controlled exclusively by a single effective parameter incorporating both layer thickness and TEB flow rate.

In the subsequent study, the influence of electron beam-induced bubbles on the emission of BN-based color centers is examined. The results demonstrate that interference effects between the bubbled material and the substrate can enhance the emission by several fold. Importantly, electron irradiation alone does not result in the formation of new emitters or the modification of existing ones. The practical application of this phenomenon requires control over the position and size of the generated bubbles. This goal was achieved through electron exposure assisted with lithographically fabricated masks.

In the final part, the effect of thermal neutron irradiation on defect-related emission in rhombohedral boron nitride (rBN) was studied. While this procedure is typically used to fabricate boron vacancies in exfoliated flakes, in MOVPE-grown, carbon-doped material, it additionally generates color centers. This result suggests an important role of vacancy-carbon complexes in the formation of these emitters. Furthermore, for the first time, neutron-induced formation of luminescent centers emitting in the blue region has been observed. Importantly, until now, the only known mechanism for creating blue emitters was electron irradiation. Should future studies demonstrate that the blue centers generated by electron and neutron irradiation originate from the same defect, the currently accepted model of their formation, which assumes the crucial role of the electric field of the electron beam, would need to be reconsidered.

The results presented in this dissertation provide a new insight into quantum emitters in epitaxial BN. The most important achievements are the determination of the relationship between growth parameters and the properties of color centers, the enhancement of their emission through the deterministic fabrication of BN bubbles, and the identification of new neutron-based mechanisms of green and blue emitter formation. The obtained results constitute an important step toward the controlled and scalable fabrication of quantum emitters in BN, advancing their prospects for practical applications.

Streszczenie

Azotek boru (BN) o hybrydyzacji sp^2 jest materiałem dwuwymiarowym (2D) o szerokiej przerwie energetycznej (~ 6 eV). Jego sieć krystaliczna może zawierać centra barwne emitujące w szerokim zakresie spektralnym - od bliskiej podczerwieni (NIR) aż po ultrafiolet (UV). Defekty te mogą być wykorzystywane w nowoczesnych technologiach kwantowych. W szczególności ujemnie naładowane luki borowe (V_B^-) służą jako ultraczułe kwantowe sensory pola magnetycznego, temperatury i ciśnienia. Z kolei defekty punktowe emitujące w zakresie widzialnym stanowią źródła pojedynczych fotonów wykorzystywane w bezpiecznej komunikacji kwantowej.

Większość badań dotyczących emiterów kwantowych w BN jest prowadzona z wykorzystaniem płatków o rozmiarach rzędu kilkudziesięciu μm^2 , eksfoliowanych z kryształów objętościowych. Takie podejście jest użyteczne do badania podstawowych właściwości centrów barwnych, ale ze względu na ograniczoną skalowalność i powtarzalność nie nadaje się do praktycznych zastosowań. Rozwiązaniem tego problemu może być wykorzystanie epitaksji z fazy gazowej ze związków metaloorganicznych (ang. MOVPE), która pozwala na wytwarzanie wielkopowierzchniowych warstw BN na kilkucalowych podłożach.

Niniejsza praca podejmuje temat wytwarzania, charakteryzacji i inżynierii emiterów kwantowych w BN wytworzonym metodą MOVPE. Co istotne, centra barwne powstają samoistnie już podczas wzrostu materiału. Zakres badań obejmuje zarówno optymalizowanie tego procesu, jak i późniejszą modyfikację już istniejących defektów.

Pierwsze omawiane wyniki dotyczą optycznej charakteryzacji defektów punktowych w wysokiej jakości warstwach BN. Badany materiał zawiera liczne centra barwne emitujące w zielonym zakresie spektralnym, które wykazują emisję pojedynczych fotonów już w temperaturze pokojowej. Analiza statystyczna wskazuje na obecność co najmniej trzech rodzajów defektów emitujących w tym zakresie spektralnym, które mogą różnić się strukturą atomową bądź lokalną symetrią otoczenia. Omawiane emitery wykazują silne sprzężenie defektu z fononami pozapłaszczyznowymi (ang. out-of-plane). Następnym kluczowym zagadnieniem jest optymalizacja warunków wzrostu BN pod kątem generowania emiterów. Jednymi z wielu parametrów determinujących właściwości BN są grubość warstwy

oraz przepływ TEB, który wpływa na ilość boru i węgla dostępnych podczas wzrostu. Uzyskane wyniki pokazują, że większa grubość warstwy skutkuje większą stabilnością emiterów. Z kolei zbyt duży przepływ TEB podczas wzrostu prowadzi do pogorszenia czystości obserwowanej emisji. Co istotne, okazuje się, że przy stałych wartościach pozostałych parametrów koncentracja zielonych emiterów zależy wyłącznie od jednego efektywnego parametru łączącego grubość warstwy i przepływ TEB.

W dalszej części pracy badano wpływ bąbli wytwarzanych w epitaksjalnym BN poprzez naświetlanie elektronami na emisję z centrów barwnych. Okazuje się, że efekty interferencyjne pomiędzy materiałem tworzącym bąbel a podłożem mogą prowadzić do wielokrotnego wzmocnienia tejże emisji. Co istotne, samo naświetlanie elektronami nie skutkuje tworzeniem nowych emiterów ani modyfikowaniem już istniejących. Praktyczne zastosowanie tego zjawiska wymaga kontroli nad pozycją i wielkością wytwarzanych bąbli. Cel ten udało się osiągnąć poprzez zastosowanie wytworzonych litograficznie masek.

W ostatniej części pracy badano wpływ naświetlania neutronami termicznymi na emisję defektową w romboedrycznym azotku boru (rBN). Chociaż metoda ta jest powszechnie stosowana do wytwarzania centrów V_B^- w eksfoliowanych płatkach, w materiale epitaksjalnym domieszkowanym węglem prowadzi ona dodatkowo do generacji zielonych centrów barwnych. Wynik ten sugeruje istotną rolę kompleksów węgiel-luka w ich powstawaniu. Ponadto po raz pierwszy zaobserwowano indukowane neutronami formowanie centrów świecących w obszarze niebieskim. Do tej pory jedynym znanym mechanizmem tworzenia niebieskich emiterów było naświetlanie BN elektronami. Jeżeli przyszłe badania wykażą, że niebieskie centra generowane przy pomocy elektronów i neutronów odpowiadają temu samemu defektowi, aktualnie przyjęty model ich tworzenia, przypisujący kluczową rolę polu elektrycznemu wiązki elektronów, będzie wymagał rewizji.

Wyniki przedstawione w niniejszej rozprawie znacząco poszerzają dotychczasową wiedzę na temat kwantowych emiterów w epitaksjalnym BN. Do najważniejszych osiągnięć należą określenie zależności między parametrami wzrostu a właściwościami centrów barwnych, zwiększenie intensywności ich emisji poprzez deterministyczne wytwarzanie bąbli w BN oraz identyfikacja nowych mechanizmów tworzenia zielonych i niebieskich emiterów w materiale domieszkowanym węglem z wykorzystaniem napromieniania neutronami. Uzyskane rezultaty stanowią istotny krok w kierunku kontrolowanego i skalowalnego wytwarzania kwantowych emiterów w BN oraz przybliżają perspektywę ich praktycznego wykorzystania.

List of Abbreviations

2D	two-dimensional	LED	light-emitting diode
3D	three-dimensional	LP	longpass
AFM	atomic force microscopy	MBE	molecular beam epitaxy
B-centers	blue centers	MOCVD	metal-organic chemical vapor deposition
BN	boron nitride	MOVPE	metal-organic vapor phase epitaxy
bBN	Bernal boron nitride	MS	metastable state
cBN	cubic boron nitride	NA	numerical aperture
hBN	hexagonal boron nitride	NIR	near infrared
rBN	rhombohedral boron nitride	ODMR	optically-detected magnetic resonance
tBN	turbostratic boron nitride	PCC	Pearson correlation coefficient
wBN	wurtzite boron nitride	PhPs	phonon-polaritons
BZ	Brillouin zone	PL	photoluminescence
CFG	continuous flow growth	PSB	phonon sideband
CL	cathodoluminescence	QD	quantum dot
CVD	chemical vapor deposition	QKD	quantum key distribution
CW	continuous wave	RMS	root mean square roughness
DAP	donor-acceptor pair	SEM	scanning electron microscopy
DUV	deep ultraviolet	SHG	second harmonic generation
e-beam	electron beam	SNOM	scanning near-field optical microscopy
EL	electroluminescence	SP	shortpass
FIB	focused ion beam	SPE	single-photon emitter
FME	flow modulation epitaxy	TCSPC	time-correlated single photon counting
FTIR	Fourier-transform infrared spectroscopy	TEB	triethylborane ($\text{B}(\text{C}_2\text{H}_5)_3$)
FWHM	full width at half maximum	TEM	transmission electron microscopy
HBT	Hanbury Brown and Twiss	TMDCs	transition metal dichalcogenides
HPhPs	hyperbolic phonon-polaritons	UV	ultraviolet
IR	infrared	XRD	X-ray diffraction
ISC	intersystem crossing	ZPL	zero-phonon line

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Motivation

The turn of the 20th century was the time of revolution in physics. It was initiated in 1900 by Max Planck, who solved the black-body radiation problem by quantizing the energy of matter oscillations [1]. Just a few years later, in 1905, Albert Einstein showed that light, previously regarded solely as an electromagnetic wave, also consists of quanta, nowadays called photons, and explained the mechanism of the photoelectric effect [2]. As a result of this discovery, he was awarded the Nobel Prize in Physics in 1921 [3]. The studies by Planck and Einstein led to the development of quantum mechanics, which redefined our perspective on the world and opened countless new scientific areas.

One of them encompasses the practical application of light quanta, described by Einstein, for quantum communication, computing, and metrology. Among the various building blocks necessary to realize these ideas, the most fundamental ones are single-photon emitters (SPEs). Obviously, they require integration within a broader photonic and electronic architecture, but the advancement of quantum technologies would not be possible without them. Therefore, over the last few decades, the scientific community has made great efforts to explore various systems that act as SPEs, ranging from single atoms, ions, and molecules, through quantum dots (QDs) and bound-excitons in two-dimensional (2D) materials, to point defects in three-dimensional (3D) semiconductors [4, 5].

Among these SPE platforms, 2D materials offer facile integration into photonic structures, mechanical flexibility, and the ability to tune quantum light emission via applying strain [4]. Unfortunately, they typically require cryogenic temperatures to operate because single-photon emission originates from bound excitons [4]. However, in 2015, layered Boron Nitride (BN), as the first 2D material, was found to host point defects that act as room-temperature SPEs[6] and immediately gained significant attention. As a result of extensive research, various emitters spanning the ultraviolet (UV), visible, and near-infrared (NIR) spectral ranges have been found in BN over the last decade, and their utility has been demonstrated in various quantum applications [6–10].

Most of these studies rely on micrometer-sized BN flakes exfoliated from bulk crystals with SPEs introduced via post-growth annealing, implantation, or

irradiation. However, such flakes lack reproducibility and scalability, so although they are a good platform for studying the fundamental properties of color centers, they are insufficient for scalable applications that require large-area materials. These obstacles might be addressed using metal-organic vapor phase epitaxy (MOVPE), which enables wafer-scale growth of BN. Moreover, the organic precursors used during growth favor the formation of carbon-related centers; therefore, as predicted by theory, engineering point defects should be possible by manipulating growth conditions [11–13]. However, despite these advantages, the controlled formation of visible SPEs during BN MOVPE growth remains largely unexplored, with only one paper linking the formation of centers emitting at ~ 580 nm to the use of carbon-containing precursors [14]. One of the goals of this work is to statistically investigate the influence of the growth conditions on the general properties of MOVPE-grown BN as well as those of visible SPEs at ~ 540 nm, whose nature remains unclear. In particular, parameters crucial for quantum applications - emission purity, stability, and broadening - are explored. The results prove the carbon-related structure of the studied SPEs. Also, successful SPE engineering via manipulation of growth conditions is demonstrated.

As mentioned above, most studies on 2D materials rely on exfoliated flakes. The transfer step might introduce contamination and structural deformations, such as bubbles, which can modify the optical properties of the studied material [15, 16]. A few years ago, our group reported the formation of bubbles under electron-beam (e-beam) irradiation of as-grown MOVPE BN [17]. The second goal of this work is to investigate the mechanical properties of BN bubbles obtained via this method and their influence on visible SPEs. Since we found that bubbles enhance quantum light emission, this work also focuses on understanding the underlying principle of this phenomenon and exploiting it. The latter includes developing a procedure for the deterministic generation of regular bubbles of predefined shapes in selected areas. Since most research groups work with BN flakes, SPE activation or enhancement protocols described in the literature typically require BN transfer onto predefined structures, such as pillars or cavities [18, 19]. Transfer-based schemes can be used when working with small flakes, but do not apply to large-area material that might be broken. In contrast, the bubble-based approach explored in this work allows for significant enhancement without transferring the material.

While this work focuses on visible SPEs, the scientific community has devoted considerable effort to exploring negatively charged boron vacancies (V_B^-), which show great potential for quantum sensing applications [7, 20]. A common strategy of V_B^- fabrication relies on irradiating BN by thermal neutrons. However, in addition to creating V_B^- centers, neutron treatment can also potentially affect the optical properties of BN in other spectral ranges. In particular, it may modify

the local environment of pre-existing defects or introduce new centers, especially vacancy-containing complexes. Although this issue should be considered in the further development of quantum sensing devices based on BN, it has not been studied to date. This work addresses this issue and aims to fill this gap. To this end, the optical properties of the MOVPE-grown BN layer are compared in a broad spectral range before and after thermal neutron treatment. The results indicate that, except for V_B^- , this procedure introduces other point defects into the lattice, thereby affecting the optical properties of BN also in a wide UV-visible range.

We believe that the discoveries described in this work will facilitate studies on SPEs in epitaxially grown BN, thereby contributing to the possible development of future everyday-life quantum applications based on this material.

Thesis Structure

The thesis is organized as follows:

Chapter 1 introduces quantum light emitters and establishes the background for the research presented in this dissertation. It begins with a discussion of the fundamental properties of quantum light, its key applications, and relevant metrics. Next, various systems that act as single-photon emitters (SPEs) are reviewed, highlighting their strengths and limitations. This part provides the broad context needed to position BN within the landscape of SPE platforms.

Chapter 2 provides the background necessary for understanding layered boron nitride (BN), the material studied in this work. In the first part, BN is introduced as a unique material at the intersection of group-III nitrides and two-dimensional (2D) materials. Its properties, applications, and growth techniques, including metal-organic vapor phase epitaxy (MOVPE), are then reviewed. The next part focuses on point defects in layered BN, including ultraviolet (UV) and blue color centers, visible SPEs, and negatively charged boron vacancies (V_B^-) that emit in the near-infrared (NIR). Their properties, proposed atomic structures, and applications are discussed. Particular attention is devoted to visible SPEs studied in this work, including a summary of fabrication schemes and methods for tuning their properties. Recent advances in the direct engineering of visible SPEs during growth are also highlighted. The final part introduces bubbles as an interesting platform for modifying the optical properties of 2D materials. It summarizes recent reports on bubbles formed in exfoliated flakes and presents electron-irradiation-induced bubbles in MOVPE-grown BN, which are investigated in this work.

Chapter 3 describes the experimental techniques used throughout this thesis, including BN MOVPE growth, sample preparation, structural characterization, and optical measurements, and also provides information on the instrumentation used.

Chapter 4 presents the results on the characterization and engineering of green SPEs in MOVPE-grown BN. First, the role of growth temperature in the formation of visible color centers is discussed. Next, the spectral properties of

the observed green-emitting point defects are analyzed statistically. In particular, three classes of green emitters are identified. The results of second-order correlation function measurements confirm that the observed green color centers serve as room-temperature SPEs and demonstrate ultrapure ($g^{(2)}(0) \approx 0.02$) single-photon emission at cryogenic temperatures. Also, temperature-dependent photoluminescence (PL) is employed to investigate phonon-mediated broadening mechanisms. The results indicate a key role of out-of-plane acoustic phonons. The latter part concerns the influence of BN thickness and the flow rate of the organic precursor (triethylborane, TEB) during growth on the formation of green SPEs. To clearly distinguish between effects originating from BN thickness and those related to the TEB flow rate, two series of BN layers were investigated: one with varying thickness and the other grown under different TEB flow rates. This part begins with a comparison of the structural properties of all the studied samples, followed by a detailed analysis of how growth conditions influence emitter formation. A simple model describing the dependence of emitter density on BN thickness and growth parameters is proposed, and its limitations are critically discussed. Next, an excessively high TEB flow rate is shown to degrade single-photon emission from green color centers. The results demonstrate a crossover between the growth regime that supports the formation of high-quality SPEs and the one that favors the generation of low-quality emitters. Finally, emitter stability is shown to increase linearly with BN layer thickness within the investigated range. The obtained results provide guidelines for optimizing MOVPE growth conditions for green SPEs in layered BN. Although the conclusions are specific to the growth conditions used in our research group, the approach presented in this chapter demonstrates a general strategy for optimizing growth conditions for SPE generation.

Chapter 5 presents the studies on bubbles induced in epitaxial BN via electron-beam (e-beam) exposure. First, the mechanical properties of bubbles are discussed. Due to the specific formation mechanism, based on the detachment of wrinkles, characteristic of MOVPE-grown BN, the bubbles exhibit unique mechanical behaviors. In particular, their geometry cannot be described within commonly used theoretical frameworks. Next, the influence of bubbles on color centers is analyzed. The detailed comparison of PL maps acquired from non-irradiated and electron-exposed BN reveals that bubbles enhance green SPEs. Based on combined PL and Raman spectroscopy mapping measurements, this effect is attributed to interference effects occurring in bubbles, which act as cavity-like systems. Finally, the problem of forming deterministic bubble arrays, a key to practical applications, is addressed. A mask-assisted strategy is developed to fabricate bubbles of the desired size in lithographically defined openings in selected

areas. Notably, the proposed approach does not disrupt the quantum properties of green SPEs hosted by MOVPE-grown BN. The results discussed in this chapter have been published in the article P. Tatarczak, et al. “Deterministic hBN Bubbles as a Versatile Platform for Studies on Single-Photon Emitters”, *Adv. Funct. Mater.* 36, no. 24 (2026): e26312, in which the author of this dissertation is the first author.

Chapter 6 discusses the formation of color centers in MOVPE-grown rhombohedral BN (rBN) induced by thermal-neutron treatment. First, the results that confirm that the investigated material is indeed rBN are discussed. Next, the optical properties of two samples, neutron-irradiated and unexposed, are compared. The combined results of PL and optically-detected magnetic resonance (ODMR) measurements indicate a successful formation of V_B^- centers in the exposed material. Then, the defect-related emission of both samples is investigated using various excitation wavelengths. The results reveal that neutron irradiation generates green emitters that plausibly contain both boron vacancies and carbon dopants in their atomic structure. In addition, neutron irradiation is found to induce the formation of emitters whose emission energy closely matches that of blue SPEs, commonly referred to in the literature as B-centers.

Chapter 7 summarizes key findings of the thesis and discusses them in the context of further studies and applications.

Chapter 1

Introduction to Quantum Emitters

1.1 Quantum Light

1.1.1 Second-Order Correlation Function

A discussion about quantum emitters undoubtedly requires a precise definition of what a quantum emitter is. Therefore, we begin by introducing the second-order correlation function $g^{(2)}(\tau)$, whose behavior is currently the most common metric to characterize the nature of light. Let's consider an experiment where many pairs of readings of the cycled-averaged intensity of light are collected, and for each pair of readings, the time delay between them is set to be equal to τ . Then, for classical light considered as a wave, $g^{(2)}(\tau)$ is defined as [21, 22]:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2}, \quad (1.1)$$

where $\langle \cdot \rangle$ represents statistical averaging over time and $I(t)$ is the intensity of the electromagnetic field at time t . In simple terms, the function describes correlations between the optical intensity measured at times t and $t+\tau$. If there is no correlation, the function returns 1. The allowed range of $g^{(2)}(\tau)$ values in the discussed classical case is limited by the Cauchy–Schwarz inequality, which implies that:

$$1 \leq g^{(2)}(0) \leq \infty \quad (1.2)$$

$$g^{(2)}(\tau) \leq g^{(2)}(0) \quad (1.3)$$

These limitations on $g^{(2)}(\tau)$ values vanish when we reconsider the degree of second-order temporal coherence in a more complex, quantum-mechanical approach [21, 22]. In this framework, the second-order correlation function is expressed in terms of electric-field quantum operators and consequently, the Cauchy–Schwarz inequality does not hold. Therefore, the above-mentioned limitations, valid in

a classical case, no longer apply, and $g^{(2)}(\tau)$ can take values which do not match Eq. 1.2 and Eq. 1.3. In such a situation, light cannot be described via classical electrodynamics, and a light source must be considered a quantum emitter. Obviously, the difference in the behavior of $g^{(2)}(\tau)$ between classical and quantum approaches does not arise from a simple mathematical trick but stems from a fundamental difference between the classical and quantum mechanical descriptions of light. In a classical picture, we considered light as a wave, whereas in a quantum-mechanical framework, light consists of quanta. Therefore, in the quantum picture, a detection of a photon at time t affects the number of photons available at time $t+\tau$. In the classical approach, this effect is not taken into account.

To simplify the analysis of $g^{(2)}(\tau)$ in the quantum picture, while maintaining the conclusions valid, we focus only on the regimes of $\tau \approx 0$ (smaller than a coherence time) and $\tau \rightarrow \infty$. In the first case, we can assume that the detected light behaves effectively like a single-mode light. Under this assumption, the second-order correlation function at zero time delay depends only on photon number statistics and takes a simple form [22]:

$$g^{(2)}(0) = 1 + \frac{(\Delta n)^2 - \langle n \rangle}{\langle n \rangle^2} \quad (1.4)$$

where $\langle n \rangle$ and $(\Delta n)^2$ are the mean value and the variance of the number of photons in the considered mode, respectively. On the other hand, while photon delay time $\tau \rightarrow \infty$, intuitively, photons become uncorrelated and consequently

$$\lim_{\tau \rightarrow \infty} g^{(2)}(\tau) = 1 \quad (1.5)$$

1.1.2 Light States

The knowledge of the behavior of the $g^{(2)}(\tau)$ function for $\tau \approx 0$ and $\tau \rightarrow \infty$ allows us to discuss different types of light sources [22]. The measurement of $g^{(2)}(0)$, described in the experimental section, is a powerful tool to study the light nature, as can be seen in the following three simple cases shown in Figures 1.1-1.2 and presented in Table 1.1. Classical thermal light sources usually emit many photons simultaneously, so the detection of one photon increases the probability of detecting others. This results in large fluctuations in the photon number and consequently leads to the appearance of a maximum in the second-order correlation function at $\tau = 0$. A phenomenon in which $g^2(\tau)$ exhibits a local maximum for any finite τ is referred to as bunching. Bunching observed for $\tau = 0$ represents the tendency of the emitter to emit many photons at once. Since the emission of thermal sources can be described by a classical electromagnetic field, the $g^2(\tau)$ function meets the limitations given by Eq. 1.2 and Eq. 1.3. In contrast to thermal sources, a laser

emits coherent light. Coherence means that the next photons generated in the stimulated emission process are identical in their properties; in particular, they exhibit long-range phase coherence. The increase in the emitted light intensity (increase in $\langle n \rangle$) results in a drop of relative fluctuations of the number of photons as $(\Delta n)^2 = \langle n \rangle$. Therefore, for all decay times, a constant value of $g^2(\tau) = 1$ is observed. The physical origin of this behavior is that subsequent stimulated emission events are independent. In case of the coherent light emission, $g^2(\tau)$ also satisfies boundaries expressed by Eq. 1.2 and Eq. 1.3. Thus, although stimulated emission in an active medium is a quantum process, the coherent light emitted by a laser can be effectively described as a classical electromagnetic wave. The last example discussed in this section is a Fock state [23], which has a well-defined photon number n and vanishing variance $(\Delta n)^2 = 0$. Fock states satisfy

$$g^{(2)}(0) = 1 - \frac{1}{n}, \quad (1.6)$$

which means that $g^2(0)$ takes values below 1. Such behavior is called antibunching. Consequently, the classical limitation expressed by Eq. 1.2 is not satisfied, and a given emitter exhibits a quantum nature.

Table 1.1: Variance of photon number $(\Delta n)^2$ and $g^{(2)}(0)$ values for different light states.

Light state	$(\Delta n)^2$	$g^{(2)}(0)$
Thermal light	$\langle n \rangle^2 + \langle n \rangle$	2
Coherent light	$\langle n \rangle$	1
Fock state	0	$1 - \frac{1}{n}$

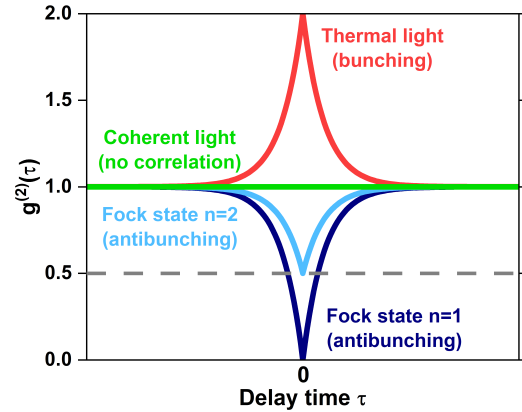


Figure 1.1: $g^{(2)}(\tau)$ curves for various light states. Gray dashed line is set at 0.5 - limit value for single-photon emission

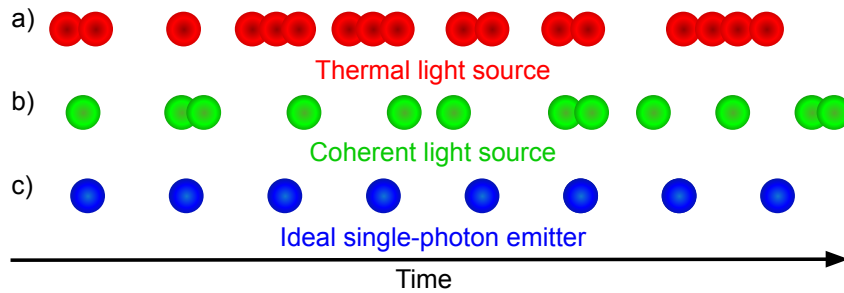


Figure 1.2: Photon separation in time for a) thermal light sources, b) coherent light sources (lasers), c) single-photon emitters.

1.1.3 Single-Photon Emitters

Single-photon emitters (SPEs) are a very special type of quantum light sources that emit photons one by one. In an ideal case, the emitted light might be modeled as the Fock state $n = 1$. Since only one photon can be emitted in a specific period of time, the probability of detecting two photons at the same time is zero. Therefore, an ideal single-photon source is characterized by $g^{(2)}(0) = 0$. However, due to imperfections of real SPE systems, it is common to slightly weaken this condition. Any source emitting multiphoton states ($n > 2$) satisfies $g^{(2)}(0) \geq 0.5$. Therefore, a commonly accepted evidence of single-photon emission is [24, 25]:

$$g^{(2)}(0) < 0.5 \Rightarrow \text{SPE} \quad (1.7)$$

The physical realization of an ideal SPE is a quantum two-level system. Since the emission of two consecutive photons is separated by a minimum time required to re-excite the system, only one photon can be emitted at once. In such a situation, the dynamic of the system is described by only one characteristic decay time t , so the antibunching curve can be described as

$$g^{(2)}(\tau) = 1 - A \cdot \exp\left(-\frac{|\tau|}{t}\right), \quad (1.8)$$

where A is the antibunching depth (for a theoretical ideal SPE, $A = 1$). However, in many systems, additional dark states that trap electrons are present. They affect the light emission and may lead to bunching behavior. The shape of the $g^{(2)}(\tau)$ curve can be reconstructed by analyzing state populations using rate equations. In the simplest case of a three-level system, it can be described as [26, 27]

$$g^{(2)}(\tau) = 1 - A_1 \cdot \exp\left(-\frac{|\tau|}{t_1}\right) + A_2 \cdot \exp\left(-\frac{|\tau|}{t_2}\right), \quad (1.9)$$

where A_1 and t_1 are the antibunching depth and antibunching temporal constant, respectively. Similarly, A_2 and t_2 are the bunching amplitude and bunching temporal constant. Second-order correlation functions for a two-level SPE and a three-level SPE exhibiting bunching are shown in Figure 1.3.

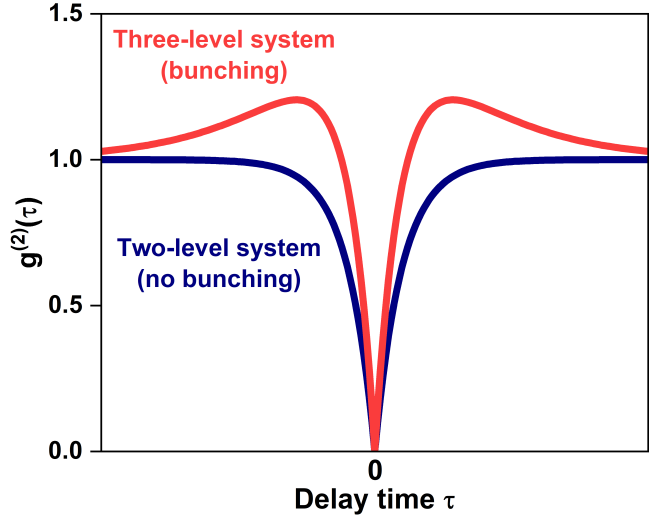


Figure 1.3: Qualitative illustration of $g^{(2)}(\tau)$ curves for two- and three-level SPEs. The three-level system exhibits bunching originating from the presence of a metastable dark state.

1.2 Applications of Single-Photon Sources

Over the last few decades, SPEs in various physical systems have been investigated. What makes them intriguing to the scientific community is not only their fascinating fundamental properties but also their applications in quantum technologies.

1.2.1 Quantum Computing

One of such promising technologies is quantum computing based on qubits [28]. Classical computers use bits to store and process information. One bit represents 0 or 1, so an N -bit register can store exactly one of 2^N different numbers. For example, a 3-bit register can take 8 different values (000, 100, ..., 111), but only one of them is realized. A qubit is a quantum system being a superposition of two states $|\Psi\rangle = \alpha_1|0\rangle + \alpha_2|1\rangle$, where $|0\rangle$ and $|1\rangle$ represents two modes of the same degree of freedom, which in case of single-photon might be, for example, orthogonal polarizations. A 3-qubit register is a superposition of 8 states realized simultaneously $(\alpha_1|0,0,0\rangle + \alpha_2|1,0,0\rangle + \dots + \alpha_8|1,1,1\rangle)$, with 8 different values $(\alpha_1, \dots, \alpha_8)$ stored at the same moment. Therefore, an N -qubit register can store 2^N numbers at once, making quantum computing much faster than classical information processing.

Many physical systems are being developed for quantum computation, including quantum dots or point defects in solids (electron spin qubits), trapped ions or atoms (state qubits), superconducting circuits, and single photons [29]. Single photons are promising for qubits since they are relatively free of decoherence, do not require cryogenic temperatures, and offer many degrees of freedom, such

as orthogonal polarization, non-overlapping optical paths, or time bins [29, 30]. However, photon-based computing also exhibits some drawbacks [29, 30]. The major issue is the lack of photon-photon interactions, which makes it challenging to build 2-qubit logic gates. The only mechanism enabling photon-based computation is interference, which imposes strict constraints on photon indistinguishability. Other problems relate to optical losses, scalability, and information storage.

1.2.2 Quantum Cryptography

SPEs play a central role in secure quantum communication due to quantum cryptography schemes [28]. The fundamental principle of cryptography is that message encryption and decryption require a secret key (a set of parameters) that must be shared between users. Classical methods of key cryptography rely on algorithms whose security depends on the assumed computational difficulty of certain mathematical operations, such as factoring large integers; however, in principle, these protocols can be broken. SPEs enable the implementation of quantum communication protocols, such as quantum key distribution (QKD), whose security is provided by the very fundamental laws of quantum mechanics. Any attempt at key eavesdropping affects quantum light states sent between users and might be detected. In such a situation, a new secret key is generated.

In recent years, much effort has been devoted to the practical implementation of quantum communication protocols. As a result, QKD has been demonstrated in many solid-state systems, promising for integration into scalable quantum networks. [31–40].

1.2.3 Quantum Repeaters

In addition to data security and high computing speed, another essential aspect for quantum networks is the ability to communicate over long distances. The optical losses in fibers limit this, so additional architecture is required. In a classical data transfer, this problem is solved by repeaters, which measure the input signal, copy it, and then resend it at higher power, providing both restoration and amplification. However, this approach is not valid for quantum communication since an unknown quantum state cannot be copied [41, 42].

Long-distance quantum communication is not based on signal retransmission; instead, it leverages quantum entanglement [28]. Two systems, such as particles or photons, are entangled when their states cannot be described independently of each other. The wavefunction of a whole system is a superposition between product states, and it is impossible to distinguish which of two (or more) possibilities forming the superposition is actually realized without performing a measurement.

An example might be a pair of photons, where it is known that one photon is polarised horizontally and the other vertically, but the individual polarisations are unspecified. In such a situation, when a quantum state of only one of them is measured, the state of the other photon is also immediately known.

An important concept in quantum communication is entanglement swapping, first demonstrated in 1998 [43]. Let's consider two pairs of photons, where photon $|1\rangle$ is entangled with photon $|2\rangle$, and photon $|3\rangle$ is entangled with photon $|4\rangle$. In the entanglement swapping procedure, one performs a joint measurement in which photons $|2\rangle$ and $|3\rangle$ are projected onto one of four Bell states that are a complete basis for the combined states of photons $|2\rangle$ and $|3\rangle$. This procedure results in the emergence of entanglement between photons $|1\rangle$ and $|4\rangle$, even though they did not interact in the past [43]. This phenomenon enables quantum communication between two users separated by a large distance. Quantum repeaters placed along the channel provide effective long-range entanglement between the users' qubits via entanglement swapping, thereby enabling the implementation of quantum communication protocols [44, 45]. In practice, a chain of many quantum repeaters, spaced at short intervals, is used to overcome transmission losses. Single-photons play a crucial role in quantum repeaters, as they are essential for entanglement swapping operations [45, 46].

In recent years, all-optical quantum repeaters that employ large photonic cluster states and loss-tolerant measurements have been proposed [47–49]. Their advantage is that, unlike typical quantum repeaters, they do not require additional quantum memories. However, they require SPEs that meet more rigorous criteria for signal purity and photon indistinguishability.

1.3 Properties of Single-Photon Sources

1.3.1 Purity

To be successfully implemented in quantum technologies, SPEs must meet certain criteria summarized in Table 1.2. The first and most straightforward requirement is the ability to emit exactly one photon at a time. The emission purity is quantified by the $g^{(2)}(0)$ value. It should be 0 for an ideal SPE, but none of the existing SPEs are perfect. Emission purity is essential for applications, as the presence of additional photons introduces errors into quantum protocols and consequently leads to communication or computational failures. As shown in Table 1.2, $g^{(2)}(0) < 0.1$ is considered to be enough for the implementation of QKD, but quantum computing, and all-optical quantum repeaters require high purity of $g^{(2)}(0) < 0.001$ [4].

1.3.2 Emission Count Rate

Even an extremely pure SPE would be useless for applications if it emitted only one photon per week. Therefore, the emission count rate is the next crucial property of single-photon sources. It depends on the nature of the given emitter, the system hosting it, and the laboratory setup. Internal limitations arise from the spontaneous emission rate Γ and non-radiative processes. In particular, in the case of solid-state emitters, the emission count rate might be reduced by the presence of additional metastable states and light phonon scattering.

Γ is not an intrinsic property of a given emitter, but depends on the local electromagnetic environment. According to Fermi's golden rule [50], if an emitter is not in a free space, its spontaneous emission rate satisfies [51, 52]:

$$\Gamma \propto \rho(\omega) \cdot |\mu E|^2, \quad (1.10)$$

where $\rho(\omega)$ is a local density of states at emitter wavelength, μ is a dipole matrix element between excited (initial) and ground (final) states, and E is the electric field intensity at an emitter position. Therefore, as proposed by Purcell in 1946 [53], it is possible to increase the emission count rate by embedding an emitter into a cavity. The proper design of a resonator allows for an increase in $\rho(\omega)$ at an emitter position, leading to an improvement in Γ . Nowadays, this approach is commonly used for enhancing the emission count rate of solid-state SPEs to meet application requirements [19, 54–63].

External limitations on emitter brightness include equipment imperfections, such as limited detector efficiency or intensity losses induced by optical elements. Applications, such as QKD, quantum computing, or quantum repeaters, require emission count rates of above GHz (Table 1.2) [4].

1.3.3 Indistinguishability

The next important property determining the utility of SPEs is their indistinguishability. To meet the criteria for various applications, emitted single photons must be identical in energy, time, and polarization. Obviously, indistinguishability is crucial for generating entangled states and for quantum repeaters. It is also essential for photon-based quantum computing, which relies on a multiphoton interference that does not occur with non-identical photons. On the other hand, it is not crucial for QKD.

The indistinguishability of photons can be quantified using the Hong-Ou-Mandel interference effect [64]. Let's consider two photons reaching a symmetric 50:50 beam splitter from opposite sides. As shown in Figure 1.4, photons have four different

options to exit a beam splitter, so the final state is their superposition. Energy conservation requires the beam splitter transformation to be unitary, implying a π phase difference between reflections from opposite sides. As a consequence, two probability amplitudes leading to one photon in each output port have opposite signs, as marked by $+$ and $-$ in Figure 1.4. When two photons are indistinguishable (all arrows in Figure 1.4 are of the same color), these amplitudes interfere destructively and cancel each other out. Therefore, a pair of indistinguishable photons always exits the beam splitter through the same output port [65]. Then, a drop in the number of coincidence events, defined as the simultaneous detection of one photon in each output port, is observed. When a time delay is introduced into one arm of the setup, the so-called Hong-Ou-Mandel dip is observed in the plot of coincidences versus time delay. Its depth is quantified by the visibility V_{HOM} defined as [65]

$$V_{HOM} = \frac{N_{max} - N_{min}}{N_{max}}, \quad (1.11)$$

where N_{min} indicates the minimum number of coincidences for indistinguishable photons and N_{max} indicates the number of coincidences for distinguishable photons (separated in time).

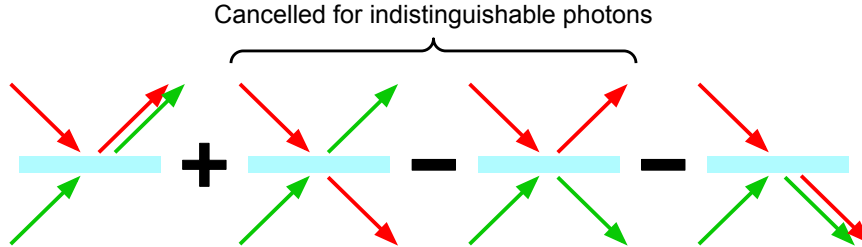


Figure 1.4: Four possibilities the photons can exit a beam splitter. Red and green arrows mark photons reaching the beam splitter from two sites. The signs $+$ and $-$ denote relative phases between final states. When two photons are indistinguishable (all arrows are of the same color), two central possibilities cancel each other out.

In solid-state SPEs, photon distinguishability arises mainly from interactions with phonons and charges; however, their influence can be limited [66, 67]. The number of interacting phonons can be reduced by lowering the temperature, while the impact of charge fluctuations can be minimized by integrating SPEs into low-noise chip devices. Also, an increase in the spontaneous-emission rate via the Purcell effect reduces interaction time and improves indistinguishability. As presented in Table 1.2, indistinguishability is not a crucial parameter for QKD implementation; however, it must be close to 1 for other applications.

Table 1.2: SPE requirements for various quantum applications. Adapted from [4].

Application	Purity $g^{(2)}(0)$	Repetition Rate	Indistinguishability V_{HOM}
Quantum key distribution	<0.1	GHz	Not crucial
Photon-based quantum computing	<0.001	GHz	>0.99
Memory-based quantum repeaters	<0.01	GHz	>0.9
All-optical quantum repeaters	<0.001	GHz	>0.99

1.4 Types of Single-Photon Sources

Researchers explore various systems to find SPEs that meet the above-mentioned requirements and offer both scalability and operation at room temperature. Below, we briefly summarize some of them.

1.4.1 Atoms, Ions and Molecules

Let's start our considerations with cold single atoms and single ions with discrete energy levels, placed in optical cavities and cooled using magneto-optical traps. Typically, the employed atom has a Λ -like energetic structure, shown in Figure 1.5a, with two metastable ground states $|g_1\rangle$, $|g_2\rangle$, and one excited state $|e\rangle$ [5, 68]. The transition of $|g_2\rangle \rightarrow |e\rangle$ is in resonance with the cavity mode, while the energy of the used pump laser corresponds to $|g_1\rangle \rightarrow |e\rangle$ transitions. When $|0\rangle$ and $|1\rangle$ are states of zero and one photon number, respectively, the eigenstates of the atom-cavity system are $|g_1, 0\rangle$, $|g_2, 1\rangle$, and $|e, 0\rangle$, according to the Jaynes-Cummings model [69]. Laser pumping induces the transition from $|g_1, 0\rangle$ into $|e, 0\rangle$, which is strongly coupled to $|g_2, 1\rangle$. Therefore, a Raman-like transition occurs with a single photon being emitted into a cavity mode [5, 68]. Using an appropriate laser pump, it is possible to achieve a situation in which the atom is never excited, so it cannot emit a photon into any mode other than the cavity mode.

Exemplary used atoms and ions are Rb, Cs, Ca^+ , or Yb^+ [70–73]. Due to the coupling into only one cavity mode and the lack of interactions with the environment, atom-based SPEs exhibit very high purity and the narrowest possible bandwidth, which is crucial for high indistinguishability. However, integrating the entire trap-cavity system with additional photonic and electronic architecture is technologically challenging. Also, one magneto-optical trap must contain only one atom, which strongly limits the scalability.

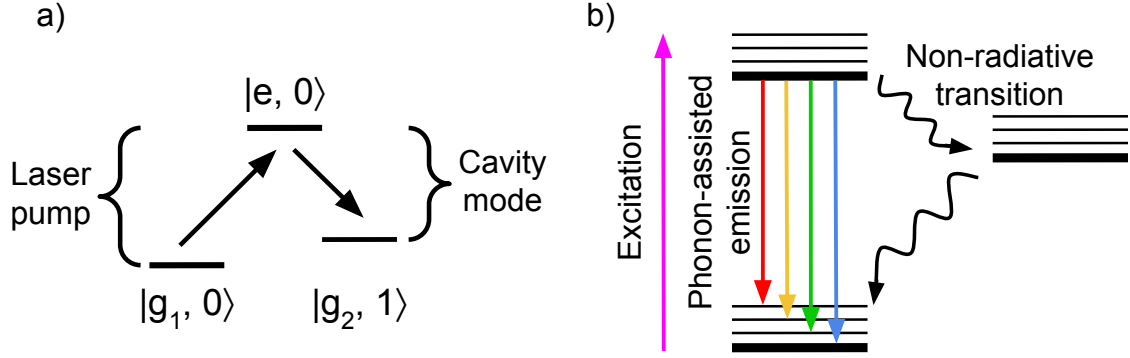


Figure 1.5: a) Λ -like energetic structure of an atom-microcavity system. b) Energy levels and emission from a molecule.

Like atoms and ions, molecules can also act as SPEs, but exhibit some differences [5, 74, 75]. In general, the emission mechanism is simple. Under laser irradiation, an electron is transferred to the excited state and then returns to the ground state, emitting a single photon. However, in a molecule, each electronic energy level is coupled to many vibrational states. Therefore, the emission bandwidth is not as narrow as in atomic SPEs, but it is broadened due to interactions with phonons, as shown in Figure 1.5b. Moreover, an excited electron might be trapped in a long-living dark state. This mechanism introduces long-timescale intensity fluctuations, leading to photon bunching.

Single molecules, particularly organic ones, have been extensively studied for single-photon emission [76–82]. The main challenge related to the practical applications of molecule-based SPEs is their instability. Due to the interaction with the local environment, such as a solvent, laser excitation, possible chemical reactions, and others, light emission from molecules suffers from bleaching and blinking [5, 75, 83].

1.4.2 Quantum Dots

The next discussed group of SPEs is quantum dots (QDs). They are nanocrystals consisting of a small region of a semiconductor, up to ~ 10 nm in size. In typical core-shell systems, the core is surrounded by a wider-bandgap material that provides a potential barrier for charge carriers in the conduction and valence bands, thereby leading to quantum confinement in all three directions. In single-material QDs, the dot surface and the environment constitute a barrier. In both cases, confinement results in a discrete energetic structure, similar to that of a single atom, and an electron (hole) density of states that can be approximated by a delta-like function. Electrons excited to the conduction band and holes formed in the valence band interact via strong Coulomb attraction, forming excitons. Since the energetic

structure is quantized, the excitonic recombination leads to the emission of single photons [84, 85].

Depending on the fabrication methods, two main groups of QDs can be distinguished. The first group is colloidal QDs. Typically, their growth originates from a rapid injection of a first precursor into a hot mixture of a second precursor and a solvent. This step results in the rapid formation of many crystal seeds at once. When the temperature is lowered, the seeds grow until they reach a given size [85, 86].

The second group comprises epitaxial QDs, typically grown by metal-organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE). Typically, epitaxial QDs are obtained in the Stranski-Krastanov growth mode [87]. In this approach, the material is grown on a substrate with a different lattice constant. Therefore, the lattice mismatch induces strain at their interface. Initially, growth is layer by layer, but at a critical thickness, it becomes energetically favorable to relieve strain and induce island nucleation, leading to QD growth. [84, 85]. Notably, QDs might be also obtained through post-growth etching.

Over the last few years, due to their advantages and mature fabrication techniques, QDs have emerged as one of the leading SPE platforms. First, the energy of a photon emitted by a quantum dot depends on core and shell bandgaps, the size of the grown quantum dot, and strain [85, 86]. Therefore, QDs of different compositions and various geometries have been studied to tune their emission properties, summarized in Figure 1.6. QD-based emitters have been realized over a wide spectral range from infrared (IR), including In(As, P), (In, Ga)As, or Ga(Sb, As) QDs [88–91], through the visible region, such as (Zn, Cd)Se, Zn(Te, Se), or ZnO QDs [92–95], up to the ultraviolet (UV) regime with GaN/AlGaN QDs [96, 97]. Moreover, QDs have been shown to operate even at room temperature [97–101] and to reach $g^{(2)}(0) < 0.001$ [88, 91, 102], providing a promising platform for quantum applications. An additional advantage of QDs is that they can be easily fabricated within or integrated into optical cavities, waveguides, or other photonic structures, making them extensively developed for quantum communication over long distances [37–40].

Like other SPEs, QDs also exhibit some technological challenges. First, surface charge traps and photo-induced charges cause spectral diffusion of QD emission, affecting photon indistinguishability [84, 103, 104]. Moreover, emission purity and efficiency are reduced by multiple-exciton generation, which leads to the simultaneous emission of more than one photon in a single pumping cycle, as well as by non-radiative Auger recombination, when the energy is transferred to a third carrier [85, 86, 105, 106]. Also, forming many QDs with the same optical properties is challenging due to variations in size and composition, as well as induced strain.

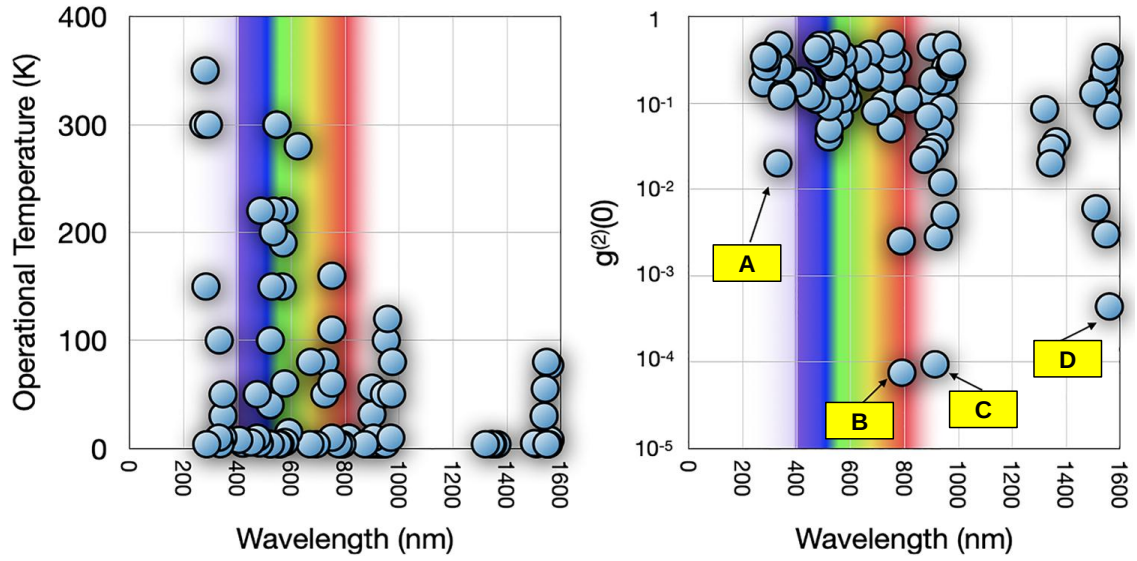


Figure 1.6: Operation temperature and purity of QDs reported in the literature. Marked points correspond to data reported in: A - [96], B - [102], C - [91], D - [88] (original citation numbers have been replaced with letters). Picture adapted from [84].

1.4.3 Point Defects in Semiconductors

From the perspective of this work, the most important SPEs are point defects, also called color centers, existing in semiconductors. In crystals, the regular arrangement of atoms results in a periodic potential and the formation of energy bands. However, atomic-scale point defects can locally disrupt the crystal's periodicity and thereby introduce new atomic-like discrete energy states into the bandgap. These states are isolated from the continuous energy bands, so they can trap charge carriers. Under laser or electrical pumping, an electron is excited from the ground state to the excited state and then emits a single photon during radiative de-excitation [85, 107].

Color centers in semiconductors include intrinsic defects, such as vacancies, interstitials, or antisites, and extrinsic ones, including impurities [108]. Typical point defects existing in crystals are shown in Figure 1.7. They can be introduced into the crystal lattice in many ways. First, they can form during growth due to non-perfect growth conditions. Such point defects do not require further post-growth fabrication; however, their positions cannot be controlled. Moreover, optimizing growth conditions to generate specific SPEs is challenging and requires detailed statistical studies on many samples. SPEs can also be introduced during post-growth processes, such as ion implantation and irradiation with a focused ion beam (FIB), neutrons, or electrons [107, 109–115]. Such processes cause damage to the crystal lattice, leading to defect formation. They provide control over defect concentration and localization, but excessively high irradiation dose can also significantly degrade crystal quality, introduce unexpected defects, create additional

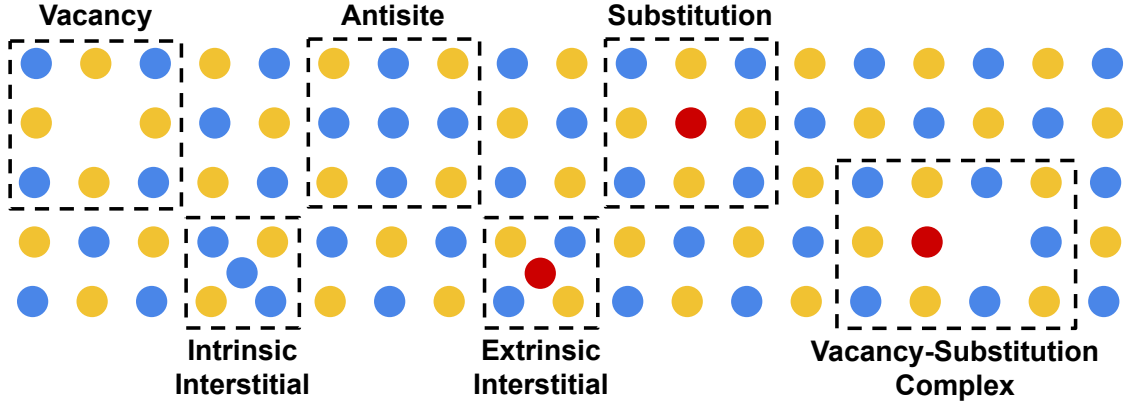


Figure 1.7: Typical point defects occurring in crystals. Blue and yellow dots represent native atoms in the host lattice, while red dots denote impurity atoms incorporated into the crystal.

non-radiative recombination channels, or cause defect clustering. Defects obtained in such a way often have to be reorganised in the lattice via annealing at high temperature of around 1000 °C, which increases defect mobility [115]. In layered boron nitride (BN), annealing activates optical defects created by irradiation and increases their spectral stability, but it also leads to the formation of new color centers [6, 114]. Another technique for post-growth generation of point defects is laser printing [116, 117]. In this approach, the energy that causes lattice damage is deposited by high-power laser pulses, providing very high precision in defect positions, limited by the laser spot size. Notably, well-isolated individual point defects are crucial for single-photon emission. If the defect concentration is too high, single-color centers are unavailable. Instead, defect ensembles form, affecting the emission energy and linewidth and decreasing signal purity.

Like in the case of molecules, single-photon emission from solid-state color centers is affected by phonons. Therefore, the emission spectrum of a point-defect SPE typically consists of a zero-phonon line (ZPL), originating from the purely electronic transition between the ground and excited electronic states, and phonon sidebands (PSBs) associated with the phonon-assisted transitions involving vibrational sublevels. The important metric of solid-state SPEs is the Debye-Waller factor, defined as the ratio of ZPL emission to the total luminescence intensity (ZPL + PSBs) [107, 118]. A Debye-Waller factor close to unity is desired to achieve a high emission rate and efficiency for a particular photon energy. Another important property, also affected by phonons, is the emission linewidth, which must be narrow to achieve sufficient photon indistinguishability.

Point defects in wide-bandgap materials possess many advantages over other single-photon sources [4, 85, 107]. First, compared with atoms, molecules, and QDs, color centers offer facile integration into other solid-state systems, such as cavities or other photonic circuit elements, thanks to the mature, well-developed

growth and nanofabrication techniques discussed above. Moreover, many of them have been shown to act as SPEs at room temperature without requiring cryogenic setups, which still constitutes a challenge for other systems. In addition, some color centers possess spin and thereby offer natural spin-photon interfaces useful in many applications. However, point-defect SPEs also present some challenges [4, 85, 107]. One of them is the light collection efficiency. Since an emitter is embedded in a high-refractive-index medium, only a small part of the isotropically emitted light might be collected in a free space. In addition, interactions with charges (which are significant for surface-close emitters), switching between charge states, and the presence of metastable states cause energy fluctuations and blinking, thereby reducing emission purity and brightness. Moreover, due to variations in the local environment, some color centers exhibit broad spectral distributions, which poses a significant issue for indistinguishability and for designing appropriate architectures, such as cavities.

Since the quantized atomic-like energy levels are introduced into the bandgap, the most important platforms for quantum light emission are wide-bandgap semiconductors such as diamond, silicon carbide (SiC), gallium nitride (GaN), aluminium nitride (AlN), or BN - the material explored in this work, which has recently emerged as an important platform in the landscape of quantum emitters [4, 107, 119]. ZPLs of exemplary color centers observed typically in semiconductors are shown in Figure 1.8.

One of the most important classes of quantum emitters in semiconductors is spin-possessing centers. The most-studied representative is the negatively charged nitrogen-vacancy (NV^-) center in diamond [120]. It consists of a nearest-neighbour pair of a substitutional nitrogen atom and a vacancy, with one extra electron. NV^- exhibits single-photon emission with ZPL at wavelength $\lambda_{\text{ZPL}}=637$ nm (1.945 eV) followed by a strong and spectrally broad PSB resulting from phonon-assisted transitions. Despite this drawback, NV^- has gained significant attention for its extremely high photostability and spin properties, which are well-suited to quantum sensing. In brief, the spin sublevels of the spin-triplet ground state with different spin projections along the NV^- 's intrinsic quantization axis are split via spin-spin interactions. The splitting, which is further strongly affected by the external magnetic field and the defect's local crystal environment, can be probed via optically detected magnetic resonance (ODMR). Due to this mechanism, NV^- centers act as highly sensitive sensors of magnetic fields, temperature, strain, and pressure, and are particularly used in biosensing and bioimaging [120–124]. ODMR, essential for quantum sensing, is discussed in more detail in Section 2.4.4. In addition to NV^- , diamond hosts other color centers with similar atomic structures, such as silicon-vacancy (SiV) or germanium-vacancy (GeV) centers [119].

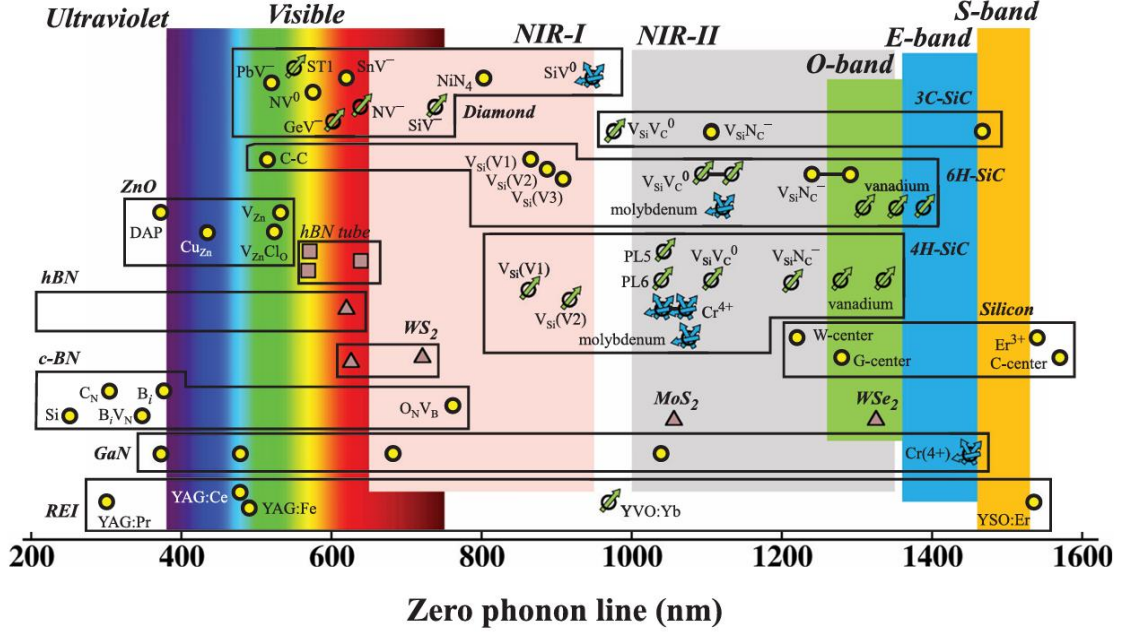


Figure 1.8: ZPL energy distribution for exemplary color centers in semiconductors. Picture adapted from [119].

Obviously, telecom-wavelength and near-telecom-wavelength SPEs are of particular interest for quantum communication. Among materials hosting color centers emitting in this spectral range, silicon carbide (SiC) and silicon show great potential due to their well-developed growth technologies and suitability for device integration. Across different SiC polytypes, numerous SPEs operating in the NIR region, such as $V_{Si}V_C$ divacancies, have been reported [119, 125]. In addition, telecom-range color centers have been observed in cubic SiC, although their microscopic nature remains poorly understood [126]. Similarly, considerable effort has been devoted to exploring telecom-range color centers in silicon [127]. The so-called G-center, consisting of an interstitial Si atom between two substitutional C atoms, is the most well-known and technologically advanced in terms of fabrication and integration into photonic structures [109, 128–130].

Gallium nitride (GaN) and aluminium nitride (AlN) are other widely used materials that have been shown to host SPEs. Like SiC and silicon, GaN and AlN are mature semiconductors with well-developed growth and post-growth processing techniques; therefore, SPEs hosted by them are promising for applications. In both materials, individual color centers spanning the visible-NIR range have been observed [131–136].

All the above-discussed hosting systems for color centers are sp^3 -hybridized, three-dimensional (3D) semiconductors. However, a decade ago, point defects acting as SPEs were also discovered in a sp^2 -hybridized, two-dimensional (2D), layered BN [6]. The 2D nature of BN offers many advantages. First, color centers

embedded in high-refractive-index 3D materials deep beneath the surface suffer from low light-extraction efficiency due to internal reflections. In contrast, SPEs in thin BN layers are free of this problem because all defects are near the surface. The 2D nature and lack of dangling bonds support mechanical flexibility and transferability to various substrates, making the integration of BN into photonic structures easier than in the case of 3D semiconductors [4, 86, 107, 137, 138]. In addition, like other 2D materials, BN is highly sensitive to applied strain, which can tune its optical and electronic properties. In particular, the tuning of a color center ZPL energy via mechanical strain has been demonstrated [139, 140]. Moreover, bending BN by transferring it onto predefined substrates, such as micropillars, allows the creation of SPEs via the generation of a strong deformation potential [18, 141]. Such strain-related features are not available for 3D crystals. Due to these advantages, SPEs in BN have been extensively studied over the last decade. During this time, many different color centers that emit across the UV, visible, and NIR ranges have been found in BN [6–9]. Their utility has been demonstrated in applications such as ODMR-based quantum sensing (like NV^- center in diamond), quantum random number generators, QKD, or quantum computing [10, 20, 32–34, 142–145]. The properties of BN and color centers hosted by it are discussed in detail in the next Chapter.

1.4.4 Bound Excitons in Two-Dimensional Materials

Obviously, BN is not the only 2D material hosting SPEs. The second important group is transition metal dichalcogenides (TMDCs) - a class of materials with the chemical formula MX_2 , where M is a transition metal, X is a chalcogen. In contrast to BN, quantum light emission in TMDCs typically originates from bound excitons localized in strain fields or defects, which can be introduced into TMDCs via methods similar to those used for BN [86, 137, 138]. In recent years, many TMDCs such as WSe_2 , MoS_2 , MoSe_2 , or MoTe_2 have been reported to host emitters spanning the visible-NIR range, including telecom-range SPEs [146–149]. Like BN, TMDCs offer advantages related to their 2D nature: flexibility, facile integration into photonic structures, and the ability to tune the ZPL energy via strain. However, while color centers hosted by BN can work as SPEs even at room temperatures, quantum emitters in TMDCs require cryogenic temperatures [86, 137, 138].

Chapter 2

Introduction to Layered Boron Nitride

2.1 Layered Boron Nitride in the Landscape of Semiconductors

2.1.1 Group-III Nitrides

Group-III nitrides play an important role in modern optoelectronics. The best-known members of this family are indium nitride (InN), gallium nitride (GaN), and aluminum nitride (AlN). In general, they crystallize in two sp^3 -bonded polymorphs: the equilibrium wurtzite structure and the metastable zinc-blend structure [150, 151]. Wurtzite forms exhibit direct bandgaps of ~ 0.7 eV for InN, ~ 3.4 eV for GaN, and ~ 6.2 eV for AlN [150–152]. As shown in Figure 2.1, their alloys are suitable for bandgap engineering and can cover a wide spectral range from ultraviolet (UV) to infrared (IR) [153, 154]. Therefore, they are widely used in light-emitting devices that operate at various wavelengths. In particular, group-III-nitrides-based light-emitting diodes (LEDs), micro-LEDs and laser diodes, covering a broad UV-green range, have been fabricated [155–161]. The crucial role of group-III nitrides for optoelectronics was underlined by awarding the Nobel Prize in Physics in 2014 to Isamu Akasaki, Shuji Nakamura, and Hiroshi Amano for the invention of GaN-based blue LEDs [162].

GaN, AlN, and their alloys (AlGaN) are good candidates for high-power electronics [163–166]. High values of the breakdown electric field (E_{crit}), combined with high thermal and chemical stability, as well as excellent thermal conductivity (κ_{th}), which enables effective heat dissipation, allow GaN/AlN-based devices to operate under extreme conditions. In addition, the high electron mobility (μ_e) and saturation velocity (v_s), as well as the ability to obtain both highly n- and p-doped

crystals, make group-III nitrides an excellent platform for all transistor types. In particular, the built-in electric polarization induces a two-dimensional (2D) electron gas at the AlGa_N/Ga_N interface, which is exploited in high-electron-mobility transistors. Table 2.1 presents numerical values of the mentioned parameters for Ga_N and Al_N and compares them with those of other materials.

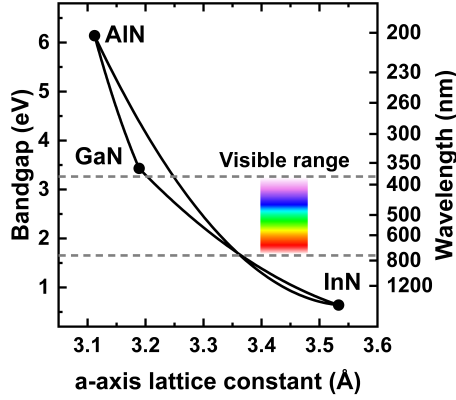


Figure 2.1: Bandgap energies and a -axis lattice constants for In_N, Ga_N, Al_N, and their alloys. Adapted from [154].

Table 2.1: Values of breakdown electric field (E_{crit}), electron mobility (μ_e), saturation velocity (v_s), and thermal conductivity (κ_{th}) for discussed wurtzite Ga_N and Al_N, as compared with Si and GaAs, commonly used in electronics. Adapted from [163].

Material	GaN	AlN	Si	GaAs
E_{crit} (MV cm ⁻¹)	3.3	15	0.3	0.4
μ_e (cm ² V ⁻¹ s ⁻¹)	1400	450	1440	9400
v_s velocity ($\times 10^7$ cm s ⁻¹)	2.4	1.4	1	0.9
κ_{th} (W cm ⁻¹ K ⁻¹)	2.5	2.85	1.3	0.55

2.1.2 Two-Dimensional Materials

In recent years, 2D materials have gained significant attention. They occur in an sp²-hybridized layered form, where atoms within a single atomic plane are linked via strong covalent bonds, while subsequent atomic planes interact by weak van der Waals coupling. The extremely weak out-of-plane interactions enable the isolation of monolayer or few-layer sheets via mechanical exfoliation from bulk crystals. This property enables stacking of thin layers of various compounds into so-called van der Waals heterostructures that do not suffer from lattice mismatch [167].

The extensive research on layered materials was stimulated in 2004 by the isolation of graphene (a graphite monolayer) [168], a discovery that was awarded the Nobel Prize in Physics in 2010 [169]. Since then, the family of 2D materials has expanded to include many new materials, such as transition metal dichalcogenides (TMDCs), black phosphorus, silicene, MXenes (compounds of transition metals with carbon or nitrogen), MBenes (compounds of transition metals with boron), 2D oxides, and many others [167, 170–174]. Layered materials span a broad spectrum of properties, ranging from insulators and semiconductors, through half-metals and semimetals, to metals, and even superconductors, as well as magnetic materials. The possibility of combining any number of ultrathin layers of different 2D compounds enables the engineering of very exotic artificial systems for various applications.

Compared with three-dimensional (3D) crystals, layered materials offer additional mechanisms for tuning their properties. First, in many 2D materials, the bandgap depends strongly on thickness (number of atomic layers); in particular, indirect-to-direct bandgap crossover is observed in TMDCs and other systems [175–178]. Furthermore, weak van der Waals interactions between atomic planes facilitate strain engineering of the electronic structure [179, 180] and make 2D materials bendable, opening the way towards flexible optoelectronics [181]. However, many layered materials, such as TMDCs, MXenes, and black phosphorus, are environmentally sensitive and prone to degradation when exposed to light, air, or humidity [182, 183]. Therefore, they require additional protective coatings to operate in ambient conditions.

2.1.3 Layered Boron Nitride as a Bridge Between Group-III Nitrides and Two-Dimensional Materials

BN, first synthesized in 1842 by reacting boric acid with potassium cyanide [184], belongs to the family of group-III nitrides; however, unlike other members, it typically occurs in a sp^2 -hybridized layered form similar to that of graphite [185]. Therefore, layered BN combines the 2D nature and associated advantages with the typical properties of nitrides. This combination makes it a unique material, used in the engineering of van der Waals heterostructures, possessing many advantages.

First, like other group-III nitrides, BN is highly chemically stable, so unlike many other van der Waals crystals, it does not degrade under ambient conditions. It is also atomically smooth and provides a clean, highly uniform dielectric environment with minimal charge disorder. These features, combined with its impermeability to oxygen and water, make BN an excellent encapsulation protective layer for sensitive materials such as 2D ferromagnets or TMDCs, preserving their structural and functional properties [182, 183].

Additionally, it has an ultra-wide-bandgap of ~ 6 eV, similar to that of AlN [186]. This value is among the largest for all 2D materials, so layered BN is often used as an insulating component in van der Waals heterostructures. Also, a high breakdown electric field, reported to be $E_{crit} \approx (10 - 20) \text{ MV cm}^{-1}$ [187–189], makes this material a good tunneling barrier. sp^2 -hybridized BN exhibits high in-plane thermal conductivity which changes from $\kappa_{th} \approx 7.5 \text{ W cm}^{-1} \text{ K}^{-1}$ for a BN monolayer to $\kappa_{th} \approx (2-4) \text{ W cm}^{-1} \text{ K}^{-1}$ observed in a multilayer regime [190]. Such high thermal conductivity enables effective heat dissipation in 2D material-based structures, thereby prolonging device lifetime and enhancing stability. In consequence, layered BN is widely used in van der Waals heterostructures to enhance their functionality.

2.2 Fundamental Properties and Applications of Layered Boron Nitride

2.2.1 Structural Properties

B and N atoms within a single atomic plane of layered BN are covalently-bonded and arranged in a honeycomb lattice shown in Figure 2.2a. The unit cell of such a single monolayer, marked by green, is spanned by two lattice vectors $\bar{v}_1 = a(-\frac{1}{2}, \frac{\sqrt{3}}{2})$ and $\bar{v}_2 = a(\frac{1}{2}, \frac{\sqrt{3}}{2})$, where $a = 2.504 \text{ \AA}$ is the lattice constant. Subsequent atomic layers are stacked into a graphite-like structure shown in Figure 2.2b. However, although each atomic plane of layered BN is arranged in the same way, various polytypes with different interlayer stackings are possible [191]. Some of them are presented in Table 2.2.

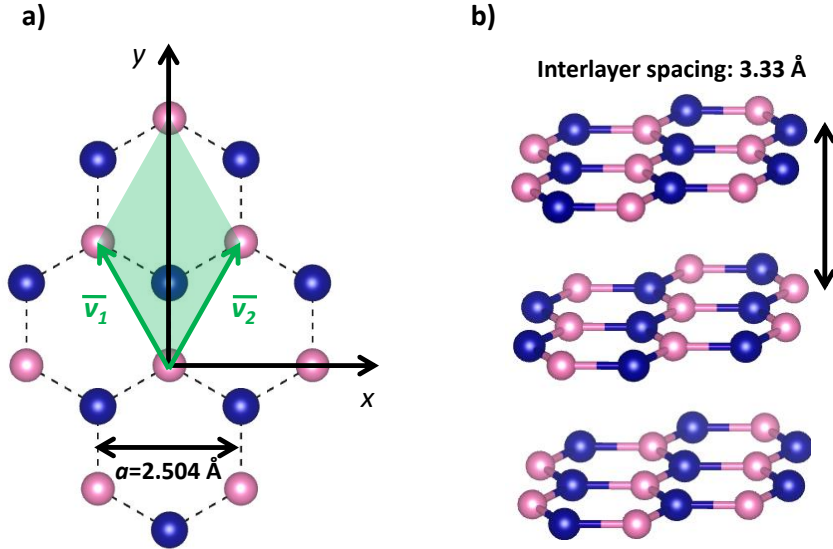
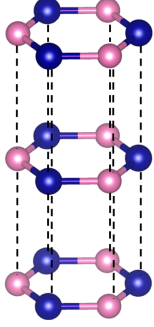
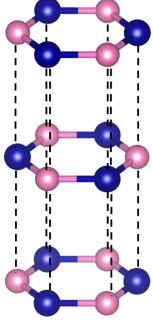
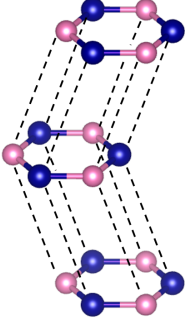
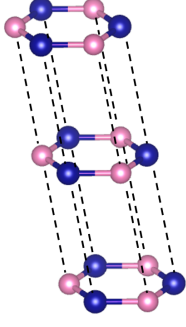


Figure 2.2: Schematic illustration of the crystallographic structure of BN. a) A monolayer sp^2 -bonded BN with a unit cell (marked by green color) spanned by lattice vectors $\bar{v}_1$ and $\bar{v}_2$. b) Multilayer sp^2 -bonded BN in its most stable AA'-stacked form. Atomic structures were prepared using VESTA software [192].

We start the discussion with an AA-stacked BN structure, in which successive atomic planes lie directly above one another, forming monoatomic columns of B and N atoms along the c -axis. Intuitively, the B-B and N-N repulsion makes this structure thermodynamically unstable [191, 195]. In particular, interlayer spacing equal to $3.55 \text{ \AA}$ is larger than for other polytypes [194]. Although a wafer-scale growth of AA-stacked BN on GaN substrates has recently been demonstrated [194], it is still considered an exotic material, and there is a lack of systematic studies of that particular BN form. In contrast, AA'-stacked hexagonal boron nitride (hBN) is the best-known and most studied BN polytype. In this structure, adjacent

Table 2.2: Crystal structures, symmetries and lattice parameters for various sp^2 -hybridized BN polytypes. Crystal structures were prepared using VESTA software [192].

Structure				
Stacking sequence	AA -	AA' (hBN)	AB (bBN)	ABC (rBN)
Space group symmetry	$P\bar{6}m2$	$P6_3/mmc$	$P\bar{6}2m$	$R3m$
a lattice constant ($\text{\AA}$) (theory) Ref. [191]	2.476	2.478	2.477	2.476
a lattice constant ($\text{\AA}$) (experiment) Ref. [193]	-	2.504	-	2.504
Interlayer spacing ($\text{\AA}$) (theory) Ref. [191]	3.468	3.177	3.160	3.226
Interlayer spacing ($\text{\AA}$) (experiment) Ref. [193, 194]	3.55	3.328	-	3.33

atomic planes are rotated by 60° with respect to each other. B and N atoms are alternately aligned along the c -axis, so the B-N attraction makes hBN much more stable compared to AA-stacked BN and leads to lower interlayer spacing 3.33 $\text{\AA}$ [191, 193, 195]. In the AB-stacked form of layered BN, referred to as Bernal boron nitride (bBN), subsequent layers are laterally shifted with respect to each other in such a way that half of the atoms in the upper plane lie above the centers of hexagons in the underlying plane. In contrast, the remaining atoms are located directly above atoms of the opposite species. Therefore, the stacking sequence repeats every two atomic planes. In ABC-stacked rhombohedral boron nitride (rBN), the lateral shift between adjacent atomic planes is smaller, so the structure repeats every three layers. The attraction between vertically aligned

B and N atoms provides structural stability to bBN and rBN and makes their interlayer spacing similar to that of hBN. While the stacking sequence can affect the distance between adjacent atomic planes, it does not affect the in-plane separation between covalently-bonded atoms. Therefore, in-plane lattice constant predicted by the theory for all polytypes is almost the same $a=(2.476-2.478)$ Å [191]. Although the experimentally observed value of $a=2.504$ Å is higher than expected, it does not vary along polytypes [193]. Notably, not all BN crystals follow any of the above symmetric structures. In particular, during the growth of layered BN, it is common to obtain also material that lacks perfect crystalline periodicity. In this disordered polytype, referred to as turbostratic boron nitride (tBN), atomic planes are randomly translated and twisted relative to one another.

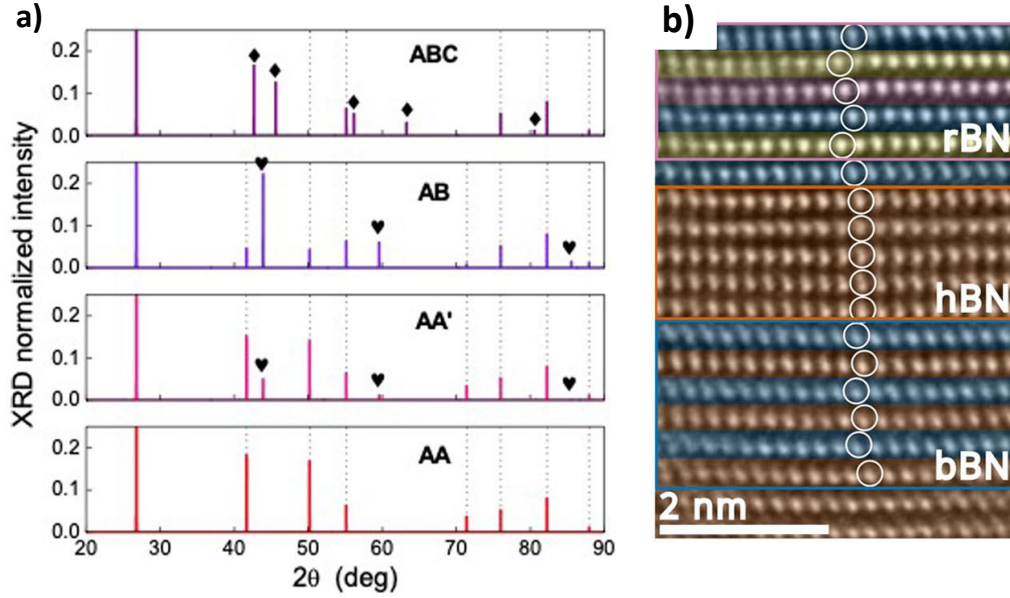


Figure 2.3: Methods of identifying sp^2 -bonded BN polytypes. a) Simulated XRD spectra for various BN stackings. Common peaks are marked by dashed, gray lines. Diamonds (hearts) indicate peaks unique to rBN (hBN and bBN) forms. Adapted from [196] b) TEM cross-section image of an exemplary epitaxial BN layer. Three colors correspond to different lateral shifts of atomic planes. Picture analysis allows for the identification of rBN, hBN, and bBN forms present in the studied sample. Adapted from [197].

Although adjacent layers of 2D BN interact only via weak van der Waals coupling, their arrangement determines the crystal symmetry. It therefore influences fundamental properties of the material, such as electronic and vibrational properties, selection rules, and defect-related transitions. In particular, non-centrosymmetric bBN and rBN support ferroelectricity, as well as second-harmonic generation (SHG) and other non-linear optical processes, which are forbidden in centrosymmetric hBN [198–202]. These examples illustrate the crucial role of polytypism in layered BN; thus, the distinction between various forms of sp^2 -bonded BN is of key importance. It can be directly achieved using X-ray diffraction (XRD)

measurements; however, this is experimentally challenging [196]. Figure 2.3a shows simulated XRD spectra for various BN polytypes when using a standard $\text{CuK}\alpha$ X-ray source with a characteristic wavelength $\lambda = 1.542 \text{ \AA}$. Obviously, due to their similar structures, all the above-discussed polytypes exhibit many common peaks marked by gray, dashed lines. In particular, based on (001)-type reflections, it is impossible to distinguish between AA'-, AB-, and ABC-stacked phases, since the diffraction angle $2\theta \approx 26.7^\circ$ is the same for all of them. Polytype identification requires access to non-(001) diffraction peaks. rBN exhibits unique reflections marked by diamonds in Figure 2.3a, while those marked by hearts are observed only in hBN and bBN. The last two phases might be distinguished by analyzing the intensity ratios between various diffraction peaks. The stacking sequence can also be studied locally using transmission electron microscopy (TEM), which directly shows the atomic arrangement. As shown in Figure 2.3b, the analysis of the lateral shift between adjacent layers enables polytype identification.

At this point, it is worth mentioning that although sp^2 hybridization is preferred in BN crystals, sp^3 -bonded BN structures - cubic and wurtzite boron nitride (cBN and wBN, respectively) are also possible. cBN crystallizes in the zinc-blende structure analogous to that of diamond. The relationship between cBN and rBN phases resembles the one between diamond and graphite, as sp^3 -bonded cBN can be obtained from sp^2 -bonded rBN under high-pressure and high-temperature conditions, which induces the compression of layered material and the transformation of the crystal lattice [203, 204]. cBN exhibits extreme hardness, similar to that of diamond, revealing potential for protecting coatings. However, compared to diamond, it shows higher both oxidation and graphitization temperatures, which expand its range of tooling applications [203]. Similar to layered BN forms and other III-group nitrides, cBN has an ultra-wide bandgap ($\sim 6 \text{ eV}$) and very high thermal conductivity $\kappa_{th} \approx 12 \text{ W cm}^{-1} \text{ K}^{-1}$, revealing a potential for high-power electronics. [204, 205]. wBN can be obtained at high temperature and high pressure hBN compression process similar to the transformation of rBN into cBN [203]. wBN is a metastable form of BN, so obtaining phase-pure material and conducting detailed studies of its properties are challenging.

Since the studies described in this thesis focus only on sp^2 -hybridized BN, sp^3 -bonded forms have been briefly discussed above to provide a broad perspective on the variety of BN crystalline structures; however, they will not be considered further in this work. From now on, the term BN refers only to sp^2 -hybridized boron nitride. Notably, all the studied samples described in Chapters 4-6 consist of a mixture of various sp^2 polytypes.

2.2.2 Vibrational and Optical Properties

The symmetry of different layered BN polytypes determines their vibrational properties [191, 206, 207]. In particular, it affects the number of vibrational modes: six for AA-stacked BN and rBN, twelve for hBN and bBN (in all cases, three acoustic modes are included). The difference arises from the unequal numbers of atoms in the primitive unit cells. Moreover, although vibrational modes have comparable frequencies across different polytypes, their IR and Raman activities may differ.

In all BN polytypes, high-energy phonon modes of E or E' symmetry and the energy $\sim 1367 \text{ cm}^{-1}$ occur. They are related to in-plane vibrations, in which B and N atoms within the same layer move in opposite directions. Observation of these modes is typically taken as evidence of the layered nature of the studied BN sample. In AA-stacked BN, bBN, and rBN, all these high-energy modes are both IR- and Raman-active. In contrast, in hBN, two nearly degenerate modes are observed at $\sim 1367 \text{ cm}^{-1}$, but one of them is IR-active only (E_{1u}) and the second one is Raman-active only (E_{2g}^{high}) [191, 206–209]. For the E_{2g}^{high} mode, the next vertically aligned B and N atoms move in the same direction, whereas for E_{1u} they are in the opposite phase.

Another important energy region is $700\text{--}800 \text{ cm}^{-1}$, where phonons of A symmetry occur. In rBN, the A_1 mode is both IR- and Raman-active, while in other polytypes, modes of A symmetry are IR-active only. Therefore, the Raman signal in this energy region might be attributed to the presence of ABC-stacked BN [207, 210–212].

Finally, low-energy $0\text{--}100 \text{ cm}^{-1}$ vibrations are concerned. In AA-stacked BN and rBN, only acoustic phonons exist in this energy range, so no IR or Raman signal is expected. By contrast, AA'- and AB-stacked BN possess low-energy optically active modes [207, 210]. While the E' mode in bBN is both IR- and Raman-active, the E_{2g}^{low} mode of the energy $\sim 50 \text{ cm}^{-1}$ in hBN can be observed only in Raman spectroscopy. Unlike the high-energy E_{2g}^{high} mode, in the case of the E_{2g}^{low} phonon all atoms within a single atomic plane move in the same direction, and subsequent layers move in opposite phase [208, 213, 214].

To better illustrate differences across various BN stackings, the literature hBN and rBN Raman spectra are shown in Figure 2.4 [210]. Both polytypes exhibit peaks at $\sim 1367 \text{ cm}^{-1}$. However, a weak signal at $\sim 800 \text{ cm}^{-1}$ is present in the rBN Raman spectrum only. On the other hand, the breathing mode E_{2g}^{low} of the energy $\sim 50 \text{ cm}^{-1}$ is observed only in hBN.

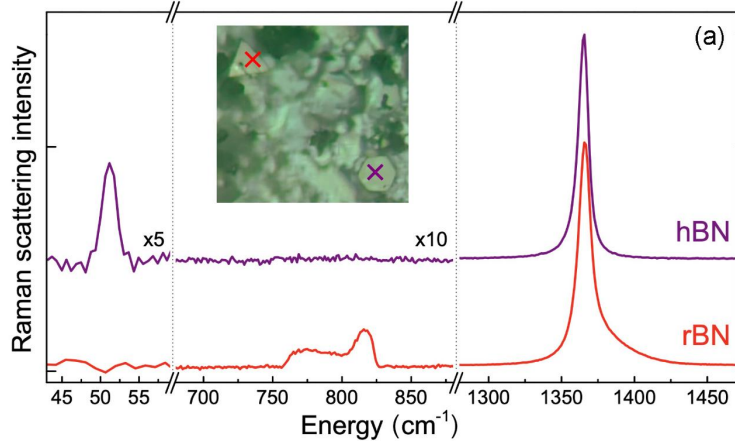


Figure 2.4: Literature Raman spectra of hBN and rBN crystals, revealing the presence of Raman-active phonon modes in different energy ranges. Adapted from [210].

Optical properties of layered BN are strongly affected by its vibrational properties, as we discuss using hBN as an example. Figure 2.5a shows the Brillouin zone (BZ) of a BN monolayer with high-symmetry points labeled. Theoretical calculations predict that monolayer BN is a direct-bandgap material with band extrema aligned at the K point of the BZ (Figure 2.5b). On the other hand, bilayer hBN is expected to exhibit an indirect bandgap with valence band maximum near the K point and conduction band minimum at the M point (Figure 2.5c) [215–219]. Doubling the number of atoms in the primitive cell (from two in monolayer BN to four in hBN) increases the number of interacting orbitals. This leads to the formation of additional electronic bands, changing the bandgap from direct to indirect. However, despite this indirect bandgap, hBN exhibits strong deep-UV (DUV) bandgap emission, more intense than that of ultrabright direct-bandgap materials such as diamond or zinc oxide [220, 221]. Intuitively, such a pronounced PL signal suggests that the hBN bandgap is direct. This discrepancy between theory and experiment was solved in 2016 by the group of G. Cassabois and B. Gil, who performed two-photon optical spectroscopy measurements providing evidence for the indirect bandgap of 5.95 eV [186].

As shown in Figure 2.5d-e, the band-edge photoluminescence (PL) spectrum of hBN consists of a very weak emission at 5.95 eV (marked as iX), originating from the forbidden recombination of indirect excitons, followed by strong phonon-assisted transitions. As marked by green arrows, the relative positions of phonon replicas correspond to vibration modes at the T point in the KT direction in the BZ. This result perfectly fits the theory since the ΓT vector is equivalent to the MK vector. The intense hBN band-edge emission originates from a very strong electron-phonon coupling and the formation of flat bands along KH and ML directions (Figure 2.5f-g), leading to a higher density of states [186, 222]. Notably, the indirect-to-direct crossover in the monolayer regime has been demonstrated experimentally [223].

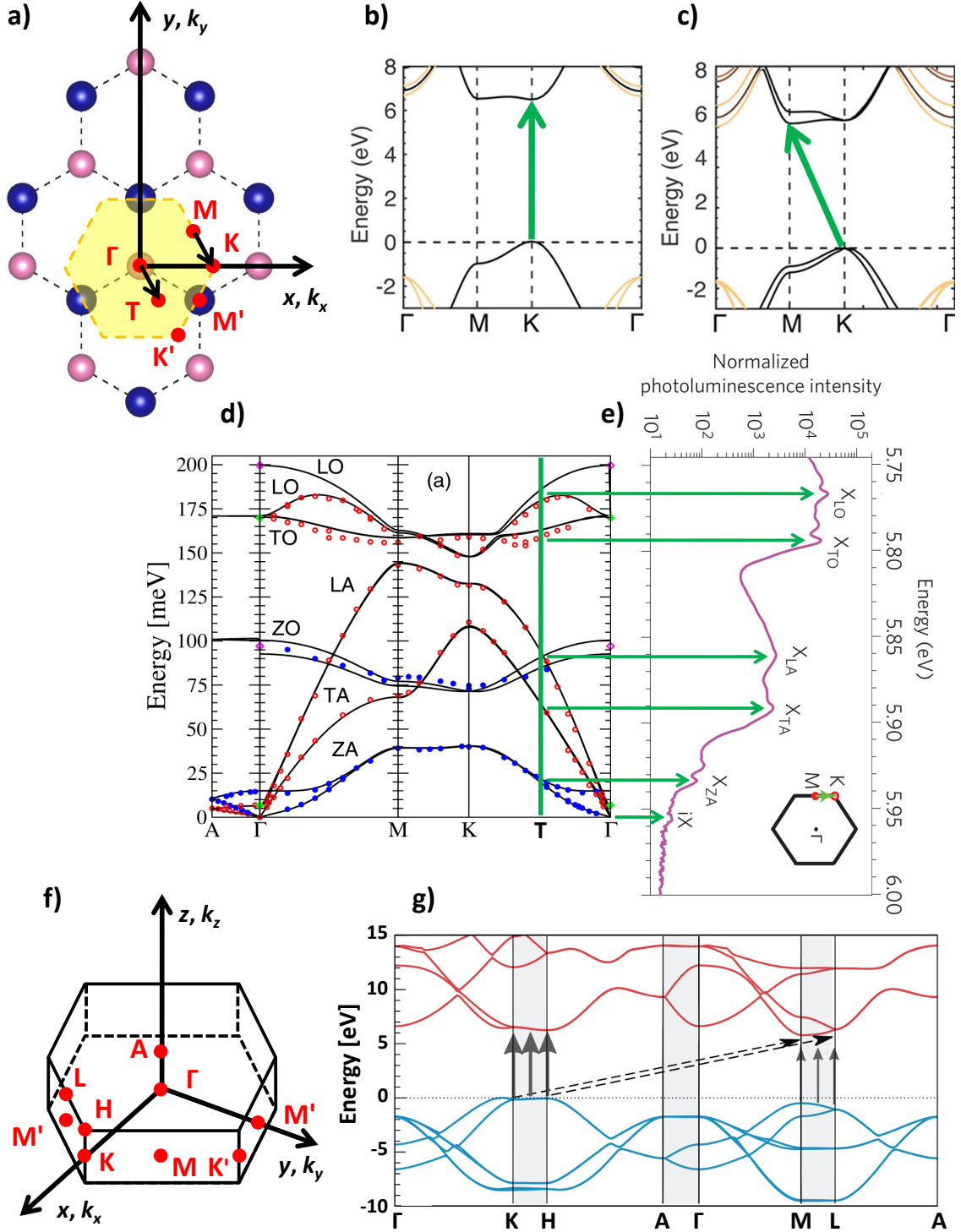


Figure 2.5: a) Atomic structure of the BN monolayer and BZ (yellow hexagon) with marked high-symmetry points (red dots). Black arrows mark equivalent ΓT and MK vectors in reciprocal space. The atomic structure was prepared using VESTA software [192]. (b-c) Theoretical calculations of band structure for monolayer BN and hBN, respectively. Green arrows mark bandgap transitions. Adapted from [219]. d) Phonon dispersion in hBN: points - experimental data, solid curves - calculations. Adapted from [224]. e) PL spectrum of hBN. Adapted from [186]. Green arrows between d) and e) show the relation between hBN PL spectrum and phonon dispersion. f) BZ of hBN with marked high-symmetry points. g) Full calculated band structure for hBN, including all high-symmetry points in BZ. Solid (dashed) arrows mark direct (indirect) optical transitions. Formed flat bands are marked in gray. Adapted from [222].

2.2.3 Applications

Layered BN possesses unique properties, making it useful in a wide range of applications. As mentioned previously, unlike most other 2D materials, BN exhibits high thermal and chemical stability, as well as high thermal conductivity. Therefore, it is commonly used to encapsulate other layered materials and van der Waals heterostructures, protecting them from degradation in ambient conditions and providing effective heat dissipation. Moreover, some 2D materials have been reported to reveal more stable emission and narrower spectral lines when embedded between BN flakes [225, 226], as shown in Figure 2.6a. In addition, due to its wide bandgap and high breakdown electric field, BN can be used as an insulating component, particularly to separate the gate from the transistor channel or from the studied material [227, 228].

Due to its bendability, BN can be used in flexible optoelectronics [181, 227, 228]. Apart from serving as a support for small, flake-sized devices, BN plays an important role in so-called van der Waals epitaxy. In this method, a 2D material is used as a substrate for growing a new material. Due to the layered nature of the substrate, no covalent bonds are formed at the interface, so lattice mismatch is not an issue [229]. BN has been shown to serve as a perfect substrate for the growth of other 2D materials, such as graphene and TMDCs [230, 231]. Moreover, van der Waals epitaxy on graphene or hBN enables the growth of sp^3 -bonded materials and their heterostructures, which can be easily transferred off the original substrate, giving rise to elastic optoelectronics [229]. In particular, flexible μ LEDs and quantum well-based structures, obtained via the growth on BN-coated substrates, have been demonstrated [232–235]. An example of such an elastic light-emitting device is shown in Figure 2.6b-c.

As discussed in section 2.2.2, despite being an indirect-bandgap semiconductor, layered BN exhibits remarkably efficient DUV emission under optical excitation. Although this spectral range is crucial for disinfection and sterilization, effective light sources remain limited. Consequently, BN has emerged as a promising candidate for DUV-emitting devices. Notably, BN has been reported to exhibit much stronger bandgap PL emission than AlGaN, which currently acts as a benchmark for DUV optoelectronics [236]. Unfortunately, the development of BN-based electrically-driven LEDs is hindered by the lack of effective doping methods. However, as shown in Figure 2.6d-e, electroluminescence (EL) DUV emission was observed in graphene/BN/graphene heterostructures [237].

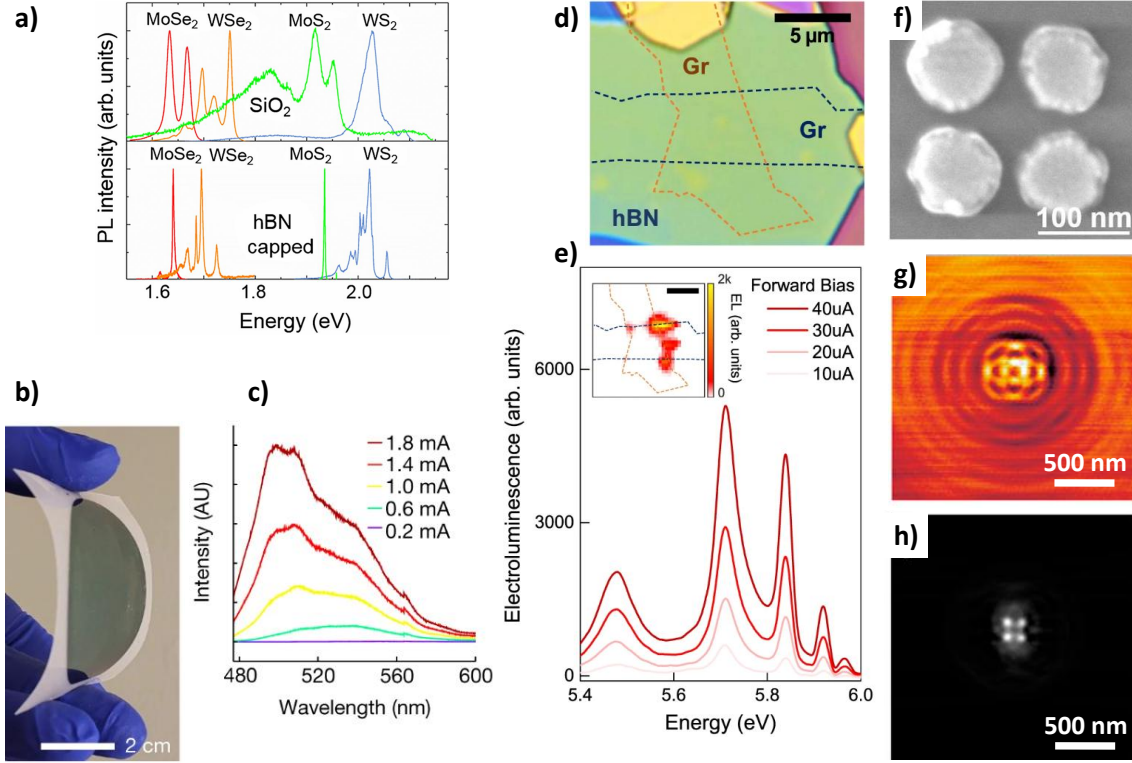


Figure 2.6: a) Low-temperature (4K) spectra of common TMDCs deposited directly on SiO₂ substrate (upper panel) and capped with layered BN (bottom panel). Adapted from [225]. (b-c) Photo and EL emission spectra of flexible InGaN-based LEDs grown on BN, respectively. Adapted from [234]. (d-e) Microscope image and EL emission spectra of graphene/BN/graphene heterostructure, respectively. Adapted from [237]. (f-h) SEM image of four 44 nm diameter discs, amplitude of the SNOM signal collected at frequency 1480 cm⁻¹ from BN flakes transferred onto discs, and a visual representation of the embedded disc obtained from the SNOM image via a reconstruction algorithm, respectively. Adapted from [238].

The strong coupling between IR-active transverse optical phonons and electromagnetic radiation gives rise to phonon-polaritons (PhPs). Their dispersion is photon-like at small wave vectors and phonon-like at larger momenta. As a result of its strong structural anisotropy, layered BN exhibits open hyperbolic isofrequency surfaces, which support the propagation of hyperbolic PhPs (HPhPs) with very large wave vectors at a fixed frequency [239, 240]. Consequently, the associated electromagnetic field can be confined to subwavelength dimensions, thereby making layered BN an attractive platform for nanophotonics. HPhPs cannot be observed in the far field due to the momentum mismatch between HPhPs and photons. Typically, they are observed in scanning near-field optical microscopy (SNOM). To provide momentum compensation and launch HPhP waves in BN, the light is scattered by a tip, used in an atomic force microscopy (AFM) setup [239, 240]. The utility of HPhPs in BN has been demonstrated in subdiffraction sensing and imaging, molecular-scale detection, and thermal imaging [238, 241–245]. SNOM measurements followed by appropriate reconstruction algorithms enable

HPhP-based imaging of subwavelength-sized objects. Figure 2.6f shows a scanning electron microscope (SEM) image of 44 nm-diameter discs, which cannot be observed via typical optical methods. However, when they are covered with a BN flake, SNOM measurements under IR excitation enable their imaging (Figure 2.6g-h).

Interestingly, BN can be used in neutron detectors [246–248]. Such devices take advantage of the fact that the ^{10}B isotope has one of the highest cross-sections for thermal neutron absorption across all isotopes, which is ~ 3840 barns [249]. For comparison, for other group-III isotopes, it ranges between 0.01-200 barns [249]. When a ^{10}B atom captures a neutron, ^7Li and an α particle are formed. They travel through the BN crystal lattice and lose energy by generating electron-hole pairs. Generated current is the measured quantity [246–248].

Finally, point defects in the BN crystal lattice, acting as single-photon emitters (SPEs), have been demonstrated to be sufficient for quantum technologies such as quantum key distribution (QKD), quantum random number generators, and quantum computing [10, 32–34, 144, 145]. Notably, due to its resistance to cosmic radiation [250], layered BN is being studied for quantum communication in space. In particular, the QUICK³ mission aims to demonstrate a quantum communication architecture that uses BN-based SPEs [251, 252]. Moreover, spin defects in layered BN are used for quantum sensing. Compared to nitrogen-vacancy (NV^-) centers in diamond, they offer close-proximity probing, since a few-atom-thick BN layer can be put directly onto the studied sample. The utility of spin defects in BN has been demonstrated in magnetic field, temperature, and pressure sensing [20, 142, 143, 253]. The properties of quantum emitters in BN are discussed in section 2.4.

2.3 Growth of Layered Boron Nitride

2.3.1 Growth of Bulk Crystals

Various methods of BN growth have been developed. Crystals of the highest structural quality are obtained by the group of Taniguchi and Watanabe via the temperature-gradient method under High-Pressure High-Temperature (HPHT) conditions [254, 255]. In this approach, BN powder or BN discs are dissolved in $\text{Ba}_3\text{B}_2\text{N}_4$. The source material and the solvent are encapsulated in a molybdenum sample chamber. Then, the sample is compressed at a high pressure of 4-5 GPa and heated up to 1500-1700 °C for 20-80 h. Before growth, the BN source is annealed at ~ 2000 °C in a nitrogen atmosphere to remove oxygen impurities. Crystals obtained via this approach exhibit excellent properties. In particular, intense excitonic emission at 5.765 eV from these crystals was observed [220, 254, 255]. However, the size of the crystals obtained by this method does not exceed a few mm^3 .

BN bulk crystals are also obtained via the metal-flux method [256]. In this approach, boron nitride powder is mixed with Ni and Cr powders. Such a powder mixture is loaded into a crucible and placed in a furnace filled with nitrogen gas. Then, the system is heated to a soak temperature of around 1500 °C for a few hours, allowing the Ni-Cr flux to saturate with boron and nitrogen. In the next step, the temperature is slowly decreased to around 1200 °C. This results in the crystallization of BN crystals, whose quality is similar to that obtained by Taniguchi and Watanabe [257]. Recent work has also explored growth using Ni and Ni-Cr solutions at high N₂ pressure, leading to the growth of thicker crystals ($\sim 30\text{ }\mu\text{m}$) of excellent quality [258]. Other solvents, including Fe-Cr and pure Fe fluxes, have also been demonstrated to support the growth of BN crystals [259, 260]. The size of bulk crystals obtained via this method is limited to a few mm³.

2.3.2 Epitaxial Methods

While the quality of bulk BN crystals is very high, their small sizes make them insufficient for scalable applications. The growth of large-area material can be achieved via epitaxial methods. Epitaxy is the growth of a crystalline layer whose crystallographic orientation is determined by the substrate. If the epitaxial layer is grown on the substrate made of the same material, the process is called homoepitaxy. On the contrary, when the substrate is made of a different material from the grown layer, then the process is called heteroepitaxy. In the latter case, the choice of an appropriate substrate, with a lattice constant similar to that of the grown material, is crucial. A large lattice mismatch between an epilayer and a substrate can generate strain at the interface and induce the growth of three-dimensional islands.

Depending on the way the crystalline layer is formed, two main approaches can be distinguished. One of them is molecular beam epitaxy (MBE). In this technique, ultra-pure elements are deposited onto a substrate. In the case of BN growth, the elemental boron is introduced into the growth chamber via thermal evaporation from an effusion cell. At the same time, highly-reactive nitrogen species involved in BN growth are supplied by a radio-frequency plasma source that dissociates and excites N₂ gas. The growth is carried out under ultra-high vacuum (typically $\sim 10^{-11}$ Torr) to avoid introducing impurities and to ensure a ballistic transport of boron and nitrogen species. A successful MBE growth of layered BN has been reported on various substrates, including Ni(111), graphite, and sapphire [261–264]. Depending on the substrate, high temperatures of 800-1700 °C are required. The advantages of MBE growth of BN are the precise control of the sample thickness and the high purity of the obtained epilayer. The drawback is a slow growth rate, ranging from 1 monolayer in a few minutes to 1 monolayer in a few hours [262, 263, 265, 266].

The second method is chemical vapor deposition (CVD). In this approach, BN is obtained using gaseous precursors that decompose at high temperatures into highly reactive species, which are then deposited onto a chosen substrate [267, 268]. One type of substrate is metallic, such as copper, platinum, nickel, or iron [269–272]. Notably, the growth mechanism is not the same for all of them [267]. When growth occurs on copper or platinum, which exhibit low solubility for boron and nitrogen, BN forms via surface reactions. On the other hand, if nickel or iron substrates are involved, boron and nitrogen can be dissolved. In such a case, cooling down results in the formation of the BN layer via precipitation on the metal surface. Growth on metallic substrates requires an additional transfer step that can introduce contamination or break the material. Moreover, controlling BN thickness over large areas remains challenging. These problems might be overcome by the growth on insulating substrates such as sapphire [267, 268]. This approach provides wafer-scale uniformity and facilitates integration with other materials while eliminating the need for transfer. Given these advantages, the further discussion focuses on the BN growth on insulating substrates. Both boron and nitrogen can be introduced via a single reactant, such as borazine ($\text{B}_3\text{N}_3\text{H}_6$) [273, 274]; however, usually two precursors are used [267, 268]. A common source of nitrogen is ammonia (NH_3), while two typically used boron precursors are trimethylborane (TMB, $\text{B}(\text{CH}_3)_3$) and triethylborane (TEB, $\text{B}(\text{C}_2\text{H}_5)_3$). Notably, both of them contain carbon, which might incorporate into BN lattice. The growth of crystalline layers using metal-organic compounds is called metal-organic chemical vapor deposition (MOCVD) or metal-organic vapor phase epitaxy (MOVPE). Both names are used in the literature. When the primary focus is on the chemical reactions leading to material formation, the term MOCVD is used. On the contrary, the term MOVPE emphasizes crystal quality and the relationship between the crystallographic orientations of the grown layer and the substrate. During MOVPE growth of BN, gaseous TMB or TEB are decomposed and interact with NH_3 , leading to the formation of an epilayer on a wafer-scale substrate. BN grown via this approach still has worse structural quality than bulk crystals and is less pure than MBE-grown epilayers. However, MOVPE enables reproducible, fast growth of large-area materials, providing a good compromise between the structural quality, scalability, and growth rate. Due to these advantages, it is considered promising for BN applications. Substantial progress has been made in recent years toward wafer-scale MOVPE growth of BN, with several groups demonstrating high-quality material [275–278]. Manipulating growth parameters, such as growth time, temperature, pressure, or the ammonia-to-boron precursor flow ratio, enables precise control of BN thickness and properties. All samples studied in this work were grown via MOVPE. Technical details are included in section 3.1.

2.4 Quantum Emitters in Layered Boron Nitride

Layered BN hosts color centers spanning a wide spectral range from UV to near-infrared (NIR). Although this work primarily focuses on the properties of visible SPEs in MOVPE-grown BN, other defect types also arise in this study. Therefore, for completeness, all types of emitters in BN are discussed below, ordered from higher to lower emission energies. Visible SPEs are introduced in detail in Section 2.4.3. It provides the background necessary to discuss the results presented in Chapter 4, which focuses on the influence of growth conditions on the properties of quantum emitters in MOVPE-grown BN and on their temperature-dependent spectral properties. Section 2.4.4 motivates the studies presented in Chapter 6.

2.4.1 UV Defects

UV-emitting point defects in BN were first reported in 1975 [279]. As shown in Figure 2.7a, their emission spectrum consists of a ZPL at ~ 4.1 eV accompanied by phonon replicas detuned by ~ 200 meV. Recently, the ZPL energy of the UV center has been demonstrated to serve as a fingerprint of the BN layer stacking sequence. In hBN, it is ~ 4.10 eV, whereas a value of ~ 4.14 eV was reported for rBN by our group [197] (Figure 2.7a). In bBN, two peaks at ~ 4.14 eV and ~ 4.16 eV, with significantly lower intensity than in hBN and rBN, were identified (Figure 2.7b) [280].

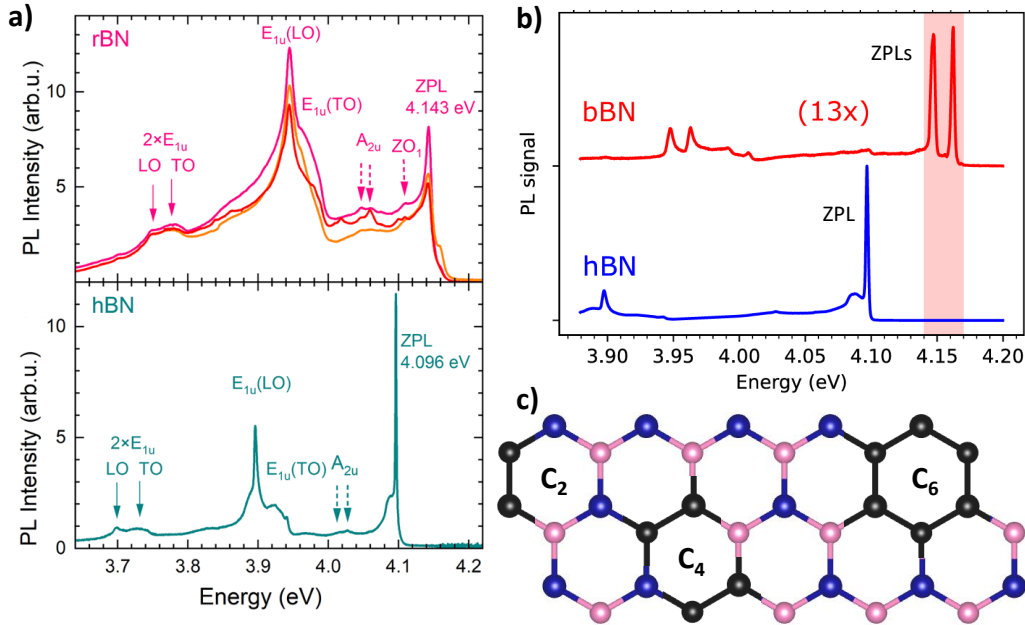


Figure 2.7: a) Comparison of low-temperature (8 K) PL spectra of UV-emitting defects in epitaxially-grown rBN (upper panel) and in bulk hBN (bottom panel). Phonon replicas are marked. In rBN, ZPL is blueshifted by ~ 40 meV compared to the one observed in hBN. Adapted from [197], b) Comparison of low-temperature (6 K) PL spectra of UV-emitting defects in bulk bBN and hBN. Adapted from [280]. c) Proposed carbon-related UV emitters in BN. Prepared using VESTA software [192].

Typically, UV centers are observed in carbon-doped BN, and their emission intensity correlates with carbon concentration [254, 281–284]. Therefore, based on theoretical calculations, carbon-related point defects, such as carbon dimers (C_2), tetramers (C_4), or rings (C_6) are proposed as sources of 4.1 eV emission (Figure 2.7c) [11, 197, 285–289]. In contrast, no direct correlation between carbon concentration and 4.1 eV emission intensity was found in [290], suggesting the key role of carbon-free lattice imperfections, such as the Stone-Wales defect, which is also predicted to emit light in the UV range [291]. However, recent results involving studies of 4.1 eV emission in BN samples with different polytypic and isotopic composition, complemented by pressure-dependent measurements, clearly indicate the crucial role of C_2 [289].

Due to experimental challenges, true single-photon emission from the UV defect in BN has been reported only once to date [9]. In this experiment, a hyperspectral cathodoluminescence (CL) map with an 18 nm step size was acquired to identify a well-isolated point defect, exhibiting a highly localized emission spot (~ 80 nm). $g^{(2)}(0)$ measurements performed on this defect under electron beam excitation proved that it acts as an SPE. Unfortunately, conducting second-order correlation function measurements with optical excitation is extremely challenging because it requires addressing individual point defects and ensuring efficient laser excitation and signal collection. Meeting these requirements in the UV range within a conventional optical setup is experimentally difficult due to aberrations. This strongly limits the facility of UV emitters in quantum applications.

2.4.2 B-Centers

The next class of color centers in layered BN is the blue centers (B centers), first observed in 2019 [8]. In hBN, the emission spectrum consists of the ZPL centered at ~ 2.85 eV (436 nm) followed by PSBs. Like in the case of UV defect, the emission energy of B centers in rBN is blue-shifted by ~ 40 meV compared to the value for hBN [292], as shown in Figure 2.8a. There is no scientific consensus on the atomic structure of these defects; however, they are present only in BN samples that exhibit UV defect-related emission [293, 294]. Therefore, the presence of carbon appears crucial for B center formation. One of the candidates of greatest interest is a carbon tetramer (C_4^{trans}) in the *trans* configuration [295] shown in Figure 2.8b. The predicted ZPL energy of 3.13 eV is in good agreement with the experimental results. Similarly, the calculated radiative lifetime 1.62 ns aligns well with the reported value of 1.85 ns [296].

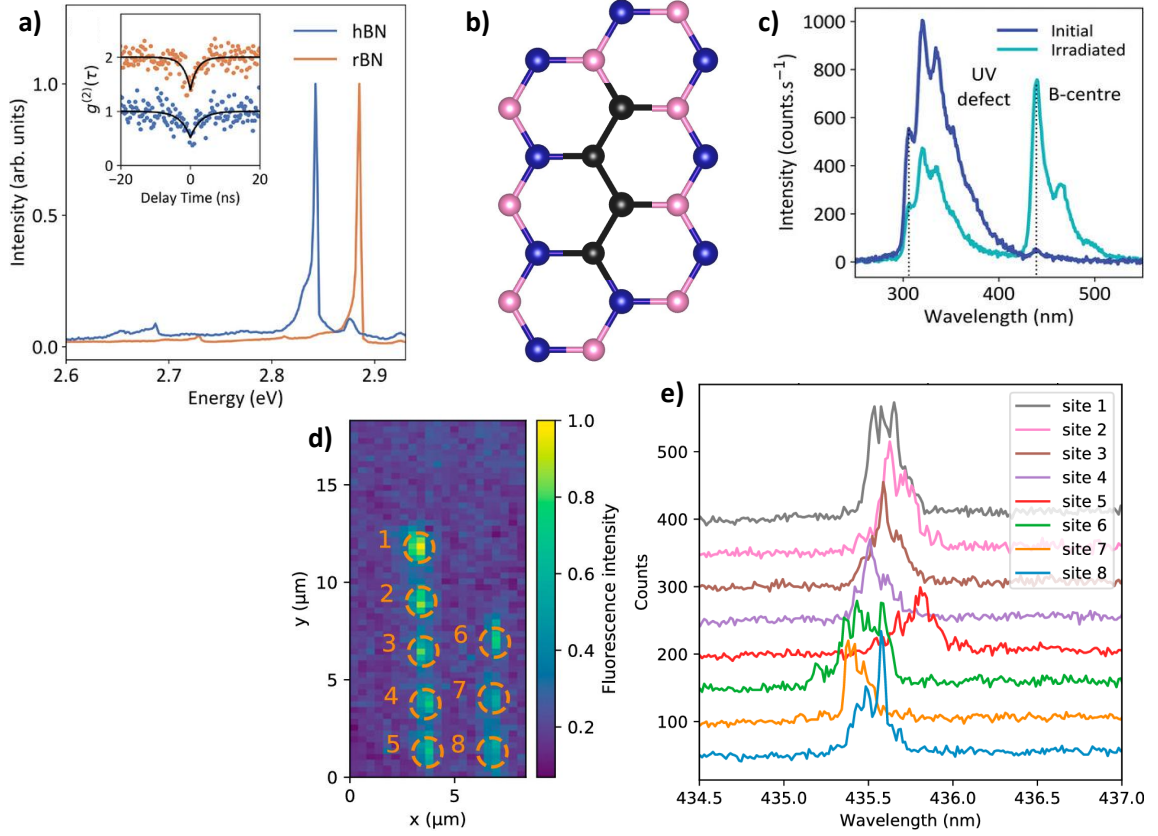


Figure 2.8: a) Comparison of low-temperature (5 K) PL spectra of B center emission in hBN (blue) and rBN (orange). In rBN, the ZPL is blueshifted by ~ 40 meV compared to the one observed in hBN. Inset - results of $g^{(2)}(\tau)$ measurements providing quantum nature of the emitters. Adapted from [292]. b) Structure of C_4^{trans} defect - a candidate for B center. Prepared using VESTA software [192]. c) CL spectra of hBN flake acquired before (dark blue) and after (cyan) e-beam exposure. Irradiation results in the formation of B centers, accompanied by a decrease in UV defect-related emission. Adapted from [294]. d) PL map of B center emission intensity in hBN flake treated by an e-beam at selected points. Bright spots correspond to irradiated regions, indicating that B-center generation is a deterministic process. e) Low temperature (5 K) PL spectra collected at bright spots shown in d). The spectral distribution of the observed ZPL is very narrow. Both d) and e) are adapted from [296].

Although the presence of carbon in the BN crystal lattice is necessary to observe blue defect-related emission, additional activation is required. Namely, B centers form in carbon-doped BN irradiated with an electron beam (e-beam), and to date, this is the only reported protocol for their generation [293, 294, 296–298]. As shown in Figure 2.8c, an increase in B center emission is accompanied by a decrease in 4.1 eV defect emission. This behavior indicates that the formation of blue-emitting centers arises from the restructuring of existing carbon-related defects, responsible for UV emission [293, 294, 297]. The electrons typically used in the experiments have too low energies (5-10 keV) to induce B center formation by knocking an atom out via momentum transfer [293]. Instead, bond breaking induced by electron-electron collisions, followed by the drift of ionized atoms in the e-beam electric field, is

considered the primary mechanism for the reorganization of carbon-related UV defects into B centers [293, 294].

Blue emitters offer many advantages for quantum technologies, both in fabrication and properties. First, since e-beam irradiation is necessary to create B centers, they are formed only at precisely selected points, providing spatial control on their positions [293, 294, 296–298]. As shown in Figure 2.8d-e, such deterministically obtained blue emitters are highly reproducible, and the ZPL energy exhibits a very narrow spectral distribution. Notably, the same ZPL emission energy has been reported in many different BN samples by many groups. Even at room temperature, B centers act as pure SPEs reaching $g^{(2)}(0) \approx (0.1–0.2)$ [34, 293, 296–301]. Recently, the utility of blue emitters has been demonstrated in QKD [34]. Interestingly, the ZPL emission energy is very close to the water absorption minimum (417 nm), so B centers hold great promise for underwater quantum communication [34]. In addition, in 2023, the first reported results of the Hong-Ou-Mandel two-photon interference experiment performed on B centers revealed photon indistinguishability with $V_{HOM} = 0.56 \pm 0.11$ [299]. Recently, $V_{HOM} > 0.9$ was reported under resonant excitation, demonstrating the potential of B centers in quantum applications [302].

2.4.3 Visible Single-Photon Emitters

In this section, we discuss the so-called visible color centers studied in this work. Unlike the 4.1 eV defect and the B center, they do not exhibit a single emission energy but instead span the entire visible range [303], as shown in Figure 2.9. In 2016, they were reported to act as SPEs [6], gaining significant attention.

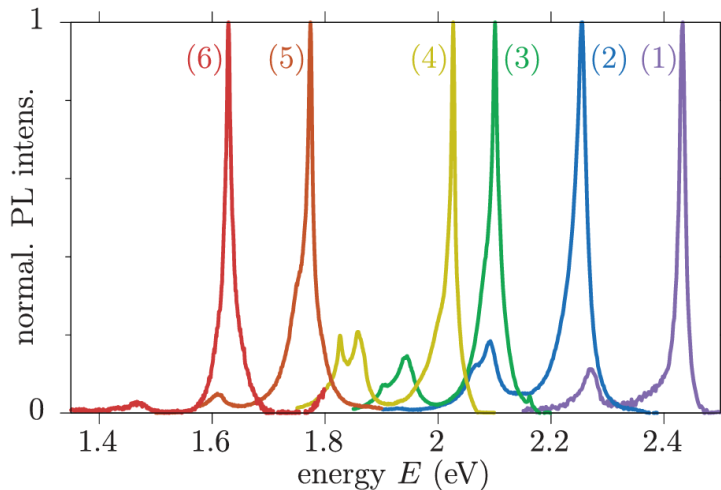


Figure 2.9: Exemplary PL spectra of visible SPEs consisting of strong ZPLs followed by phonon replicas with energy detuning of 150–200 meV. The observed emission covers the entire visible spectral range. Adapted from [303].

Over the last decade, various protocols for obtaining visible centers have been demonstrated. In the simplest case, emitters are activated via annealing BN at high temperatures ~ 1000 °C in an inert argon environment [6, 114]. An increase in the annealing temperature results in a higher emitter density, indicating the crucial role of lattice relaxation and defect diffusion [114]. This behavior suggests that vacancy-related defects contribute to visible emission. The annealing method has been extended to non-inert environments. In particular, BN annealing in oxygen and carbon-rich conditions also introduces visible SPEs into the BN lattice [304–306], suggesting the important role of oxygen- and carbon-related point defects. Similarly, common approaches are also argon and oxygen plasma treatments [305, 307–309].

Other methods for fabricating visible SPEs rely on bombarding BN with high-energy particles. In [310], ~ 2 MeV electron irradiation has been reported to increase the density of bright spots by a factor of 2-4 compared to non-exposed samples. Notably, the distribution of created emitters was similar in both carbon-doped and high-purity BN, suggesting that carbon is not involved in the atomic structure of the obtained defects. Similarly, irradiation via fast neutrons (~ 1.2 MeV) or heavy ions, such as Ta or Ge, with energies exceeding 100 MeV also results in the formation of visible SPEs [311, 312]. In all these cases, the authors have considered vacancy-related defects as the source of visible emission.

All the above-mentioned methods enable efficient fabrication of visible SPE over large areas of BN, but do not provide spatial localization. However, this can be achieved by transferring a BN flake that hosts emitters onto a graphene mask. As shown in Figure 2.10a-b, in such a case, point defects localized in predesigned holes arranged into an array can emit light, while the rest of them are quenched,[313]. In addition to the mask-based approach, many techniques developed over the last decade provide precise spatial control over the created emitters. A common method is BN irradiation with a focused ion beam (FIB), using Ga^+ , Xe^+ , or He^+ ions accelerated to energies of 5-30 keV [314–317]. Precise spatial control provided by electrostatic lenses allows for the fabrication of SPEs in selected areas (Figure 2.10c-d). Similar to FIB, irradiating BN with electrons of the energy of a few keV also introduces visible color centers into the BN lattice. Figure 2.10e shows a regular array of yellow emitters obtained via this method [318]. The energy that induces lattice damage and thereby introduces point defects may also be deposited via short, high-power light pulses used in so-called laser writing. Spatial resolution and position control are limited by a laser spot, facilitating regular SPE array fabrication shown in Figure 2.10f-g [319, 320]. The BN lattice may also be mechanically damaged using a very precise AFM tip in a technique known as nano-indentation [321, 322] (Figure 2.10h-j).

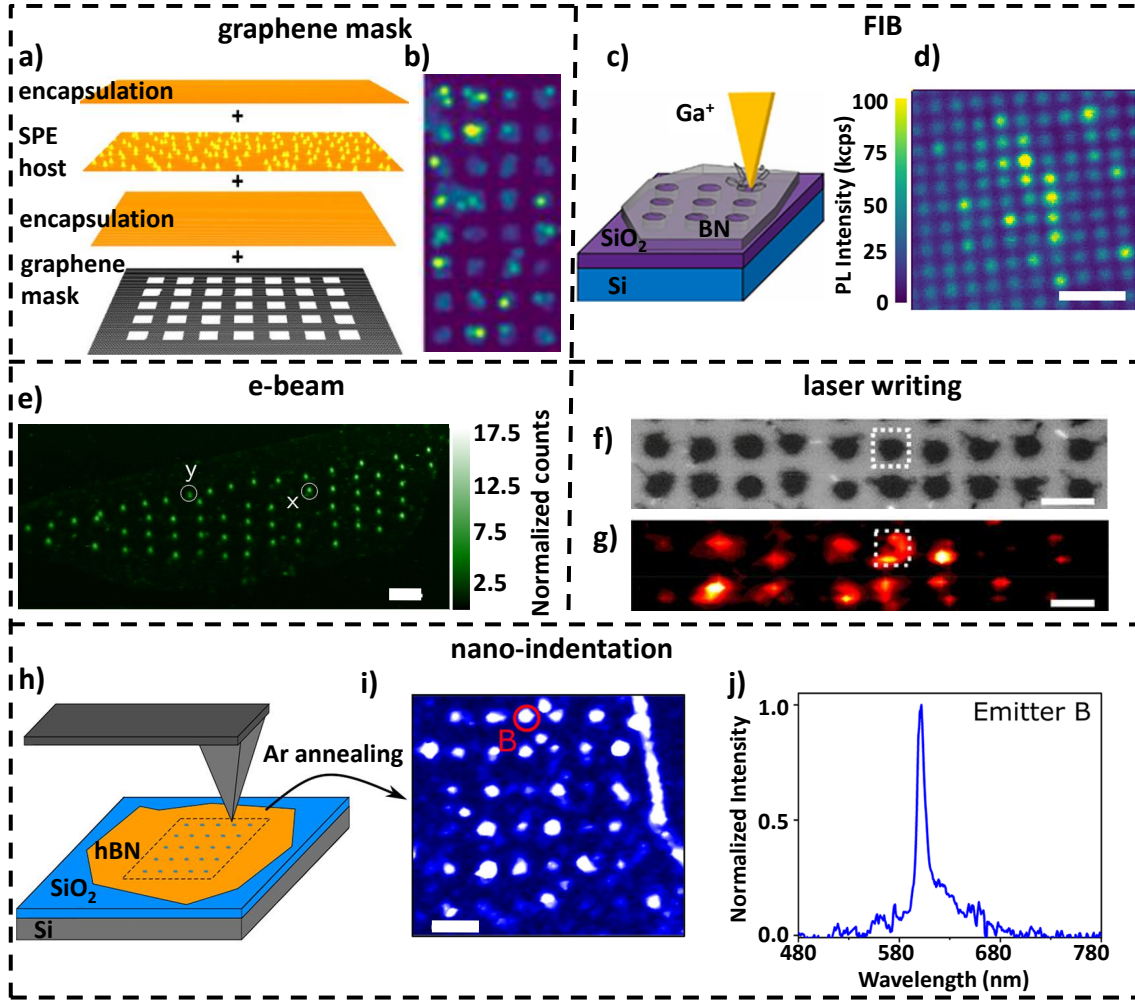


Figure 2.10: Selected techniques of deterministic fabrication of SPEs in BN. (a-b) Graphene mask approach. Adapted from [313]. a) Scheme of localizing SPE emission via a graphene mask: BN layer hosting color centers is encapsulated within two pure BN layers and put onto a graphene mask. b) PL map of an emitter array obtained by the use of a graphene mask with $1\mu\text{m} \times 1\mu\text{m}$ holes. (c-d) FIB-based approach. Adapted from [317]. c) scheme of FIB fabrication of SPEs. A focused beam of Ga^+ ions damages the BN lattice in precisely selected points. d) PL map of an emitter array obtained via FIB. Scalebar is $3\mu\text{m}$. e) PL map of a BN flake irradiated via e-beam in selected points. Bright spots correspond to the presence of yellow emitters. Scalebar is $5\mu\text{m}$. Adapted from [318]. (f-g) Laser writing technique. Adapted from [320]. f) SEM image of holes created in a BN flake by short laser pulses. g) PL map of the area shown in f). Bright spots, corresponding to visible color centers, are located around holes. Scalebars in f) and g) are $5\mu\text{m}$. (h-j) Nano-indentation technique. Adapted from [321]. h) The scheme of nano-indentation - AFM tip damage BN in selected regions, forming holes similar to those obtained via laser writing. i) PL map of emitter array obtained via nano-indentation. Scalebar is $2\mu\text{m}$. j) PL spectrum of the emitter marked as B in i).

Other methods of visible SPE activation are based on the material bending. In particular, the transfer of exfoliated BN flakes onto lithographically predefined pillar arrays or silica microspheres has been demonstrated to generate strong quantum light emission at points of the highest curvature [18, 141]. The proposed mechanism relies on the carrier trapping in the quantum-well-like deformation potential [18].

Unfortunately, such transfer-based methods apply only to small exfoliated flakes and are not scalable. However, successful bending of large-area BN has recently been achieved via direct growth on SiO₂ nanopillar arrays [323]. Interestingly, while as-grown BN located on pillars exhibited bright quantum light emission, the authors did not observe the formation of SPEs in the reference sample consisting of an exfoliated BN flake transferred onto a pillar array, in contrast to results described in [18, 141]. Therefore, the role of strain in color center formation remains incompletely understood, and further research is required.

The variety of methods for generating visible SPE in BN suggests the possible role of multiple point defects with different atomic structures. Therefore, to date, the identification of these color centers remains an open issue. Approaches that damage the lattice, such as FIB, e-beam irradiation, nano-indentation, or laser writing, should intuitively generate vacancy-related defects or dangling bonds. On the other hand, the formation of visible emitters during annealing in oxygen- or carbon-rich environments indicates that at least some of these emitters contain impurity atoms. As a consequence, over the last decade, researchers have proposed many point defects, acting as visible centers, such as native N_BV_N [6, 324], V_{B3N1} [311], carbon-related ones like V_NC_B [325–327], V_BC_N[−] [14], C_B and C_N [328, 329], C₂C_N and C₂C_B [328, 330], oxygen-related V_BO_N [309, 331], V_BO₂ [305, 309], or dangling bonds [314, 332]. Interestingly, while most of the proposed candidates are point defects within a single atomic plane, interlayer C_XC_X pairs have also recently been analyzed for visible emission [333].

Probably at least a few of the proposed defect atomic structures are realized in BN, as various studies have reported different classes of visible emitters. In particular, recent reports concerning visible emitters created via laser writing or nano-indentation indicate that, even within a single BN sample, SPEs can be grouped into a few distinct classes depending on their emission energy [320–322]. Another classification of visible emitters is based on the shape of the emission spectrum. In [114], the authors observed the emergence of emitters from two distinct groups. Centers belonging to the first group cover the region 580–650 nm. These emitters exhibit highly asymmetric ZPLs with a pronounced long-energy tail arising from coupling to low-energy phonons, followed by strong characteristic double-structure PSBs. The second group consists of color centers with narrower and more symmetric ZPLs and relatively weak phonon replicas. Typically, these emitters cover the region 680–760 nm. Recently, a large-scale statistical analysis of over 10000 color center spectra collected from BN nanoflakes has been reported [334]. The authors identified 11 defect families with distinct properties, including ZPL energy, PSB shape, and the Debye-Waller factor. Notably, they also linked the formation of particular defect classes to the BN morphology.

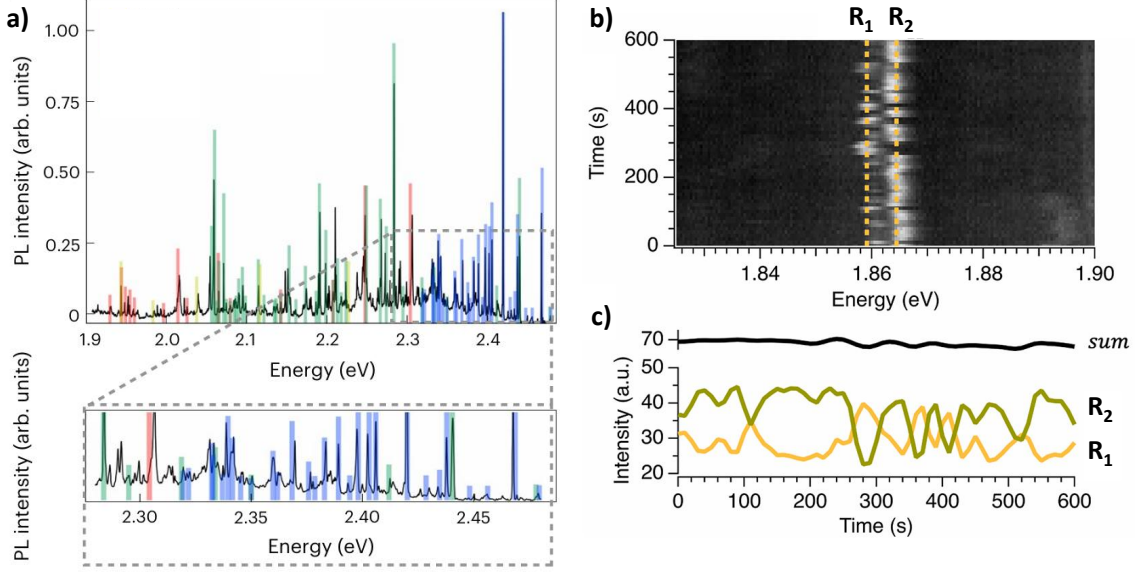


Figure 2.11: Experimental results suggesting DAP transitions as sources of visible SPEs. a) Low temperature (8 K) PL spectra in the visible range collected from a defective BN flake. Color bars correspond to four series of DAP transitions given by Eq. 2.1 (one color - one series). Adapted from [335] b) Time evolution of selected exemplary SPEs. Rapid, discrete spectral jumps between two emission energies, which correspond to two different distances R_1 and R_2 between a donor and an acceptor, are observed. As shown in c), the total emission intensity remains constant in time. b) and c) were adapted from [336].

Typically, either intracenter transitions between defect states or transitions between the BN bands and defect states are considered. However, recent reports suggest that the observed variety of SPEs may be associated with donor-acceptor pair (DAP) transitions [335–337]. This mechanism relies on the recombination of an electron provided by a donor with a hole bound to an acceptor. Due to the Coulomb interaction, the energy of the emitted photon might be described as:

$$E_{SPE} = E_{DA} - \frac{e^2}{4\pi\epsilon R_m}, \quad (2.1)$$

where E_{DA} is the energy difference between the energetic level of a donor and an acceptor, e is the electron charge, ϵ is the dielectric constant, and R_m is the donor-acceptor distance that can take discrete values determined by the crystal lattice. Therefore, DAP transition results in the appearance of a series of sharp, isolated spectral lines, corresponding to various R_m . As shown in Figure 2.11a, almost all peaks present in the low-temperature visible PL spectrum acquired from a BN flake by the authors of [335] match very well to four series of DAP transitions (with four different E_{DA} values). Moreover, as shown in Figure 2.11b-c, the DAP-based model explains ZPL energy fluctuations typically observed in BN [336]. When we consider a single donor, multiple recombination pathways are possible, as multiple acceptors, which might be involved in photon emission, are available.

Each of such transitions corresponds to a specific ZPL emission energy given by Eq. 2.1. Subsequent recombination events are independent and may involve different acceptors, so the next photons can have different energies. Therefore, although the total emission intensity is constant, rapid spectral jumps are observed.

The utility of visible color centers has been successfully demonstrated in various applications [10]. In particular, QKD using visible SPEs was implemented [32, 33]. Although at this stage the transmission rate is $\times 40$ slower than in systems based on much more mature NV^- centers [33], these reports prove that quantum communication based on room-temperature SPEs in layered BN is possible. The high resistance to cosmic radiation makes this material a promising platform for space quantum communication [250]. Notably, a quantum communication architecture that utilizes visible SPEs in BN is currently being tested on a satellite platform as part of the project QUICK³ [251, 252]. Another area of interest is quantum computing. JenQuant, introduced in [145], is a pioneering quantum processor based on visible quantum emitters in BN. The qubits are encoded in the polarization of photons. Compared to other devices, JenQuant exhibits very good stability and achieves high-precision single-qubit operations [338, 339]. Although it currently works properly only as a single-qubit quantum computer, multi-qubit operations might be achieved in the future via entangling gates, which require high photon indistinguishability. Visible SPEs have also been used to implement quantum random number generation [144]. The emitter is coupled into a photonic chip and distributed across multiple outputs. Due to its quantum properties, every single photon enters a random output unpredictably. Finally, some visible emitters possess spin and, similarly to N_V^- centers in diamond, exhibit optically-detected magnetic resonance (ODMR), described in detail in Section 2.4.4 [340, 341]. This property makes them promising for quantum sensing applications.

While visible SPEs are a promising platform for quantum technologies, most studies on quantum emitters rely on exfoliated BN flakes, which are insufficient for practical applications due to limited scalability and reproducibility. These issues might be addressed via MOVPE, which enables the growth of large-area (wafer-scale) BN layers in a relatively short time compared to other methods. In addition, commonly used metal-organic precursors such as TMB or TEB favor the formation of carbon-related visible SPEs during the growth. Therefore, intuitively, engineering these emitters should be possible by manipulating TEB flow and other growth parameters, such as temperature, that affect chemical reactions. This hypothesis is also supported by theoretical calculations that link specific growth conditions with the preferred formation of particular point defects [11–13]. Their formation energies depend on technological parameters, such as the introduced B-to-N ratio, the carbon content during growth, and temperature, all of which can be adjusted. However, to

date, most studies have focused on developing and optimizing the above-discussed post-growth methods for SPE fabrication in BN flakes. In contrast, studies on the direct formation of visible SPEs during epitaxial growth and on how growth conditions influence emitter properties remain limited, particularly for MOVPE growth.

Attempts to optimize growth conditions to achieve controlled formation of visible SPEs have been reported in the CVD growth of BN on Cu foils. As presented in [342], for this type of growth, controlling boron diffusion is an effective tool for the selective formation of visible SPEs belonging to different defect classes with distinct emission energies. As shown in Figure 2.12a, all the emitters observed by the authors in BN grown via a standard CVD method emit in the 600-650 nm range. However, if BN is obtained via so-called gettered growth, in which the amount of boron is limited by mitigating its diffusion through Cu foil, the majority of generated SPEs emit in the 550-600 nm range (Figure 2.12b). This research has recently been further extended to the controlled formation of carbon-related emitters by adjusting carbon diffusion through regulating its concentration in the Cu substrate [343]. As shown in Figure 2.12c, when it is low, the visible PL spectra of BN exhibit emission peaks, centered at 600-610 nm, attributed to the formation of C_B . The increase in carbon concentration in Cu foil leads to the appearance of new emission lines shifted to 630-640 nm (Figure 2.12d). Combining experimental data and theoretical calculations, the authors attribute them to the formation of $C_2B - C_N$ defects. As expected, when the carbon concentration is further increased, formation of defects, which include more carbon atoms in their atomic structure, is preferred (Figure 2.12e). Obviously, defect identification is a very complex problem, so further studies are required to confirm or refute the authors' hypothesis regarding the role of C_B and $C_2B - C_N$ defects. However, regardless of the exact atomic structure of the observed emitters, the results described in [342, 343] clearly demonstrate that by changing the BN growth conditions, it is possible to manipulate visible color centers in large-area BN.

Although MOVPE offers faster growth, better thickness homogeneity, and greater scalability, current progress in controlling SPEs in as-grown material has been limited. The previous report has shown that when the TEB flow during the MOVPE growth of BN increases, the density of color centers emitting at ~ 580 nm in the obtained material becomes higher [14]. As shown in Figure 2.13a, BN grown under a low TEB flow rate exhibits individual SPEs with narrow ZPLs. In contrast, increasing the flow rate leads to the formation of defect ensembles with much broader emission (Figure 2.13b). This result demonstrates that carbon is undoubtedly involved in the formation of the observed emitters, whose concentration can be modified by adjusting TEB flow. However, almost all BN epilayers investigated by

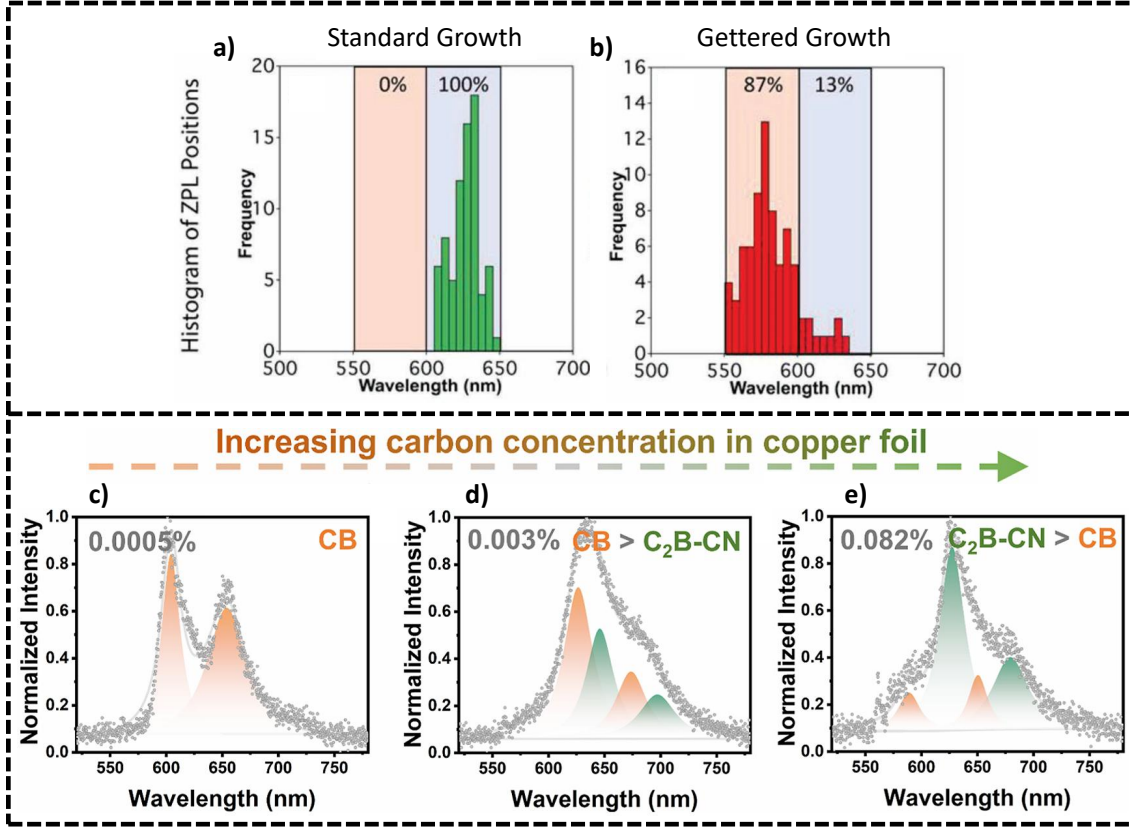


Figure 2.12: Results on the controlled formation of visible SPEs in BN grown via CVD on metal foils. (a-b) Histograms of the observed ZPL positions in BN films grown via standard method and via gettered growth with the mitigated boron diffusion through Cu foil substrate. Two growth regimes favor the formation of two distinct defect types that emit at 600-650 nm and 550-600 nm, respectively. Adapted from [342] (c-e) PL emission spectra acquired from BN layers grown on Cu foils with different carbon concentrations ranging from 0.005 % to 0.082 %. By adjusting the carbon concentration, one can favor the formation of particular color centers. Adapted from [343].

the authors were grown in the high TEB-flow regime, where the formation of defect ensembles is favorable; only one sample was grown under low TEB flow and exhibited well-isolated visible SPEs. Consequently, while the results discussed are extremely valuable for identifying carbon-related defects as quantum light sources at ~ 580 nm, to date, there is still no literature on how MOVPE growth conditions influence SPE properties, such as purity and energy distribution, which are key to applications. Moreover, point defects emitting at different wavelengths have not been studied. These issues are addressed within this dissertation. Chapter 4 provides a detailed analysis of the influence of growth parameters on the properties of quantum emitters centered at ~ 540 nm embedded in MOVPE-grown BN.

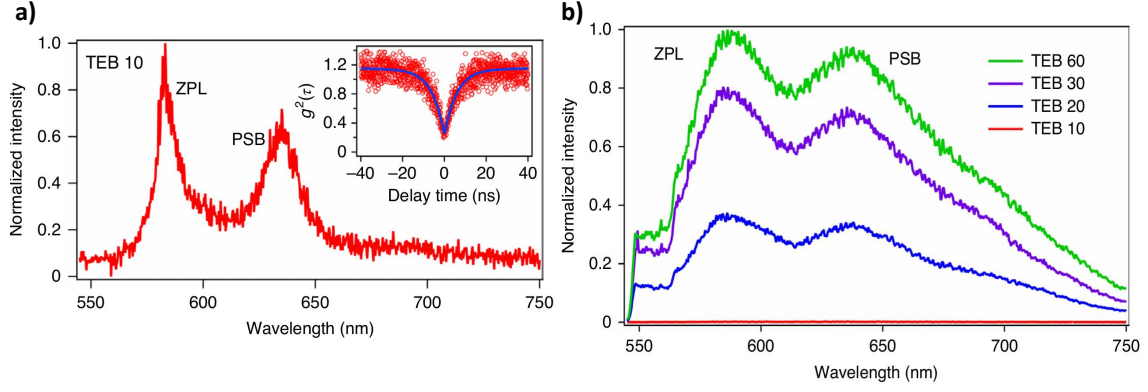


Figure 2.13: Literature results on the formation of visible SPEs in MOVPE-grown BN. a) PL spectrum acquired on a BN layer grown under TEB flux equal to 10 $\mu\text{mol min}^{-1}$. The spectrum consists of a narrow ZPL at ~ 580 nm followed by a PSB. The inset shows results of $g^2(\tau)$ measurements, which prove that the studied centers are true SPEs. b) PL spectra of BN layers grown under TEB fluxes varying from 10 to 60 $\mu\text{mol min}^{-1}$. Under TEB flows higher than 10 $\mu\text{mol min}^{-1}$, the formation of defect ensembles that exhibit broad emission, rather than isolated SPEs, is preferred. Adapted from [14].

While the generation of visible SPEs is the first and most fundamental issue, much effort has also been devoted to tailoring their properties for specific applications. In particular, an enhancement of quantum light emission has been achieved by integrating BN-based emitters into various cavity types, including Fabry-Perot cavities, photonic crystal cavities, microdisk resonators, and microring resonators [19, 60–63].

Another important issue is controlling the emission energy. As demonstrated in [139, 140], it can be tuned by applying strain to the BN lattice. In the simplest case of a defect with a C_S symmetry, the first-order change in the ZPL energy induced by strain is given by [140]:

$$\Delta E_{ZPL} \approx \varepsilon(\kappa_{xx}\cos^2\phi + \kappa_{yy}\sin^2\phi), \quad (2.2)$$

where ε is the amplitude of the applied strain, κ_{xx} and κ_{yy} are linear strain susceptibility parameters, and ϕ is the angle between the emitter dipole moment and the applied strain. As shown in Figure 2.14a, this approach has been demonstrated to induce ZPL energy shift by tens of meV [140]. The emission energy of visible color centers in BN might also be tuned using the Stark effect, as reported in [344–347] (Figure 2.14b). When the electric field $\vec{E}$ is applied to the emitter with a dipole moment $\vec{\mu}$ and polarizability $\vec{\alpha}$, the change in the ZPL energy might be approximated by:

$$\Delta E_{ZPL} \approx -\vec{\mu}\vec{E} - \frac{1}{2}\vec{E}\vec{\alpha}\vec{E} \quad (2.3)$$

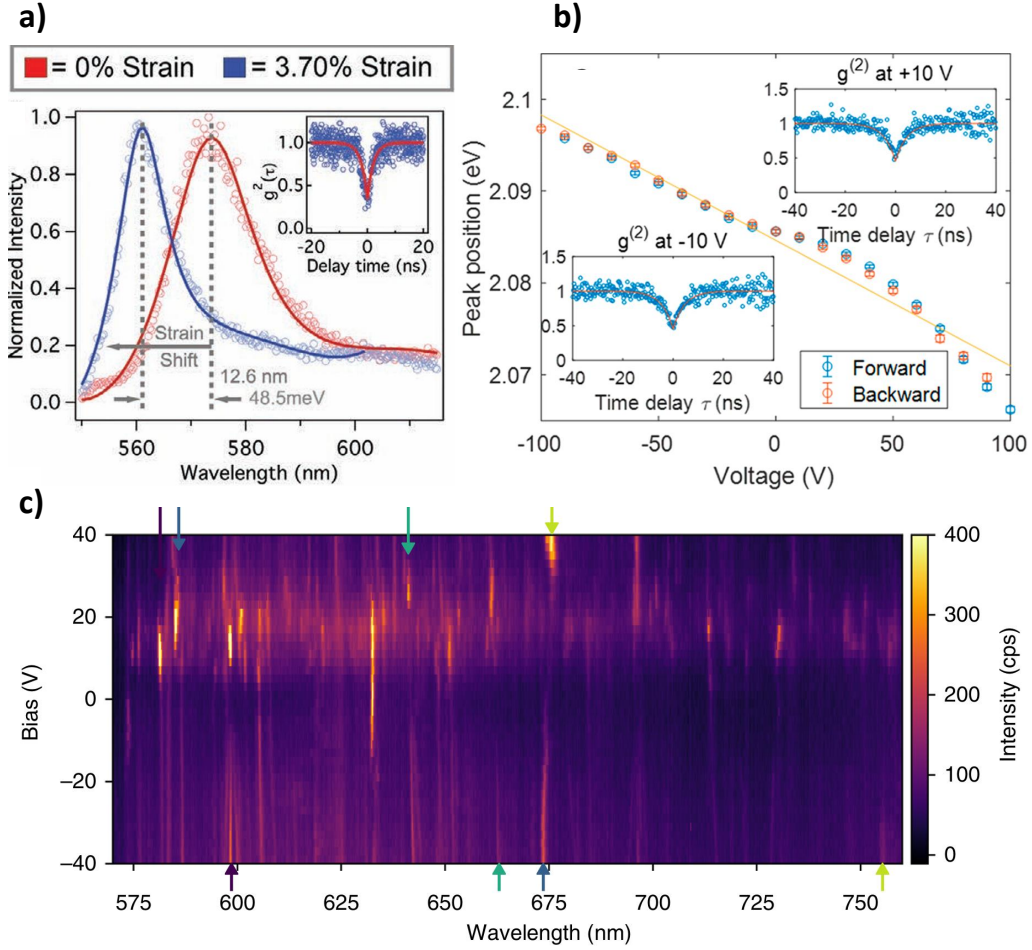


Figure 2.14: The emission control over visible SPEs in layered BN. a) PL spectra of a visible SPE in BN without strain (red curve) and with applied tensile strain of 3.7% (blue curve). The strain causes a blue shift by around 50 meV. Inset - results of $g^{(2)}(\tau)$ measurements. Adapted from [140]. b) Change of the visible SPE emission energy via the Stark effect. Applying an electric field shifts the ZPL by around 30 meV. Insets - results of $g^{(2)}(\tau)$ measurements with different directions of the applied electric field. Adapted from [346]. c) Electrical control over SPE emission. Several ZPLs are observed only in a specific range of the applied bias voltage. Emission activation and deactivation are attributed to changes in the defect charge state. Adapted from [348].

In addition to tuning the SPE emission energy, the application of an electric field has been reported to alter the charge state of a defect. Such a change, originating from tuning the Fermi level, may result in emitter activation or deactivation, as well as in a shift in the observed ZPL, as shown in Figure 2.14c [348, 349].

Despite significant effort put into controlling visible SPEs, some aspects remain challenging. The most important one is the emission photostability, which is disturbed by three main mechanisms: photobleaching - disappearance of the emission after prolonged laser exposure, blinking - switching between *on* and *off* states in which the emitter emits or does not emit light, and spectral diffusion - fluctuations of ZPL energy [350–355]. These phenomena seem to depend strongly

on the local environment of a particular color center, as emission stability varies significantly from point to point. Typically, they are attributed to photochemical reactions involving color centers and oxygen, as well as the interactions with localized charges. Consequently, the stacking of additional BN layers, providing an oxygen-free atmosphere, introducing a passivation layer between BN and a substrate, as well as applying an electric field, were reported to enhance the emission photostability, which is crucial for the utility of SPEs [347, 352, 354, 356].

Spectral diffusion is also one of the mechanisms leading to ZPL broadening. In the so-called Fourier transform limit, when the interactions of a given color center with the environment are negligible, the emission full-width at half maximum (FWHM) is determined solely by the excited-state lifetime. For SPEs in BN, it is reported to be as low as $\sim 0.2 \mu\text{eV}$ [357]. However, if the spectral acquisition time is larger than the time between spectral jumps, then inhomogeneous broadening, resulting in a Gaussian shape, is observed [358]. While spectral diffusion is important at low temperatures, other mechanisms of emission broadening, associated with lattice vibrations, become crucial at around tens of K. The impact of many of them on FWHM value versus temperature T can be approximated as T^α , with α varying for different mechanisms. Typically, $\sim T^3$, $\sim T^5$, or $\sim T^7$ dependencies are considered [359–361]. The term T^7 comes from the electron-phonon coupling when only non-degenerate electronic states of a defect are involved [362], while T^5 dependence is associated with a dynamic Jahn-Teller effect [363, 364]. T^3 behavior is typically observed in defect-rich diamond samples and is associated with two-phonon elastic scattering processes [337, 360, 365–367]. For visible color centers in BN, $\sim T^3$ dependence is typically observed [337, 347, 366, 367]. As in the case of defects in diamond, such a behavior is attributed to fluctuating fields generated by acoustic waves that influence atomic distances.

The mechanism of temperature-dependent broadening is often considered to be mediated by an effective single-frequency phonon. In this framework, taking into account the phonon occupation at a given temperature, the emission linewidth Γ might be described as [368, 369]:

$$\Gamma(T) = \Gamma_0 + \frac{a}{\exp\left(\frac{E_{ph}}{kT}\right) - 1}, \quad (2.4)$$

where Γ_0 is the emission linewidth at $T = 0$ and k is the Boltzmann constant. The second term is proportional to the occupation factor of a phonon mode with energy E_{ph} , and a is the coupling constant. Notably, only one phonon energy appears in Eq. 2.4, while many phonons can be involved. Also, the phonon density of states is not accounted for. Therefore, the fitted E_{ph} effectively represents the characteristic energy scale of phonons that most efficiently affect the optical transition.

Electron-phonon interactions result in the homogenous broadening of the emission, thereby inducing the Lorentzian shape of a ZPL. Emission broadening is undesirable because it degrades photon distinguishability and reduces the count rate at a specific central wavelength, thereby limiting the utility of SPEs. Therefore, a proper understanding and description of phonon-mediated broadening of the ZPL are crucial for applications. In most reports studying this phenomenon, hBN flakes or small transferred parts of CVD-grown films were considered [337, 347, 358, 361, 367, 370, 371]. However, as-grown large-area BN, which can be obtained via MOVPE, exhibits different mechanical properties [273, 372–374]. Consequently, the temperature-dependent properties of the studied emitters, which are influenced by lattice vibrations, may also vary. Therefore, Chapter 4 contains the results on the temperature broadening of quantum emitters in as-grown, non-transferred BN layers grown by MOVPE.

2.4.4 Boron Vacancies

Another type of point defect existing in BN is the boron vacancy, which typically occurs in a negatively charged state (V_B^-). As shown in Figure 2.15a, it exhibits a very broad emission centered at ~ 850 nm (1.46 eV) [7]. The phonon-free emission of this defect is dark due to symmetry reasons, and the whole observed signal is related to phonon-assisted transitions [375]. A ZPL centered at 773 nm (1.60 eV) was observed only from defects embedded into a microcavity [376]. By changing its length, the authors tuned the cavity mode to match the V_B^- phonon-free emission, which could then be observed, as shown in Figure 2.15b. Due to the low brightness, V_B^- emission is typically studied in ensembles, while the observation of individual defects is hindered. However, despite this drawback, V_B^- is a promising platform for quantum applications.

Similar to an N_V^- center in diamond, V_B^- is a spin-active defect used in quantum sensing via optically detected magnetic resonance (ODMR) [7, 120]. While this technique was previously just mentioned in Sections 1.4.3 and 2.4.3, here, treating V_B^- as a textbook example, we explain the principle of ODMR. We start with considering the energetic structure of V_B^- shown in Figure 2.15c. Both the ground and excited states are spin-triplet states ($S=1$) with three possible spin-projection quantum numbers $m_s \in \{-1, 0, 1\}$, defined with respect to the quantization axis perpendicular to the BN atomic planes. When applying the external magnetic field $\vec{B}$, the spin Hamiltonian is given by [7]:

$$H = D \left(S_z^2 - \frac{S(S+1)}{3} \right) + E(S_x^2 - S_y^2) + g\mu_B \vec{B} \vec{S}, \quad (2.5)$$

where D and E are zero-field splitting parameters, g is the Landé factor, μ_B is the Bohr magneton, $\vec{S}$ is total electron spin. In the above, we put the z -axis as the principal symmetry axis. The axial zero-field splitting parameter D originates from spin-spin interactions, while the off-axis zero-field splitting parameter E is related to local strain and anisotropy. In further discussion, we assume that $\vec{B}$ is applied perpendicular to the BN surface. As shown in Figure 2.15c, due to spin-spin interactions $|0\rangle$ and $|\pm 1\rangle$ states are separated by the frequency $\nu_0 = D/h$ (h is the Plack constant), which in the case of V_B^- is equal to 3.48 GHz. $|\pm 1\rangle$ state is further splitted onto $|-1\rangle$ and $|+1\rangle$ states of energies corresponding to frequencies:

$$\nu_{1,2} = \nu_0 \pm \frac{1}{h} \sqrt{E^2 + (g\mu_B B)^2} \quad (2.6)$$

The defect can be optically excited to the spin-triplet excited state via spin-conserving transitions and then relax, emitting light. However, as shown in Figure 2.15c, if the defect is excited from the $|\pm 1\rangle$ ground state to the $|\pm 1\rangle$ excited state, additional spin-selective non-radiative intersystem crossings (ISCs), involving metastable state (MS), are allowed. In such a situation, PL signal intensity is lower. This spin-dependence of V_B^- emission is the principle of ODMR. In this technique, one measures PL intensity as a function of the applied microwave field frequency. When it is tuned to $\nu_{1,2}$, the spin population is transferred from $|0\rangle$ to $|\pm 1\rangle$ ground state. As a consequence, a drop in the measured emission intensity is observed, as shown in Figure 2.15d. The analysis of the ODMR contrast (relative change of PL intensity) versus microwave frequency provides information about the V_B^- energy-level structure, which is highly sensitive to the external magnetic field and changes in the local environment. Therefore, V_B^- has been demonstrated to be a good sensor for magnetic field, temperature, strain, and pressure [20, 142, 143, 253]. Although NV^- center in diamond is a much more mature quantum sensor, commonly integrated into AFM tips, V_B^- has one significant advantage. Namely, a BN flake with V_B^- sensors can be placed directly on the studied object, enabling sensing at the atomic distance scale. This approach has allowed for a successful imaging of the magnetic field produced by magnetic 2D material flakes [142, 253], as well as detection of spin waves [377, 378].

Various methods for V_B^- generation have been developed, including FIB, electron irradiation, ion implantation, or laser writing [379–383]. The first studied V_B^- were obtained via thermal-neutron irradiation [7], an approach that remains commonly used. In this procedure, defect generation is mediated by neutron capture reactions, which induce V_B^- formation via removing a boron atom from the BN crystal lattice. The high efficiency of this method originates from the high cross-section of ^{10}B for neutron absorption. Notably, in contrast to high-energy neutron irradiation,

where both B and N atoms might be removed via ballistic knock-on processes, the use of thermal neutrons strongly favors the formation of V_B^- and suppresses the generation of nitrogen vacancies. Intuitively, this process might also affect other color centers in BN. In particular, it should modify the atomic structure of point defects that initially include boron, as well as introduce boron-vacancy-containing complexes. Also, the presence of neutron-induced V_B^- might influence properties of other emitters by modifying their local environment. Since neutron irradiation is commonly used to generate V_B^- , understanding its impact on BN's properties is crucial for the engineering of BN-based sensing devices. However, to date, there have been no systematic studies on the influence of thermal-neutron treatment on the optical properties of BN over a wide spectral range. This topic is addressed in Chapter 6, where the optical properties of unexposed and neutron-irradiated MOVPE-grown BN layers are discussed.

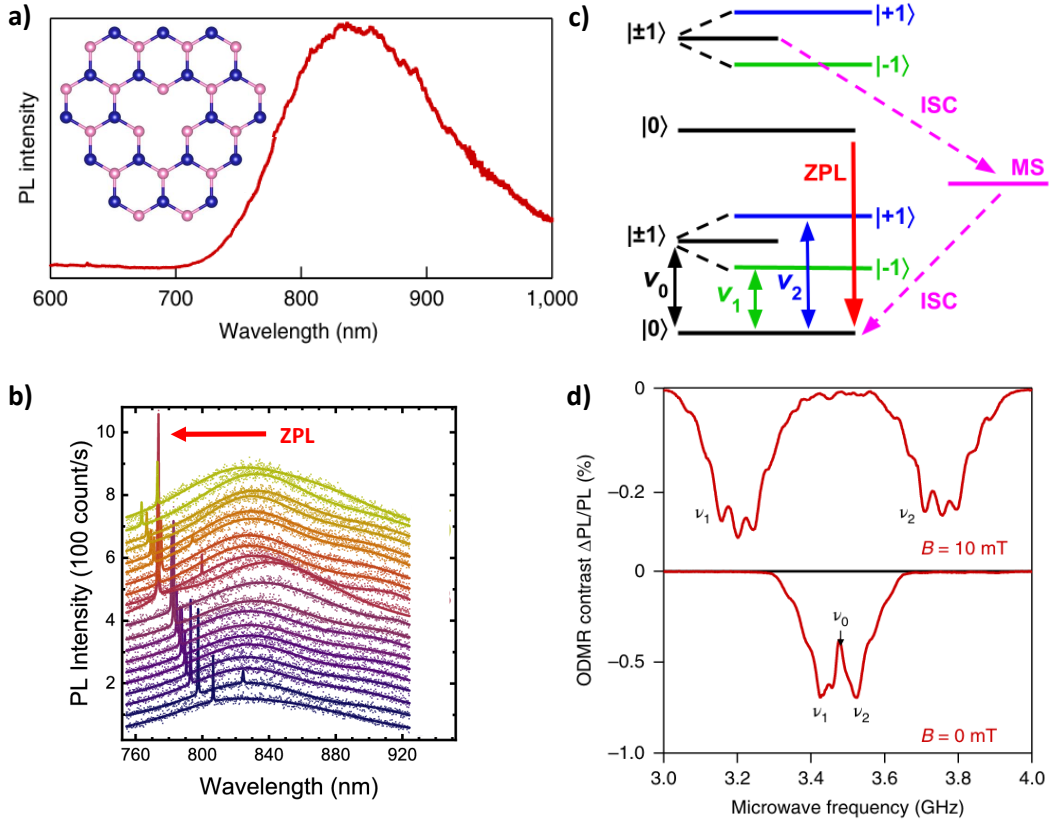


Figure 2.15: a) PL spectrum of V_B^- revealing broad emission centered at ~ 850 nm. Adapted from [7]. The inset shows the atomic structure of the defect prepared using VESTA software [192]. b) Detuning-dependent PL spectra of V_B^- embedded into a cavity. When the cavity mode is adjusted to 773 nm, a strong ZPL is observed. Adapted from [376]. c) Electronic structure of V_B^- . Both the ground state and the excited state are spin-triplets. The emission from $|\pm 1\rangle$ excited state is influenced by non-radiative ISCs involving the MS state. d) The bottom and the upper panels show V_B^- ODMR spectra without and with an applied external magnetic field, respectively. The frequency separation between the two observed peaks increases with the applied magnetic field. Additional small peaks observed in the upper panel are related to the hyperfine interactions. Adapted from [7].

2.5 Bubbles in Two-Dimensional Materials

2.5.1 Bubbles in Exfoliated Flakes

The transfer of exfoliated 2D material flakes onto a new substrate might introduce structural deformations. One of these deformations is the formation of bubbles reported in such materials as graphene, TMDCs, and layered BN [384–389]. They are formed spontaneously when gas molecules or organic residuals are trapped between a thin layer and a substrate. One can also trigger bubble formation in a more controlled manner by treating exfoliated flakes with protons or plasma [390–392]. Ions penetrating 2D material monolayers induce the formation of molecules that cannot diffuse through the impermeable layer. Such trapped molecules give rise to bubbles in 2D materials. In both of the above-discussed cases, the formation of a convex bubble requires stretching the thin material that initially covers only a flat circular area. Therefore, the layer is strongly strained, and a very high pressure, on the order of hundreds of MPa or a few GPa, inside a bubble is necessary to keep it stable [384]. In particular, below the liquefaction temperature of the trapped gas, bubbles collapse [391].

A bubble geometry depends on the energy of the trapped gas, the elastic properties of a particular 2D material, its adhesion to the substrate, and the external pressure [393]. Typically, the profile of a bubble of radius R and height H is described via membrane or plate theories given by [393]:

$$y(x) = H \left(1 - \left(\frac{x}{R} \right)^2 \right)^\alpha, \quad (2.7)$$

where x is the distance from the center of a bubble. Depending on the material stiffness and bubble size, the parameter α is equal to either 1 in the thin membrane limit or 2 in a thick material regime. Sometimes the above model is modified, and α is set as a fitting parameter. In particular, profiles of multilayer hBN bubbles investigated in [389] were described with $\alpha \approx 1.5$. In this case, α was larger than 1 due to the non-negligible bending rigidity of the multilayer material. However, weak van der Waals interactions between atomic planes make the material's stiffness so small that the plate theory ($\alpha=2$) also did not describe the bubble shape correctly. As the bubble radius R increases, the influence of material rigidity on the bubble's mechanical properties decreases, and consequently α becomes closer to 1 [389, 393]. While the thin membrane model ($\alpha=1$) assumes negligible bending rigidity and $H/R \ll 1$, a more general expression for the bubble shape has been proposed in [394]:

$$y(x) = H \left(1 - \left(\frac{x}{R} \right)^q \right) \quad (2.8)$$

In this expression, q is fitting parameter, typically found to be ~ 2.2 for various 2D materials. An important metric of 2D material bubbles is their aspect ratio H/R . When the bending stiffness is negligible, the aspect ratio depends on the material and the substrate but is independent of the bubble size [394]. Such a situation occurs in bubbles formed in 2D material monolayers. In particular, for bubbles in monolayer BN, H/R values were reported to be around 0.11 [384, 390]. For multilayer BN bubbles, when the bending stiffness cannot be neglected, the aspect ratio is typically lower [389].

The optical properties of 2D materials may be significantly altered by bubble formation. First, bubbled material might exhibit large strain of up to 1-2 %. Its presence has been reported to significantly enhance excitonic emission in TMDCs and give rise to light emitters, particularly SPEs (Figure 2.16a-b) [15, 385, 391]. In addition, as shown in Figure 2.16c-d, the high strain within TMDC bubbles has been demonstrated to induce the direct-to-indirect bandgap crossover [16]. The strain may be probed by investigating IR- and Raman-active phonon modes, which can be significantly shifted (by tens of cm^{-1}) and split due to the strain anisotropy [392]. Notably, bubbles might also act like cavity-like structures. Such a behavior has been observed in graphene and TMDC bubbles, where Raman shift and intensity oscillations were reported (Figure 2.16e) [386, 387, 395]. These oscillations were attributed to the formation of standing waves between a bubble and a substrate. Similarly, interference-mediated enhancement of UV-defect emission in BN bubbles has been reported in [389]. All these reports demonstrate that bubbles can be used to modify the optical properties of 2D materials. In practical applications, it is crucial to control the position and size of bubbles. This can be achieved using masks that allow bubble formation only within predefined circular openings [391, 396]. However, all the studies mentioned were limited to small exfoliated flakes, which are insufficient for practical use and require a transfer step that may damage or contaminate the material. Addressing these limitations is a key step toward establishing bubbles as a promising platform for 2D-material-based applications.

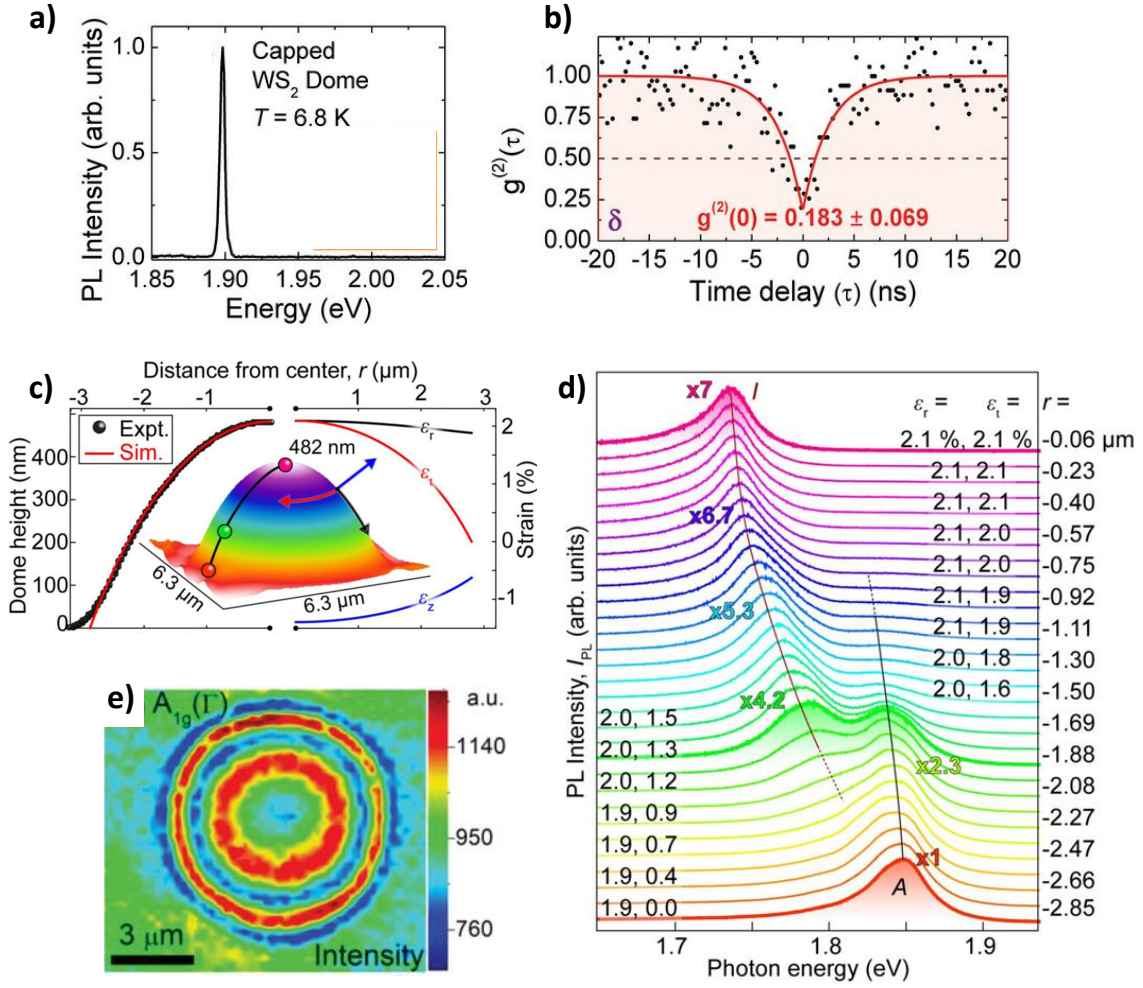


Figure 2.16: a) Low-temperature PL spectrum acquired from a bright spot observed in an exemplary WS₂ bubble. As shown by $g^{(2)}(\tau)$ measurements in b), the strong line at 1.9 eV corresponds to single-photon emission. Both a) and b) were adapted from [15]. c) The left side shows a cross-section profile of an exemplary WS₂ bubble measured by AFM. Black dots are experimental points, while the red curve was obtained from calculations. A three-dimensional AFM picture is shown in the inset. Black, red, and blue arrows mark directions of radial (ϵ_r), circumferential (ϵ_t), and out-of-plane (ϵ_z) directions, respectively. Calculated strain components along bubble radius are plotted on the right side. d) Normalized low-temperature PL spectra acquired along a radius of the WS₂ bubble shown in c). All spectra are labeled by the distance r from the bubble center and calculated strain components ϵ_r and ϵ_t . The change in strain along the bubble leads to a transition from direct excitonic emission (marked as A) at the bubble edge to indirect excitonic emission (marked as I) at the center. Both c) and d) were adapted from [16]. e) A_{1g} Raman mode intensity map in an exemplary WS₂ bubble. The observed oscillations correspond to standing waves formed between the bubble and the substrate. Adapted from [395].

2.5.2 Bubbles in MOVPE-Grown Layered Boron Nitride

In 2023, our group reported electron-irradiation-induced bubble formation in BN grown by MOVPE on sapphire substrates [17]. Notably, this phenomenon is observed only in as-grown, non-transferred material and is related to its specific morphology. BN is grown at high temperatures, typically exceeding 1000 °C, so after the growth, the whole BN/sapphire wafer cools down to room temperature. During this process, the sapphire substrate shrinks, while the epilayer tries to expand due to BN's negative in-plane thermal expansion coefficient [397], resulting in strain generated at their interface. Below some critical temperature, the accumulated strain is so high that it is energetically preferred for the BN layer to detach from the sapphire substrate and form wrinkles [374]. A schematic illustration of the formation of BN wrinkles, together with their AFM image, is presented in Figure 2.17a-c. As shown in Figure 2.17b, when the BN sample is exposed to ambient conditions, wrinkles provide an effective pathway for water intercalation from the ambient [17]. Further electron-beam (e-beam) irradiation induces radiolysis of this interfacial water. Molecular hydrogen produced in this process detaches the BN layer from the substrate, leading to bubble formation (Figure 2.17d-e).

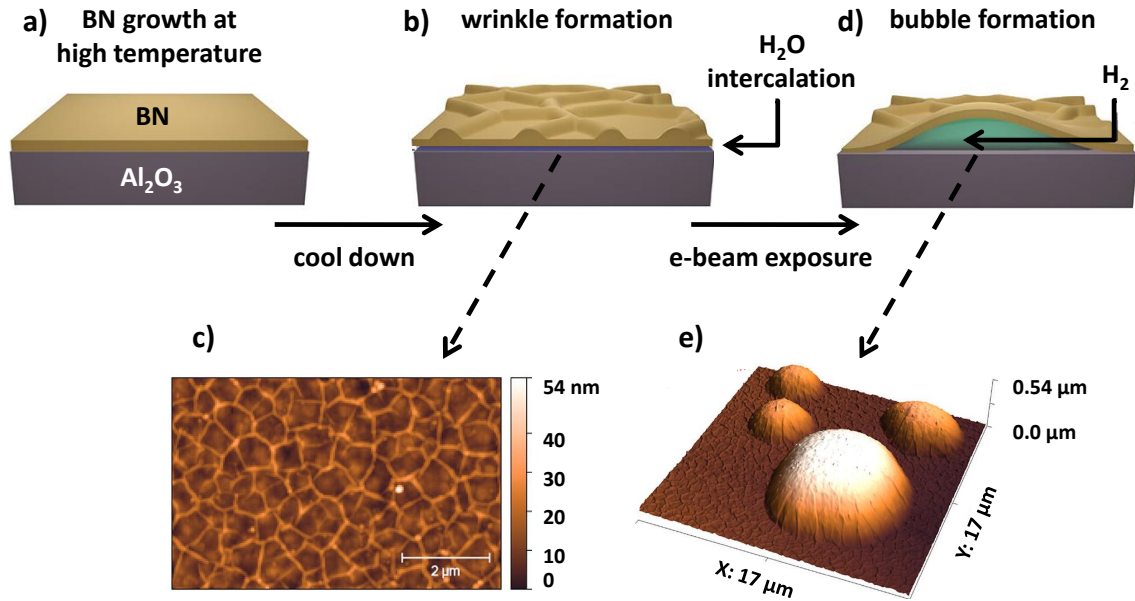


Figure 2.17: Scheme of wrinkle and bubble formation in MOVPE-grown BN. a) Schematic picture of flat BN grown on a sapphire substrate at high temperature. b) Schematic picture of BN wrinkles formed due to thermal expansion mismatch between the grown epilayer and the substrate. Wrinkles provide a channel for water intercalation. c) Exemplary AFM image of BN wrinkles. Scalebar is 2 μm . d) Schematic picture of a hydrogen-filled BN bubble formed via e-beam irradiation. e) AFM image of exemplary BN bubbles. All images adapted from [17].

Since the presence of wrinkles is necessary, the discussed procedure works only for as-grown BN. In particular, the e-beam exposure does not induce bubbles in wrinkle-free epilayers transferred onto a new substrate. The discussed strategy for bubble fabrication avoids the unwanted transfer step, thereby reducing the risk of material damage or contamination. Until now, the mechanical properties of such bubbles and their influence on the optical properties of BN have been unexplored in detail. These issues are addressed in the Chapter 5, where e-beam-induced bubbles are proposed as a new interesting platform for studies on visible SPEs in BN. In this dissertation, we focus only on e-beam-induced bubbles. However, it is worth mentioning that in 2024, an alternative approach for creating bubbles in MOVPE-grown BN was demonstrated [398]. Namely, the formation of molecular hydrogen, leading to bubble formation, might be achieved via UV laser irradiation.

Chapter 3

Methodology, Experimental Techniques, and Setups

3.1 Metal-Organic Vapor Phase Epitaxy

All BN layers investigated in this work were grown using metal-organic vapor phase epitaxy (MOVPE). In this method, the material forms through chemical reactions among gaseous precursors that supply the necessary elements. The samples discussed in this dissertation were grown in an *AIXTRON CCS 3x2"* setup. The scheme, showing its most important elements, is provided in Figure 3.1a. The nitrogen and boron precursors used for BN growth in our group are NH_3 and triethylborane (TEB, $\text{B}(\text{C}_2\text{H}_5)_3$), respectively. Both precursors are introduced into the reactor chamber via a carrier gas flow, which, for all samples discussed in this work, was H_2 . TEB in a liquid form is stored in a bubbler (Figure 3.1b). To supply it in the gas phase, H_2 is injected into the liquid TEB, forming bubbles. The carrier gas becomes saturated with TEB vapor and is subsequently transported through the outlet line. NH_3 and TEB vapor are injected into the showerhead reactor chamber through 0.6 mm-diameter openings in the reactor lid (Figure 3.1c). There, BN is formed as a result of the following chemical reaction:



The grown material is deposited on a 2-inch sapphire substrate placed in a graphite susceptor coated with silicon carbide. A heater located beneath the susceptor enables growth at temperatures reaching 1400 °C Figure 3.1d. The real substrate temperature is read with an optical pyrometer. To ensure a homogeneous temperature distribution, the susceptor is rotated during growth. The chamber pressure can be varied in the range 30-1300 mbar. The showerhead reactor is closed in a glovebox.

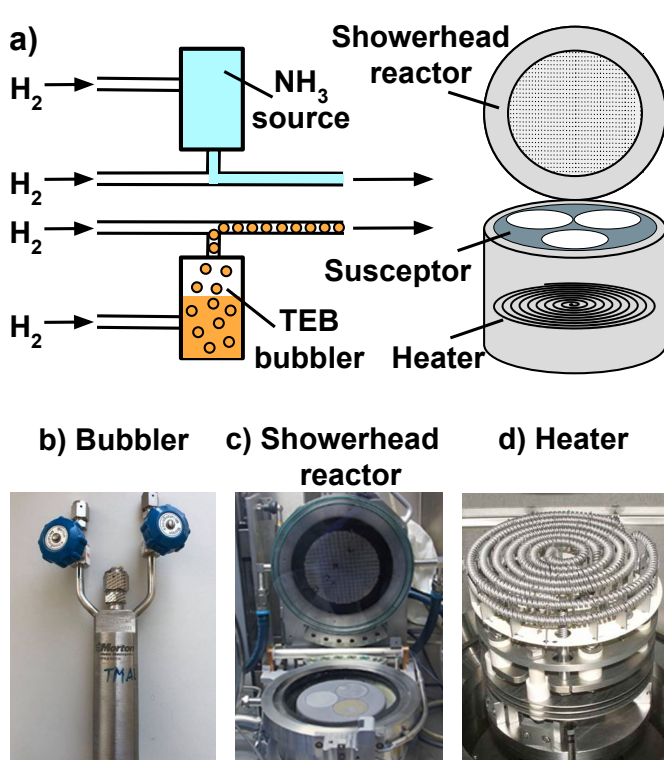


Figure 3.1: a) Schematic illustration of the MOVPE setup. Using a carrier gas, TEB vapor and NH₃ are injected through 0.6 mm-diameter openings into the showerhead reactor. The precursors are directed onto sapphire substrates placed in a susceptor. The heater located beneath the susceptor provides high-growth temperature. b) Photo of an exemplary bubbler taken by Dr Aleksandra Dąbrowska. Pure (TEB-saturated) H₂ is injected (removed) by an inlet (outlet) tube. c) Photo of the open MOVPE showerhead reactor taken by MSc Krzysztof Pakuła. d) Photo of the heater located below the susceptor, adapted from the Aixtron manual [399]

Depending on the precursor injection scheme, two main growth modes can be distinguished. In the continuous flow growth (CFG) method, both NH₃ and TEB are injected into the reactor chamber simultaneously. Growth can be carried out either under TEB-rich conditions, which promote rapid material synthesis, or under NH₃-rich conditions, where the material grows much more slowly and exhibits self-limiting behavior [400]. On the other hand, in flow-modulation epitaxy (FME), the precursors are injected into the reactor in alternating pulses, each on the order of seconds. Compared to CFG, this approach enables the growth of thicker samples (tens of nm), as self-limiting behavior is not observed. However, FME-grown epilayers typically exhibit a larger concentration of defects [401].

Recently, our group has developed a new BN growth scheme, called two-stage epitaxy, that combines the advantages of both CFG and FME [278]. In this approach, CFG is employed to form a thin BN buffer layer that serves as a template for subsequent FME growth. The material grown in such a homoepitaxial-like process exhibits better structural quality than a typical BN grown in a standard FME process.

All samples discussed in this work were grown by Dr Aleksandra Dąbrowska. The author of this dissertation did not directly perform the growth processes; however, he contributed to defining the growth conditions of subsequent samples.

3.2 X-Ray Diffraction

The structural quality of all studied samples was assessed using X-ray diffraction (XRD), a non-invasive technique that provides information on crystal lattice parameters. It utilizes the fact that X-ray wavelengths are comparable to the interatomic distances in solids. Consequently, monochromatic X-ray radiation directed onto the crystal lattice is diffracted. The waves scattered by successive atomic planes interfere, leading to the appearance of intensity maxima at diffraction angles that satisfy Bragg's law:

$$n\lambda = 2d_{hkl} \sin(\theta_B), \quad (3.2)$$

where d_{hkl} is the distance between adjacent lattice planes described by the Miller's indices hkl , λ is the wavelength of the incident X-ray beam, n is the order of diffraction, and θ_B is the incidence angle for which the diffraction maximum is observed (see Figure 3.2). Therefore, for a particular λ used in the experiment, the positions of peaks observed in the registered diffractogram can be attributed to specific interplanar distances characteristic of a given material.

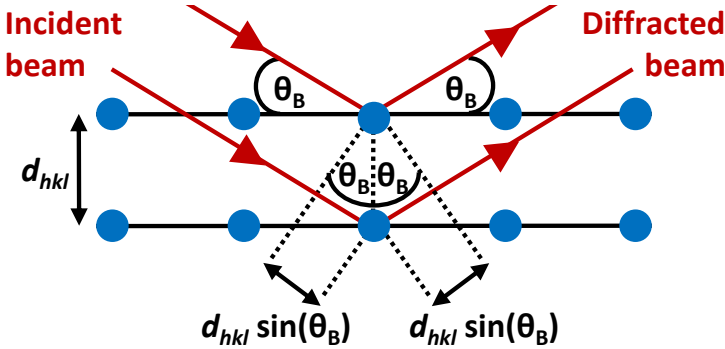


Figure 3.2: Schematic demonstration of Bragg's law. Reflection peak is observed when the condition given by Eq. 3.2 is satisfied.

All XRD diffractograms discussed in the dissertation were recorded by BSc Gabriela Szwed and Dr Mateusz Tokarczyk using a Panalytical X'pert diffractometer equipped with a Cu X-ray tube with a characteristic wavelength equal to $\lambda = 1.542 \text{ \AA}$. Using this wavelength, the presence of high-quality layered BN results in the appearance of an XRD peak centered at $2\theta_B \approx 26.7^\circ$ originating from (001)-type reflections [196].

As discussed in section 2.2.1, identification of particular sp^2 -hybridized BN polytypes based solely on the positions of (001)-type reflections is experimentally impossible since peaks originating from (002) reflections in hBN and (003) reflections in rBN appear at $2\theta_B = 26.76^\circ$ and $2\theta_B = 26.72^\circ$, respectively [402, 403]. Identification of the individual polytypes requires analysis of the reflections in the $40\text{--}50^\circ$ range, where characteristic peaks unique to each polytype are observed [196]. Such an approach was employed to identify the rBN sample discussed in chapter 6.

3.3 Scanning Electron Microscopy

The morphology of all investigated samples was assessed by scanning electron microscopy (SEM), which enables nanoscale imaging. In this method, the sample surface is scanned using a focused beam of electrons with a wavelength on the order of a few pm, much shorter than the wavelengths of photons used in optical microscopy. The scheme of a typical scanning electron microscope is provided in Figure 3.3. The electrons emitted by an electron gun are accelerated by an anode and focused on the sample surface via magnetic lenses. The current and the energy of the incident electrons can be controlled. The current determines the number of electrons and, thus, the spot size. The energy determines the electron wavelength and penetration depth.

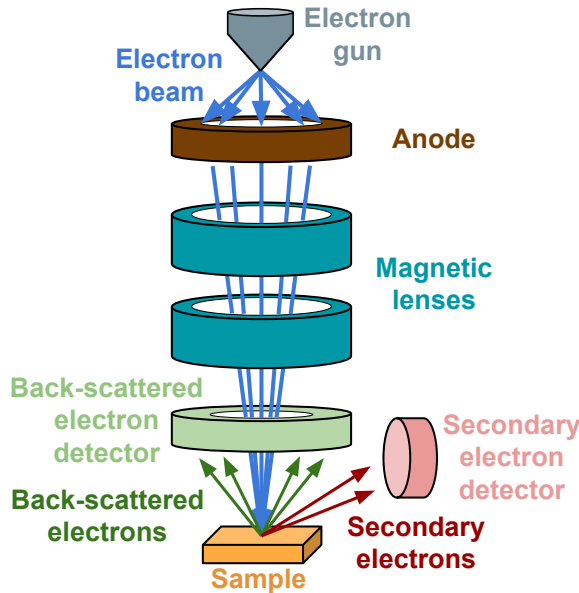


Figure 3.3: Schematic illustration of the working principle of a scanning electron microscope, including the electron gun, anode, magnetic lenses, as well as back-scattered electron and secondary electron detectors.

The incident beam interacts with the investigated sample in various ways, generating different types of signals, which are detected [404]. Two of them are of major importance for electron microscopy. First, secondary electrons are generated by removing electrons from the outer shells of atoms during inelastic scattering of the beam electrons. They exhibit low energies, typically ~ 50 eV. The secondary electrons detected during the measurements are generated at shallow depths, typically below 5 nm. Therefore, they provide detailed information on the sample surface morphology with a resolution of around 1 nm. In contrast, high-energy back-scattered electrons arise from the elastic scattering of incident electrons by sample atoms at higher depths (tens or hundreds of nm). They provide chemical contrast, as the probability of scattering increases with atomic number.

All SEM images of BN epilayers presented in this dissertation were taken by Dr Aleksandra Dąbrowska and Dr Mateusz Tokarczyk using the FEI Helios 600 Dual Beam system equipped with a RaithElphy electron lithography setup.

3.4 Atomic Force Microscopy

Complementary to SEM, atomic force microscopy (AFM) allows imaging the surface of the investigated material with atomic resolution. This technique employs a cantilever ended with a sharp tip that interacts with the sample surface via interatomic forces. During the scan, surface irregularities modulate the force acting on the AFM tip, leading to cantilever deflections that are optically analyzed. The cantilever is illuminated with a laser beam. The reflected light is detected by a photodiode, which provides information about the cantilever position to the feedback loop. It modifies the position of the piezoelectric sample stage to maintain the operating conditions characteristic of a given imaging mode. A schematic illustration of the AFM system is provided in Figure 3.4.

In contact mode, where the tip touches the sample surface, the vertical position of the piezoelectric stage is adjusted to maintain a constant cantilever deflection. In contrast, in non-contact mode, the tip does not touch the sample, but is kept a few nm above it. During the measurement, the cantilever is oscillating. The quantity kept constant is the cantilever oscillation amplitude or phase, both of which depend on the tip-sample distance, as the oscillations are affected by long-range forces. Non-contact mode imaging generally provides lower resolution than contact-mode measurements, but reduces the risk of damaging the sample and the tip. Finally, in tapping mode, the sample topography is mapped by tapping its surface with an oscillating tip. The cantilever oscillation amplitude is kept constant. This approach provides higher resolution than the non-contact mode while reducing the risk of tip damage compared to the contact mode.

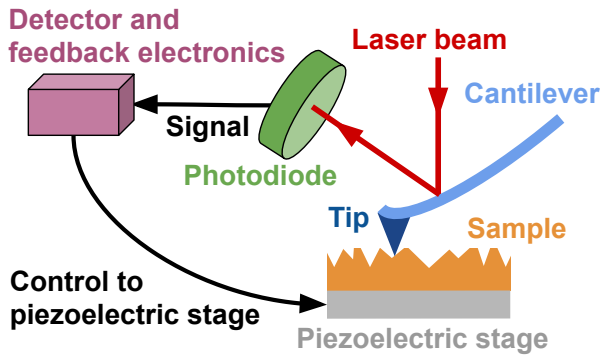


Figure 3.4: Schematic illustration of the working principle of AFM, including the cantilever-tip system, laser detection, and feedback control loop.

AFM measurements presented in this work were performed using a Dimension Icon microscope equipped with a NanoScope 6 controller (Bruker Corporation, Billerica, MA, USA). Topographical images were acquired in PeakForce Tapping mode. The AFM characterization of BN epilayers presented in chapter 4 was carried out by MSc Rafał Bożek, while the AFM imaging of BN bubbles described in chapter 5 was performed by Dr Jan Pawłowski. Data analysis was performed by the author.

3.5 Fourier-Transform Infrared Spectroscopy

The thickness of all investigated BN layers was assessed using reflectance Fourier-transform infrared spectroscopy (FTIR). In this technique, one registers the signal reflected from the sample illuminated with broadband infrared radiation. The measured response is determined by characteristic IR-active vibrations involving a change in dipole moment. They modify the specimen's dielectric function, thereby affecting the reflectance spectrum. For thin films, such as epitaxial BN, the registered signal is additionally affected by interference between light beams reflected from air/film and film/substrate interfaces [405]. In particular, for a BN epilayer of the thickness d on sapphire, the reflectance R measured at a given wavenumber $\tilde{\nu}$ is given by [406]:

$$R(\tilde{\nu}) = \left| \frac{r_1 + r_2 e^{(i\Delta\phi)}}{1 + r_1 r_2 e^{(i\Delta\phi)}} \right|^2, \quad (3.3)$$

where r_1 and r_2 are reflection coefficients at air/BN and BN/sapphire interfaces, defined in terms of BN and sapphire dielectric functions $\varepsilon_{BN}(\tilde{\nu})$ and $\varepsilon_{Al_2O_3}(\tilde{\nu})$

$$r_1 = \frac{1 - \sqrt{\varepsilon_{BN}(\tilde{\nu})}}{1 + \sqrt{\varepsilon_{BN}(\tilde{\nu})}}, \quad r_2 = \frac{\sqrt{\varepsilon_{BN}(\tilde{\nu})} - \sqrt{\varepsilon_{Al_2O_3}(\tilde{\nu})}}{\sqrt{\varepsilon_{BN}(\tilde{\nu})} + \sqrt{\varepsilon_{Al_2O_3}(\tilde{\nu})}} \quad (3.4)$$

$\Delta\phi$ is the optical path difference between beams reflected at air/BN and BN/sapphire interfaces, given by:

$$\Delta\phi = 4\pi d \tilde{\nu} \sqrt{\varepsilon_{BN}(\tilde{\nu})} \quad (3.5)$$

The principle of FTIR measurement is shown in Figure 3.5. The light source emits a broad-band radiation $I(\tilde{\nu})$ in which intensities corresponding to various wavenumbers $\tilde{\nu}$ are different. The beam is directed into a Michelson interferometer, which is the most important part of an FTIR spectrometer. Here, the incident beam is divided by a beam splitter and directed onto two mirrors. While the position of one mirror is fixed, the second mirror can move. Two reflected beams recombine and interfere, resulting in a modulated spectral distribution $J(\tilde{\nu}, x)$, which depends on both the wavenumber $\tilde{\nu}$ and the optical path difference x determined by the position of the second mirror. This radiation is then directed onto the sample, which introduces a frequency-dependent modification. Finally, the reflected light reaches the detector, which measures the total power (the field intensity integrated over all frequencies). Notably, at this stage, different frequencies are not distinguished, and the recorded interferogram $S(x)$ depends only on x . The spectral response, $R(\tilde{\nu})$, is obtained by Fourier transforming the interferogram $S(x)$ and normalizing it with a reference (background) measurement.

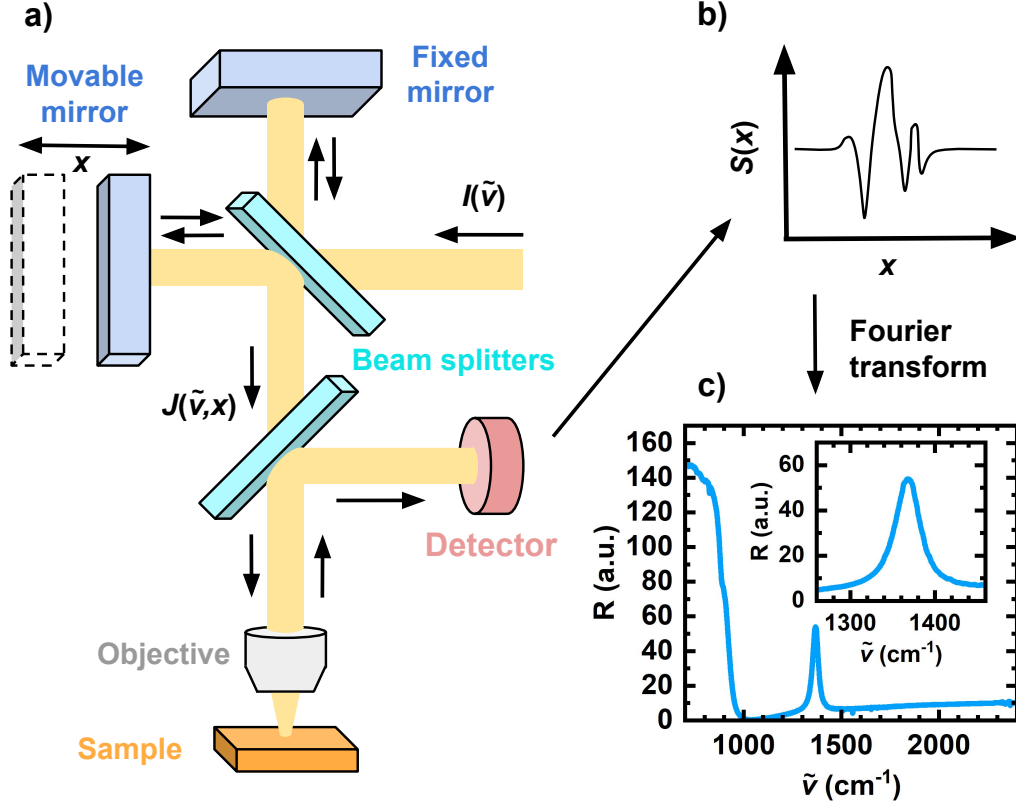


Figure 3.5: Schematic illustration of the working principle of FTIR. a) Presents the optical setup. Incident light $I(\tilde{\nu})$ passes through a Michelson interferometer. The resulting radiation $J(\tilde{\nu}, x)$ is directed onto the sample. Total intensities measured at different values of x form an interferogram, shown schematically in b). After performing the Fourier transform, $R(\tilde{\nu})$ is obtained. c) Shows an exemplary FTIR spectrum measured for a typical high-quality BN epilayer. The peak around 1370 cm^{-1} corresponds to the E_{1u} phonon mode characteristic of BN. The signal below 1000 cm^{-1} comes from a sapphire substrate.

By fitting Eq. 3.3 to experimental data, it is possible to extract properties of the IR-active BN E_{1u} vibrational mode and the epilayer thickness. Notably, in practice, the presented equations are modified by factors related to the sample roughness and porosity; however, the underlying principle remains the same.

FTIR measurements, which were used to determine the thickness of the investigated BN epilayers, were performed using a Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer equipped with a $32\times$ Schwarzschild objective (infinity-corrected) ($\text{NA} = 0.65$). Data were collected and analyzed by MSc Jakub Iwański.

3.6 Raman Spectroscopy

Complementary to XRD, which probes long-range order, the local crystal quality of all investigated BN epilayers was assessed with Raman spectroscopy. This technique utilizes the fact that a small fraction of the photons incident on the crystal undergo inelastic scattering [407]. In such a process, a photon may either excite a new phonon in the crystal lattice (Stokes Raman scattering) or absorb an existing phonon (anti-Stokes Raman scattering). Due to energy and wavevector conservation rules, the following conditions must be satisfied:

$$\begin{cases} \omega = \omega_0 \pm \Omega \\ \vec{k} = \vec{k}_0 \pm \vec{q} \end{cases} \quad (3.6a)$$

$$(3.6b)$$

where ω , ω_0 , and Ω are frequencies of the incident photon, scattered photon, and a phonon, respectively. Analogously, $\vec{k}$, $\vec{k}_0$, and $\vec{q}$ are their wavevectors. When the radiation, whose electric field can be expressed by $\vec{E}_0(\omega)$, interacts with the crystal, it induces the polarization $\vec{P}$ given by:

$$\vec{P} = \varepsilon_0 \chi \vec{E}_0(\omega) \quad (3.7)$$

where ε_0 is a vacuum permittivity and χ is an electric susceptibility tensor. Since lattice vibrations cause the movement of atoms, they also affect the electric susceptibility tensor components χ_{ij} , which in the first approximation might be described as:

$$\chi_{ij} \approx \chi_{ij}^{(0)} + \left(\frac{\partial \chi_{ij}}{\partial Q_\Omega} \right)_0 Q_\Omega \quad (3.8)$$

where Q_Ω describes the displacement of atoms from the equilibrium position (denoted by index 0) under the lattice vibration of the frequency Ω . In this approximation, polarization is expressed by [407]:

$$\vec{P} \approx \varepsilon_0 \chi_0 \vec{E}_0(\omega) + \varepsilon_0 \left(\frac{\partial \chi}{\partial Q_\Omega} \right)_0 Q_\Omega \vec{E}_0(\omega) \quad (3.9)$$

Since $\vec{E}_0(\omega)$ oscillates with the frequency ω and atomic movement Q_Ω is associated with a lattice vibration of the frequency Ω , the second term gives rise to oscillations at Stokes and Antistokes frequencies $\omega \pm \Omega$. Consequently, the scattered light spectrum consists of a strong peak centered at the frequency ω corresponding to the laser used in the experiment, and additional weaker peaks redshifted (or blueshifted) by the frequencies of phonons characteristic of a given material. Notably, as seen from Eq. 3.9, Raman-active vibrations must satisfy $\left(\frac{\partial \chi}{\partial Q_\Omega} \right)_0 \neq 0$.

Raman spectroscopy allows for the identification of materials based on the frequencies of their vibration modes. In addition, it also provides insight into local structural quality. In particular, strain, lattice disorder, and the presence of defects within a crystal lattice induce variations in phonon energies and broadening of the Raman lines [408, 409].

Raman spectroscopy measurements discussed in this work were performed using a Renishaw inVia spectrometer. The measurement principle is illustrated schematically in Figure 3.6. First, the 532 nm laser excitation beam is directed by a dichroic mirror into the microscope objective, which focuses it onto the sample surface. The sample is mounted on an XYZ motorized stage with a 100 nm step size, enabling precise mapping measurements. The backscattered light passes through a dichroic mirror and a 532 nm longpass (LP) filter, which together effectively reject the laser wavelength. Next, the signal is focused onto the entrance slit, where it is spatially filtered and subsequently re-collimated. Finally, the emission is dispersed by a diffraction grating, which spatially separates the spectral components and directs them onto a CCD detector.

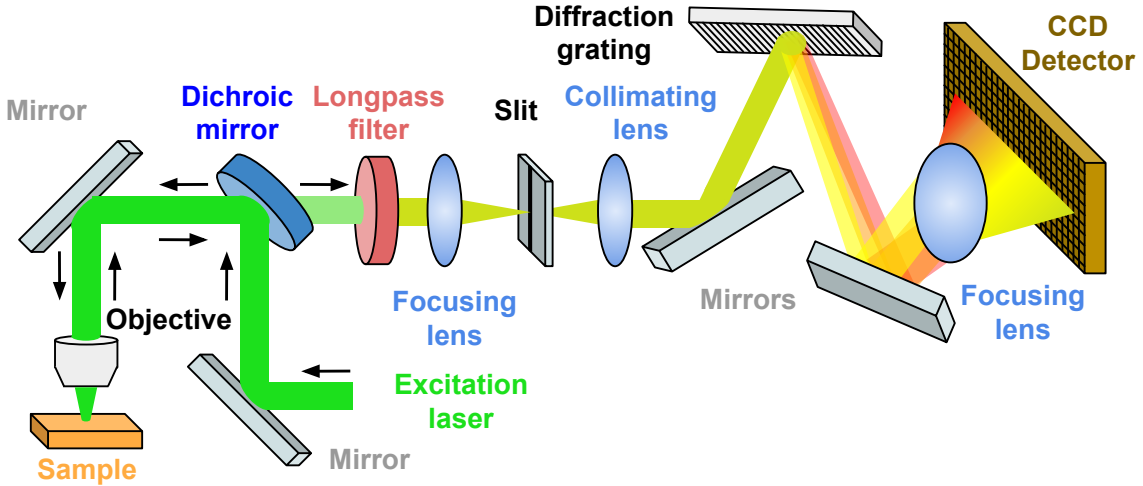


Figure 3.6: Schematic illustration of the working principle of the Renishaw inVia spectrometer during Raman spectroscopy measurements.

In this work, we investigated the properties of the Raman-active E_{2g}^{high} phonon mode characteristic of sp^2 -hybridized BN. Typically, the acquired Raman signal was accompanied by defect-related luminescence. Therefore, prior to data analysis, background correction of all spectra was performed using the RamPy Python library [410]. The obtained peaks were fitted with Lorentzian curves. The results provide an insight into the crystal quality of BN samples investigated in chapter 4. Additionally, Raman mapping measurements on bubbles discussed in chapter 5 provide information on strain distribution and interference effects within bubbled material. All Raman experiments and the data analysis were performed by the author of the dissertation.

3.7 Photoluminescence

In a semiconductor, an electron can be excited from the valence band to the conduction band. The excited electron quickly relaxes to the conduction band minimum via non-radiative processes. Then it recombines with a hole in the valence band, emitting a photon with energy close to the bandgap. This phenomenon, commonly known as luminescence, is particularly useful for measuring bandgap energies of various materials. Depending on the excitation mechanism, various types of luminescence, such as photoluminescence (PL, excitation with photons), electroluminescence (EL, excitation with electric current), or cathodoluminescence (CL, excitation with an electron beam), can be distinguished. Below, we focus on PL, which was employed in this work.

For a theoretical, perfectly pure semiconductor, strong PL emission should only occur when the incident photon energy exceeds the bandgap energy because the initial transition of the electron from the valence band to the conduction band is required. However, all real crystals contain structural defects that introduce additional electronic states. Optical transitions involving such states can also give rise to PL emission. Consequently, the PL spectrum acquired under sub-bandgap excitation can provide valuable information about defects present within the studied material. In particular, band-to-defect transitions, donor-acceptor pair (DAP) recombination, as well as intracenter transitions can be observed.

Optical transitions observed in PL satisfy the selection rules given by Eq. 3.10 [411–413]. First, energy conservation requires that the energy of the emitted photon E_p equals the energy difference between the electron excited and ground states ΔE (Eq. 3.10a). Similarly, the total change in the electron wavevector $\Delta \vec{k}$ must be zero, as photons carry negligible crystal momentum relative to electrons in solids (Eq. 3.10b). This is why indirect-bandgap semiconductors do not exhibit efficient band-edge emission. Additional selection rules arise from the form of the light-matter interaction Hamiltonian $\hat{H}_{int} \sim \vec{E} \cdot \hat{r}$ (in electric dipole approximation), where $\vec{E}$ is the electric field of the incident electromagnetic wave, and $\hat{r}$ is the position operator. The operator $\hat{r}$ acts on the spatial components of the electron wavefunctions, namely $\psi_e(\vec{r})$ for the excited state and $\psi_g(\vec{r})$ for the ground state, leading to the additional symmetry-related rule expressed by Eq. 3.10c. In contrast, it leaves spin components unchanged, so the total spin change ΔS must be zero (Eq. 3.10d).

$$\left\{ \begin{array}{ll} \Delta E = E_p & (3.10a) \\ \Delta \vec{k} = 0 & (3.10b) \\ \langle \psi_g | \hat{r} | \psi_e \rangle \neq 0 & (3.10c) \\ \Delta S = 0 & (3.10d) \end{array} \right.$$

PL was employed to explore the spectral properties of BN-based emitters. In general, the optical setup for PL measurements operates in essentially the same way as a Raman spectroscopy setup; the main difference lies in the broader spectral range. PL spectra presented in this dissertation were acquired under various excitation wavelengths (given in brackets) and using different spectrometers. In most experiments, we used the Renishaw inVia (532 nm) and the Horiba T64000 spectrometers (442 nm, 532 nm) available in our research group. The second setup can be integrated with a constant-flow Microstat HiRes cryostat (Oxford Instruments), enabling low-temperature measurements down to 4 K. To access excitation wavelengths not available in our setups, some PL measurements were performed in collaboration with colleagues in our department. In particular, 405 nm- and 288 nm-excited rBN spectra, discussed in chapter 6, were acquired using Princeton Instruments SpectraPro HRS 750-mm (405 nm) and Princeton Instruments Acton SP2300 (288 nm) spectrometers, kindly provided by Prof. Maciej Molas and Prof. Krzysztof Korona, respectively. The second system is compatible with a Cryovac Konti cryostat, enabling studies of UV defect-related emission in BN at 4 K. Additionally, the 532 nm-excited PL spectra, acquired in parallel with low-temperature second-order correlation function measurements, presented in chapter 4, were obtained using a Princeton Instruments Acton SpectraPro 2750i 750-mm spectrometer available in the Laboratory of Ultrafast MagnetoSpectroscopy (LUMS). The system is compatible with an Oxford Instruments Spectromag cryostat, which provides a stable low-temperature environment down to 1.7 K.

All discussed PL measurements were performed by the author of this dissertation, except for two cases. Temperature-dependent PL studies of an exemplary green emitter discussed in section 4.6 were carried out by BSc Bartosz Kaczmarek under the supervision of the author, while UV PL spectra of the rBN sample discussed in chapter 6 were recorded by Prof. Krzysztof Korona. In addition, the PL measurements performed using Princeton Instruments Acton SpectraPro 2750i and Princeton Instruments SpectraPro HRS-750 mm spectrometers, available in the laboratories of Prof. Jan Suffczyński and Prof. Maciej Molas, were assisted by MSc Tomasz Fąs and MSc Łucja Kipczak, respectively. All additional experimental details are provided in the discussion of the results.

3.8 Second-Order Correlation Function Measurements

The quantum properties of green emitters, discussed in chapter 4, were investigated via measurements of the second-order correlation function $g^{(2)}(\tau)$, introduced in section 1.1. In a standard Hanbury Brown and Twiss (HBT) configuration employed in this work, shown schematically in Figure 3.7, the emission from the studied emitter is divided by a 50:50 beam splitter and directed to two single-photon detectors. The detection events are recorded using time-correlated single photon counting (TCSPC) electronics, which record the arrival times of photons detected in both channels. Next, time delays τ between detection events in the two channels are calculated, and a raw coincidence histogram $C(\tau)$ is constructed, where each bin represents the number of occurrences of τ within a given interval. A proper normalization of $C(\tau)$ with respect to the detector count rates, total acquisition time, and bin width provides the $g^{(2)}(\tau)$ function [414]. As discussed in section 1.1, for an ideal SPE $g^{(2)}(0) = 0$ should be observed; however, $g^{(2)}(0) < 0.5$ is commonly accepted as evidence for single-photon emission.

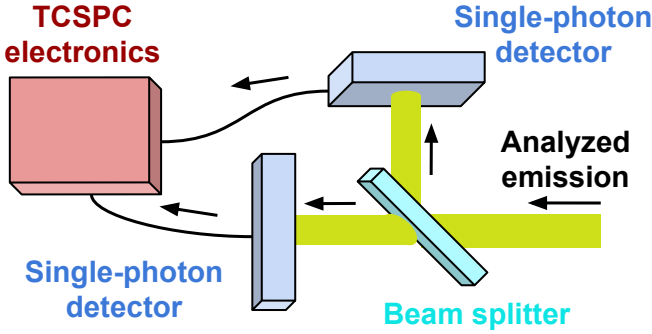


Figure 3.7: Schematic illustration of the working principle of a $g^{(2)}(\tau)$ measurement. The signal from an emitter is split by a beam splitter and directed to two single-photon detectors. Detections are analyzed by TCSPC electronics.

All second-order correlation function measurements discussed in chapter 4 were performed using the HBT configuration. For room-temperature $g^{(2)}(\tau)$ studies, the Renishaw inVia spectrometer was employed. We chose it because all its optical components are optimized for the green spectral range. Consequently, among all the optical setups available in our laboratory, this one is best suited for studying green emitters considered in this work. Therefore, we developed a custom adaptation of this spectrometer for $g^{(2)}(\tau)$ measurements. During the experiment, a sample was excited in the same manner as for PL measurements; however, instead of reaching the CCD detector, the PL signal of an emitter was redirected to the second output of the Renishaw system using a flip mirror (in practice, when finding an emitter exhibiting intense ZPL in its spectrum, the mirror was flipped to redirect the signal). Then it was focused through a lens and directed to two single-photon detectors via a 50:50 beam splitter cube. The investigated emitters typically exhibit broad

emission and strong PSB. Consequently, after dispersion by a diffraction grating, the selected spectral region became substantially broadened in space. Therefore, to collect the entire defect emission, photomultiplier tubes (Hamamatsu H10721P-110) with a relatively large active area (8 mm in diameter) were used as single-photon detectors. Additionally, the registered signal was filtered by a 600 nm shortpass (SP) filter to remove the strong emission from Cr dopants in a sapphire substrate. Photon arrival times from both detectors were recorded using a HydraHarp 400 time-tagging module in a TCSPC scheme, enabling measurement of the second-order correlation function with a temporal resolution of 1.5 ns. Depending on the emitter brightness, recording a single $g^{(2)}(\tau)$ curve typically took 1–2 hours.

Low-temperature (1.7 K) $g^{(2)}(\tau)$ measurements, discussed in chapter 4, were performed in Prof. Jan Suffczyński's laboratory. The defect-related emission, collected from the sample mounted in the Oxford Instruments Spectromag cryostat, was split by a beam splitter cube and directed to two high-resolution Princeton Instruments Acton SpectraPro 2750i spectrometers, each equipped with a single-photon detector. Since the emission of the studied point defects was very narrow (FWHM of the order of 1 meV), spectrometers were used to select a desired spectral line and route it to the detectors. As the resulting signal was not significantly spatially broadened, highly sensitive PerkinElmer AQR-14 single-photon counting modules with a much smaller active area (approximately 0.2 mm in diameter) were used as detectors instead of Hamamatsu H10721P-110 photomultiplier tubes. TCSPC was performed using a HydraHarp 400 time-tagging module, as in room-temperature measurements. The second-order correlation function, $g^{(2)}(\tau)$, was determined with an overall temporal resolution of approximately 400 ps.

The second-order correlation function measurements discussed in this work were performed by the author of this dissertation and MSc Tomasz Fał, whose expertise and assistance were essential. Single-photon detectors were kindly provided by Prof. Jan Suffczyński.

3.9 Optically-Detected Magnetic Resonance

The principle of optically-detected magnetic resonance (ODMR) was introduced in section 2.4.4. In this work, this technique is employed to demonstrate that the MOVPE-grown rBN sample irradiated with thermal neutrons, discussed in chapter 6, hosts V_B^- centers. The experimental setup is shown schematically in Figure 3.8. The 532 nm excitation laser beam, with a power of approximately 8 mW, is focused on the sample surface using an achromatic doublet lens ($f=5.2\text{mm}$, $NA \sim 0.45$), providing a spot diameter of around $1\text{ }\mu\text{m}$. Microwaves with a power of around 1 W are applied to the sample via a microwave antenna (the initial microwave power emitted by the Agilent E8257D generator is increased from 0.3 mW by means of an amplifier). The PL signal originating from V_B^- passes through 736 nm LP and 1010 nm SP filters and is detected using a Thorlabs PDA36A photodetector, which measures the total PL intensity. Notably, the relative changes in V_B^- signal induced by microwave excitation are small (below 1 %). Thus, to increase the experimental sensitivity, a lock-in detection scheme is employed. The amplitude of the applied microwave field is modulated at a frequency of 3 kHz, which serves as the lock-in amplifier's reference input. The lock-in is connected to the photodetector and demodulates the registered PL emission intensity at the reference frequency. Consequently, only those changes in emission intensity that are synchronized with the microwave amplitude modulation are extracted. Such an approach significantly improves the signal-to-noise ratio. During the measurements, the rBN sample was mounted in a cryostat and cooled down to 10 K. Notably, in this work, we discuss only ODMR results obtained in the absence of an external magnetic field. ODMR measurements, presented in chapter 6, were performed by BSc Tomasz Łopion and Dr Mateusz Goryca.

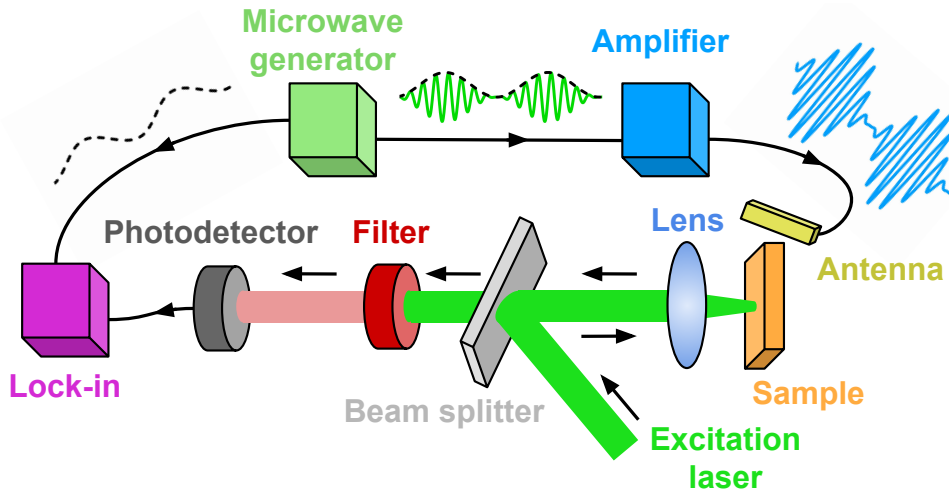


Figure 3.8: Schematic illustration of the working principle of the ODMR setup.

3.10 Electron-Beam Induced Bubble Formation

The SEM setup was used not only to investigate the morphology of MOVPE-grown BN, but also to generate bubbles, whose properties are discussed in chapter 5. As mentioned in section 2.5.2, e-beam exposure of the as-grown material induces the radiolysis of the water present at the sapphire/BN interface. Molecular hydrogen formed in this process detaches the BN epilayer from the substrate, thereby leading to bubble formation. This method is unique to MOVPE-grown material, as the presence of wrinkles, which support the intercalation of water from the ambient environment, is required [17].

The scheme of this process was previously demonstrated in Figure 2.17. Since bubble formation occurs in the electron microscope, we can observe it in situ. Figure 3.9 shows a sequence of 4 SEM images taken at an exemplary BN layer within around 20 seconds. In the next pictures, which correspond to longer exposure times, we observe the formation of new small bubbles and the merging of the existing structures into large ones.

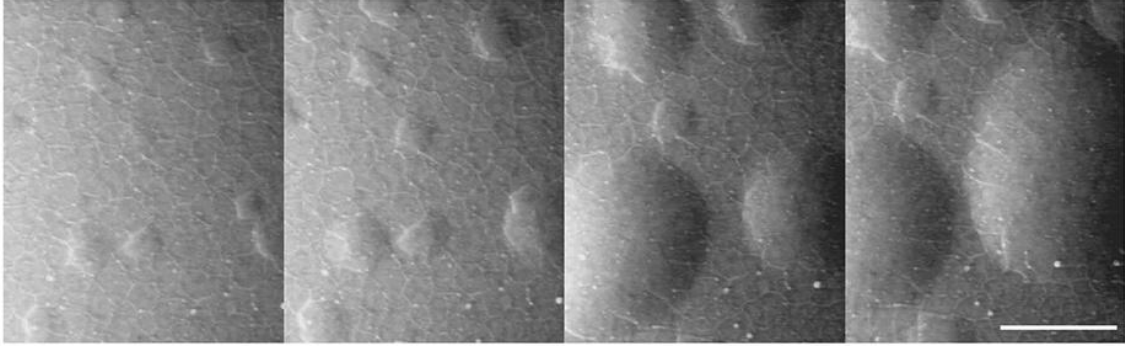


Figure 3.9: From left to right - the sequence of 4 SEM images taken within 20 seconds during e-beam exposure. The formation of new bubbles and the merging of small ones into larger structures are observed. Scalebar is 5 μm . Adapted from [17]

The bubbles investigated in this work were fabricated using an FEI Helios 600 Dual Beam system equipped with a RaithElphy electron lithography setup, the same as that used for SEM imaging. Typically, the beam current and incident electron energy were set to be around 1 nA and 5 keV, respectively. Regular matrices of circular features irradiated into the BN layer, described in section 5.4, were designed using ELPHY Quantum software. The author of this dissertation was responsible for designing the exposure patterns and performing the irradiation processes for bubble generation.

3.11 Optical Lithography for Deterministic Bubble Formation

In chapter 5, we propose a mask-assisted strategy for the formation of deterministic bubble arrays. In this approach, prior to e-beam exposure, a resist mask is fabricated on the BN surface using optical lithography. The procedure is shown schematically in Figure 3.10. First, a ma-P 1205 positive photoresist (Micro Resist Technology GmbH) is deposited onto the BN surface via spin-coating. The thickness of the obtained photoresist layer is approximately 0.4-0.5 μm . Next, the sample is baked on a hotplate at 105 $^{\circ}\text{C}$ for 45 seconds to evaporate the solvent. Then, the predefined pattern, consisting of circular features, is exposed into the resist layer using a POLOS μ Printer maskless lithography system operating at a wavelength of 436 nm. The system resolution is 2 μm . The pattern is designed using KLayout software. After exposure, the photoresist is developed in an MF331 solution (Kayaku Advanced Materials) for 60 seconds, forming a resist mask with circular openings. Finally, the BN layer is exposed to the electron beam. The mask-assisted electron irradiation induces bubble formation only in unprotected areas. The author of this dissertation was responsible for designing the exposure patterns, performing the entire lithography process, and final electron irradiation.

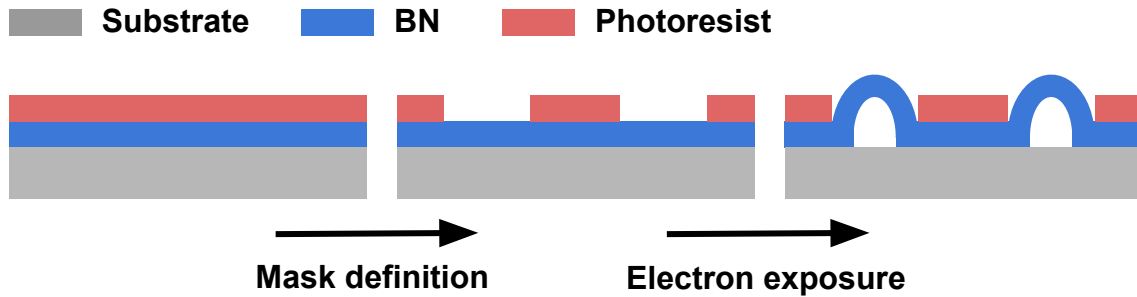


Figure 3.10: Scheme of mask-assisted strategy for bubble fabrication. A photoresist mask is defined on the sample using optical lithography. Consequently, electron exposure induces bubble formation only in the predesigned areas.

Chapter 4

Characterization and Engineering of Visible Single-Photon Emitters

4.1 Introduction

As discussed in section 2.4.3, visible quantum emitters in BN are a promising platform for various applications. However, to move SPE-based technologies from laboratories to the market, a large-area material that hosts these emitters is required. Such wafer-scale BN might be obtained via MOVPE growth, which offers a compromise between growth rate and material quality. Moreover, the presence of organic precursors, such as TEB, induces the formation of carbon-related point defects acting as visible quantum emitters [14], thereby avoiding the need for post-growth SPE fabrication. A combination of these two aspects makes MOVPE a very promising approach for establishing BN as a robust platform for quantum applications. However, although engineering visible SPEs has been demonstrated for BN grown by CVD on metal foils, similar results are lacking for BN epilayers grown by MOVPE on insulating substrates.

In this chapter, we address this issue by a systematic analysis of how growth conditions influence the properties of visible SPEs in BN layers grown by MOVPE. The previous studies of visible quantum emitters in MOVPE-grown BN focused on yellow emitters in the range 2.00-2.20 eV, which were identified as carbon-related point defects introduced by TEB [14]. Here, we instead focus on green SPEs, emitting in the 2.25-2.32 eV range, which are typically observed in our epilayers. Emitters in a similar spectral range have been previously induced in BN flakes via annealing in either carbon-rich [304] or oxygen-rich atmospheres [306]. However, to date, they have not been studied in detail in epitaxial BN, and consequently, the growth strategy for their formation has not been optimized, which we address in this work.

First, we demonstrate that increasing the growth temperature from 1300 °C to 1400 °C significantly improves BN quality and drives a transition from a growth regime in which no useful quantum emitters form, to one in which a high density of room-temperature green SPEs is achieved. The large number of emitters enables statistical analysis of their properties, including the distributions of ZPL position, linewidth, and emission purity. Notably, based on the shape of the phonon replica, the studied green emitters can be divided into three classes. In addition, phonon-induced broadening of the emission linewidth is investigated via temperature-dependent PL measurements.

In the following sections, the properties of green SPEs are investigated in BN epilayers grown at different TEB flow rates. TEB is an organic precursor, so intuitively, its concentration in the MOVPE reactor chamber strongly influences the formation of carbon-related emitters. To provide a clear distinction between effects caused truly by the change in TEB flow rate and those originating from the variations in BN thickness, a series of BN epilayers grown at the same TEB flow rate but of different thicknesses is also included in the analysis.

Our results indicate that green SPEs observed in our samples arise from carbon incorporated into the BN lattice. We demonstrate their engineering by manipulating the TEB flow rate and sample thickness. In particular, the impact of these parameters on emitter density, purity, and stability is analyzed in detail. When the TEB flow rate is too low, the BN growth rate is slow, and the formation of green SPEs is ineffective. On the other hand, when it is too high, formation of defect ensembles rather than isolated emitters is preferred and the emission purity decreases. In particular, we observe a strict crossover between growth conditions that support the formation of true room-temperature SPEs and those that induce the generation of quantum emitters that do not satisfy the $g^{(2)}(0) < 0.5$ condition.

Another key property analyzed is the stability of green SPEs. We demonstrate that for high-quality BN epilayers thinner than $\sim 20\text{-}30$ nm, it increases proportionally with BN thickness. This behavior imposes some restrictions on the minimum thickness of future hBN-based quantum devices.

4.2 Samples

All samples studied in this chapter were grown by Dr Aleksandra Dąbrowska on 2-inch sapphire substrates using the two-stage epitaxy approach [278] introduced previously in section 3.1. Boron and nitrogen precursors were TEB and NH_3 , respectively. In all cases, a thin BN buffer layer was obtained at 1300 °C under the pressure of 800 mbar using the CFG method. In this step, the NH_3 flow rate was 4000 sccm, and the TEB flow rate was 10 sccm. The procedure for buffer layer

Table 4.1: Growth parameters for all BN samples investigated in this chapter. Every studied epilayer belongs to one of three groups, each marked by a different color. Samples within one group differ in exactly one growth parameter relative to the standard growth process. For layers marked by yellow/green/blue, the changing parameter is temperature/TEB flow rate/number of pulse cycles.

Sample	Growth Temperature (°C)	TEB Flow Rate (sccm)	Number of TEB Pulses	Thickness (nm)
T ₁₃₀₀	1300	15	600	30.5 ± 0.7
T ₁₄₀₀	1400	15	600	17.5 ± 0.5
F ₁₀	1400	10	600	2.7 ± 0.4
F ₁₃	1400	13	600	10.5 ± 0.3
F ₁₅	1400	15	600	15.8 ± 0.5
F ₁₇	1400	17	600	17.6 ± 0.5
F ₂₀	1400	20	600	42.8 ± 0.2
P ₁₀₀	1400	15	100	3.2 ± 0.1
P ₂₀₀	1400	15	200	5.1 ± 0.2
P ₄₀₀	1400	15	400	9.4 ± 0.5
P ₆₀₀	1400	15	600	13.9 ± 0.9
P ₁₀₀₀	1400	15	1000	23.0 ± 1.6

growth was established over many years of research on BN in our group [278, 400]. The actual material is formed on a buffer layer using the FME approach. For each sample studied here, during this step, the chamber pressure and NH₃ flow were set to 400 mbar and 4000 sccm in a pulse, respectively. Other growth parameters were varied between samples.

As summarized in Table 4.1, the studied BN samples can be divided into three series, marked by yellow, green, and blue. In a standard FME process, 600 alternating NH₃/TEB pulse cycles are introduced into the reactor chamber. The growth is carried out at 1400 °C with a TEB flow rate of 15 sccm in a pulse. All samples within one group differ by exactly one growth parameter, which is modified relative to the standard growth procedure. Samples marked in Table 4.1 by yellow and labeled as **T** differ in the growth Temperature, which is included in the bottom index. Thus, samples T₁₃₀₀ and T₁₄₀₀ were grown at 1300 °C and 1400 °C, respectively. The comparison between these two epilayers provides insight into the influence of growth temperature on BN properties. Samples marked by green and labeled as **F** were grown using different TEB Flow rates ranging from 10 sccm in a pulse for sample F₁₀ up to 20 sccm in a pulse for sample F₂₀. Intuitively, an increase in TEB flow rate should lead to a higher density of carbon-related point defects. Therefore, studying samples from this group reveals the role of carbon in SPE

formation. Finally, samples marked by blue and labeled as **P** were obtained using a different number of NH_3/TEB Pulse cycles. It varies between 100 for sample P_{100} and 1000 for sample P_{1000} . In principle, the samples belonging to this group should differ only in thickness. The detailed analysis of the F and P samples' properties enables the distinction between effects caused by higher carbon incorporation and higher thickness. The sample thicknesses, listed in Table 4.1, were obtained from FTIR measurements by MSc Jakub Iwański.

Every group of samples includes exactly one epilayer grown under standard conditions: T_{1400} , F_{15} , P_{600} . However, as this study found, they exhibit slightly different properties. We attribute this effect to reactor-related factors such as operational conditions and system history. All measurements discussed in this chapter were performed for as-grown samples on sapphire substrates. It means that all observed changes in SPE formation can be directly attributed to variations in the growth scheme, and no point defects are unintentionally introduced during material transfer.

4.3 Growth-Temperature Dependence of Boron Nitride Properties

We start with comparing properties of BN layers T_{1300} and T_{1400} grown at 1300 °C and 1400 °C, respectively. First, although the precursor flow ratios and the number of pulse cycles were the same during the growth of both layers, T_{1300} is almost twice as thick (~ 31 nm) as T_{1400} (~ 18 nm). The drop in the growth rate for the higher temperature is related to the increase in BN quality. As the material exhibits better structural properties and its surface becomes flatter, the concentration of nucleation sites for the growth of the next atomic plane is lower, so the growth rate decreases. This interpretation is consistent with the results of SEM, XRD, and Raman measurements, discussed below.

Figure 4.1a-b show SEM images of samples T_{1300} and T_{1400} , taken by Dr Aleksandra Dąbrowska and Dr Mateusz Tokarczyk. Both surfaces are flat and covered with wrinkles, which arise from the thermal expansion mismatch between BN and sapphire and are characteristic of high-quality 2D materials [374]. Notably, the wrinkles in sample T_{1400} are more regularly arranged and intersect at angles of approximately 120°, reflecting the crystallographic directions. Also, while the surface of T_{1400} is extremely clean (Figure 4.1b), in the central upper area of the T_{1300} surface shown in Figure 4.1a, small 3D objects (debris), are observed. We attribute the debris to local nucleation at structural defects, where BN grows along crystallographic directions different from those of the surrounding layers.

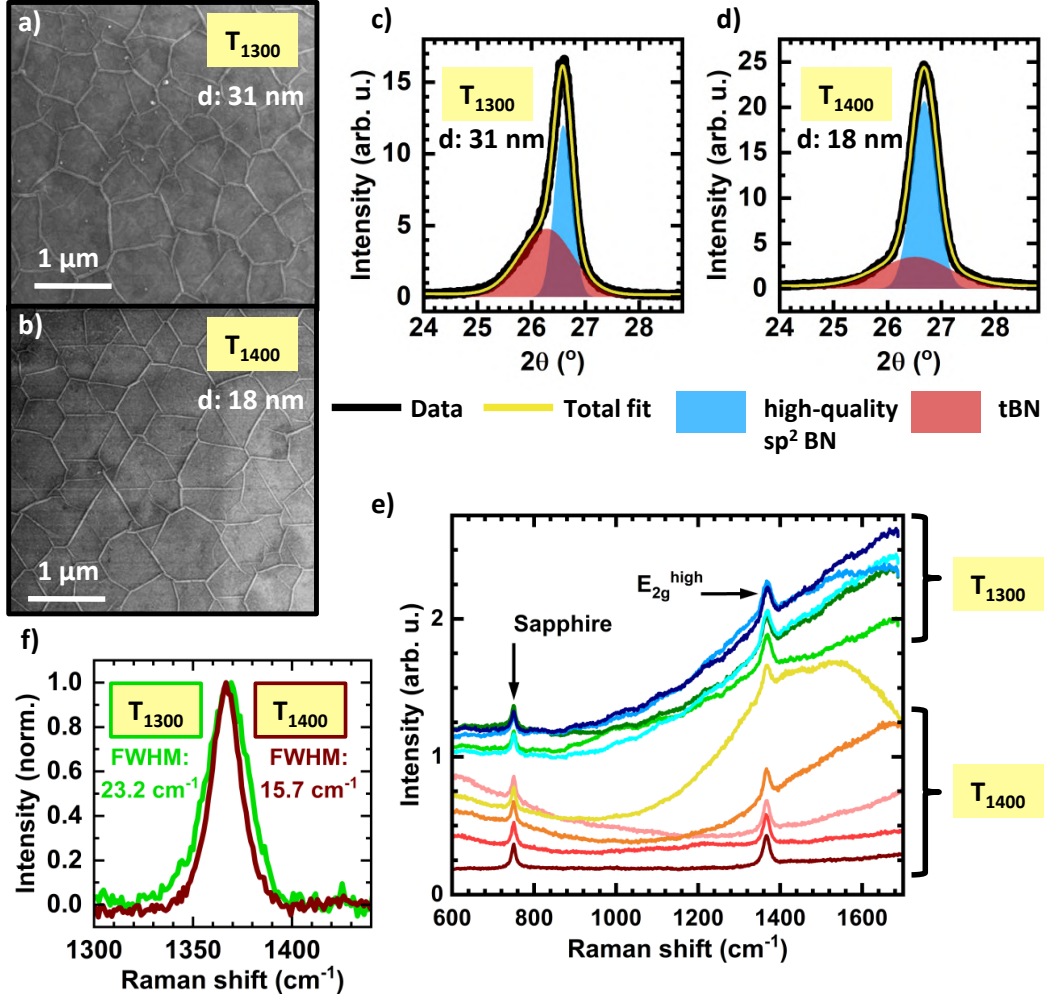


Figure 4.1: (a-b) SEM images of samples T₁₃₀₀ and T₁₄₀₀, respectively. Both samples exhibit flat morphology with wrinkles, characteristic of high-quality BN layers. Scalebars are 1 μm. (c-d) Results of XRD measurements close to the (002) peak position for samples T₁₃₀₀ and T₁₄₀₀, respectively. For both layers, signals from high-quality BN (blue-filled) and from lower-structural-quality tBN (red-filled) are observed. Experimental data and the total double-Gaussian fits are marked by black and yellow lines, respectively. e) Sets of representative Raman spectra acquired from samples T₁₃₀₀ and T₁₄₀₀. The peak at ~750 cm⁻¹ is a sapphire vibrational mode. At ~1367 cm⁻¹, the Raman-active E_{2g}^{high} mode characteristic for sp²-bonded BN is observed. f) Zoom on exemplary background-corrected Raman spectra of T₁₃₀₀ (green curve) and T₁₄₀₀ (brown curve). The epilayer grown at a higher temperature exhibits a significantly narrower Raman peak.

Table 4.2: BN (002) XRD peak positions and corresponding interlayer spacings for tBN and high-quality BN components in samples T₁₃₀₀ and T₁₄₀₀. Rows are filled in yellow consistent with the color coding used in Table 4.1.

Sample	tBN		high-quality BN	
	2θ (°)	Interlayer spacing (Å)	2θ (°)	Interlayer spacing (Å)
T ₁₃₀₀	26.29	3.39	26.59	3.35
T ₁₄₀₀	26.51	3.36	26.68	3.34

Table 4.3: Energy and FWHM of the E_{2g}^{high} Raman-active phonon mode in samples T₁₃₀₀ and T₁₄₀₀. Rows are filled in yellow consistent with the color coding used in Table 4.1.

Sample	E_{2g}^{high} Energy (cm ⁻¹)	E_{2g}^{high} FWHM (cm ⁻¹)
T ₁₃₀₀	1366.90 ± 0.17	23.16 ± 0.26
T ₁₄₀₀	1367.12 ± 0.07	15.69 ± 0.30

The detailed information on material quality was assessed with XRD measurements around the (002) peak position performed by Dr Mateusz Tokarczyk, while the data analysis was conducted by the author of this thesis. The results are shown in Figure 4.1c-d. For both samples, the total signal observed in the 2θ scan exhibits a double-peak structure arising from two BN components and can be fitted with a double-Gaussian curve. Precise values of peak positions and corresponding BN interlayer distances are included in Table 4.2. Light blue peaks are associated with the presence of high-quality sp^2 -hybridized BN of interlayer spacing close to the literature value of 3.33 Å. Red peaks correspond to tBN of poorer [415] quality and interlayer spacing above 3.35 Å. As clearly seen in Figure 4.1c-d, when the growth temperature is higher, the amount of tBN relative to high-quality BN decreases. Also, the distance between atomic planes reduces from 3.35 Å to 3.34 Å. The results indicate that the long-range order of sample T₁₄₀₀ is better than that of T₁₃₀₀.

Additionally, the local structural quality was investigated via Raman spectroscopy. To obtain information representative of an entire large-area layer, for both samples, nine Raman spectra were acquired at points separated by more than 1 mm. The measurements were performed using a Renishaw inVia spectrometer. The samples were excited via a 532 nm continuous-wave (CW) laser with a power of 20 mW. A 100× objective with a numerical aperture (NA=0.9) provided a laser spot size of about 0.5 μm. Sets of representative Raman spectra are provided in Figure 4.1e. At all points, two peaks are observed. The one occurring at ~ 750 cm⁻¹ is associated with the E_g phonon mode in sapphire substrate [416]. The peak at ~ 1367 cm⁻¹ corresponds to the Raman-active E_{2g}^{high} mode typical for sp^2 -bonded BN. All spectra of layer T₁₃₀₀ exhibit a strong defect-related luminescence signal. As we have shown in our previous work, this background emission can typically be quenched by annealing BN at ~ 700 °C or by prolonged laser illumination [329, 374]. In this work, these procedures were not implemented to avoid unintentional sample modification. Notably, the strong background appears uniform across the sample, suggesting a high and uniform concentration of optically active defects throughout. For sample T₁₄₀₀, the defect-related emission intensity is typically much lower. In fact, only one of the five T₁₄₀₀ spectra presented in Figure 4.1e exhibits as high background signal as that observed for T₁₃₀₀. This suggests a much lower concentration of point defects emitting in the visible range.

Exemplary background-corrected spectra of samples T₁₃₀₀ and T₁₄₀₀, limited to the range of the E_{2g}^{high} mode, are shown in Figure 4.1f. Raman peaks were fitted as Lorentzian curves. Table 4.3 includes average energies and FWHMs of the E_{2g}^{high} mode for the investigated samples. In both cases, the Raman peak position is very close to the literature value of 1365-1366 cm⁻¹, suggesting the absence of strain within layers. A striking difference is observed in E_{2g}^{high} FWHM, which decreases from above 23 cm⁻¹ to below 16 cm⁻¹ when the growth temperature of BN is increased from 1300 °C to 1400 °C, indicating a significant enhancement of the material quality. The results from SEM, XRD, and Raman spectroscopy clearly show that sample T₁₄₀₀ has much superior structural properties compared to T₁₃₀₀. This proves that the growth temperature is a key parameter that determines BN's crystalline properties. The slow growth rate of higher-quality material might be attributed to a lower concentration of structural imperfections that could act as initiation points for the growth of subsequent atomic planes.

4.4 Spectral Properties of Green Emitters

After studying the general structural properties of samples T₁₃₀₀ and T₁₄₀₀, we focus on their defect-related emission in the visible range. To this end, 34×34 μm² room-temperature PL maps with a step size of 0.4 μm were acquired from both layers over the spectral range 2.01-2.32 eV (533-616 nm). The experimental setup was the same as that used for the Raman measurements discussed above, but the incident laser power was set to 2 mW. Figure 4.2a-b show maps of the total integrated intensity for both studied samples. Representative spectra acquired at exemplary bright spots, marked by blue circles, diamonds, and squares, are presented in Figure 4.2c-d. The gray-filled spectra represent the average emission from 7396 pixels for each map.

As shown in Figure 4.2c, the epilayer grown at 1300 °C exhibits strong and uniform defect-related emission at all points. The spectra collected at bright spots do not differ significantly in shape from the average background emission, but are more intense. Typically, the observed signal consists of two broad structures centered at ~2.1 eV and ~2.3 eV. The strong, spatially uniform emission indicates a high concentration of optically active defects. It suggests that the applied growth conditions favor the formation of defect ensembles over well-isolated point defects, for which characteristic sharp ZPLs would be expected.

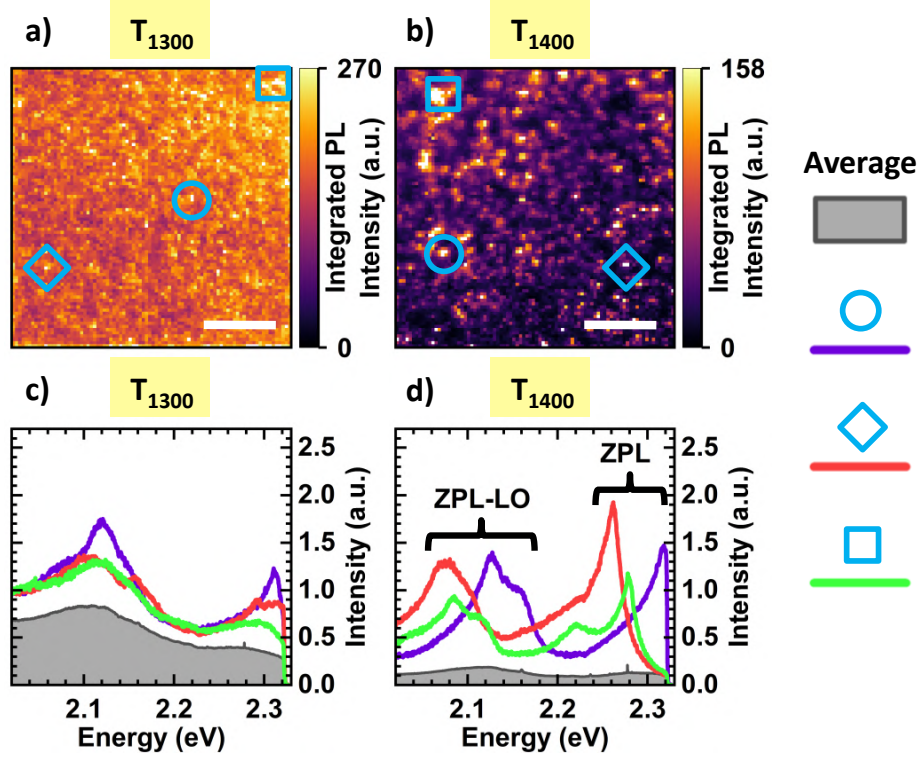


Figure 4.2: Results of PL mapping measurements for samples T₁₃₀₀ and T₁₄₀₀. (a-b) $34 \times 34 \mu\text{m}^2$ maps of the total integrated emission intensity in the range 2.01-2.32 eV. Step size is $0.4 \mu\text{m}$. Scalebars are $10 \mu\text{m}$. Intensity color scales can be directly compared. For clarity, they were limited such that the brightest 1% of points lie outside the displayed range. (c-d) PL spectra acquired at bright spots marked by blue circles, diamonds, and squares in a) and b), respectively. The gray-filled spectra are the averaged PL signals from the whole maps (7396 pixels). Intensity scales can be directly compared.

In contrast, many individual well-isolated bright points are found across sample T₁₄₀₀ (Figure 4.2b), while the average visible PL emission from this layer is low, as shown in Figure 4.2d. At bright points, an intense and highly asymmetric ZPL is typically observed. The pronounced low-energy tail is attributed to strong coupling to acoustic phonons and is commonly reported for BN-based quantum emitters [114, 303, 417]. The ZPL is followed by an optical-phonon replica (ZPL-LO), detuned by 160-200 meV, which is another frequently observed feature [114, 303, 417].

Sample T₁₄₀₀ supports the formation of well-isolated emitters due to its higher crystal quality and significantly lower defect density compared to T₁₃₀₀, in which defect ensembles form. Therefore, the growth temperature seems to be a crucial parameter for obtaining individual color centers. For the growth scheme typically used in our group, it should be as high as 1400 °C. One could expect that even higher growth temperatures could further improve BN structural properties and emitter formation; however, we cannot verify this hypothesis due to the limitations of our MOVPE reactor.

To identify emitters across the acquired PL map of sample T₁₄₀₀ and other PL maps analyzed further in this work, we developed the following procedure consisting of three steps: background correction, identification of local intensity maxima, and application of intensity-based filtering criteria. Each recorded spectrum S_N ($N \in \{1, 2, \dots, 7396\}$) consists of r values $S_{N,i}$ ($i \in \{1, \dots, r\}$), which correspond to intensities measured for energies E_i (r is the number of pixels of the CCD detector). Analogously, the average emission spectrum (the gray-filled spectrum in Figure 4.2d) consists of r values A_i . We define so-called corrected spectra. Each corrected spectrum C_N consists of r values $C_{N,i}$ given by:

$$C_{N,i} = S_{N,i} - A_i \quad (4.1)$$

Then, for each C_N , we determine index j satisfying:

$$C_{N,j} = \max\{C_{N,1}, C_{N,2}, \dots, C_{N,r}\} \quad (4.2)$$

and we label each map pixel with value u_N defined as:

$$u_N = C_{N,j} \quad (4.3)$$

If the value u_N for a given map pixel exceeds values found for nearest-neighboring pixels, the corresponding spectrum S_N is classified as bright. This prevents the same emitter from being counted multiple times, since only the brightest spectrum within a bright spot is analyzed further. However, before being classified as emitters, bright spectra undergo additional intensity-related tests. Let k be such an index that E_k is approximately ZPL energy (bright spectra without a clearly identifiable ZPL are manually discarded). The first test is passed if

$$C_{N,k} > 4A_k \quad (4.4)$$

requiring the ZPL intensity in the corrected spectrum to be at least four times the average signal at a given energy. It is useful for samples with low average emission, allowing us to discard very weak local maxima. The second test is passed when

$$C_{N,k} > A_k + 4T_k, \quad (4.5)$$

where T_k denotes the standard deviation calculated from the set $\{S_{1,k}, S_{2,k}, \dots, S_{N,k}\}$. At first glance, this condition may appear non-intuitive; however, it enables the selection of only these emitters whose emission is statistically significant relative to the background fluctuations. The last condition is met if

$$S_{N,k} > 3 \times \min\{S_{N,1}, S_{N,2}, \dots, S_{N,r}\} \quad (4.6)$$

which implies that the ZPL must be at least 3 times more intense than the background level. This condition discards color centers that are not considered useful, because their emission appears on top of a very strong background signal. In summary, the applied procedure selects only spatially isolated emitters that are sufficiently bright, exhibit intensities statistically higher than those of weaker emitters, and whose emission is not artificially enhanced by a strong background.

Using the procedure described above, 102 bright isolated emitters were identified in sample T₁₄₀₀. This gives the spatial emitter density of 0.13/ μm^2 , which is similar to values reported for BN flakes annealed in carbon- or oxygen-rich atmosphere [418, 419], but is one order of magnitude lower than reported for CVD-grown BN layers [342, 356].

In the next step, we investigated the spectral properties of the found emitters. Notably, the emission of some observed color centers was very close to the longpass (LP) filter edge or even beyond it. Therefore, the ZPL energy and FWHM can be assessed only for 92 and 85 emitters, respectively. Figure 4.3a presents the energy distribution of the observed ZPLs. Although SPEs in BN are known to cover the entire visible range, in our material, almost all the observed color centers emit in the range 2.25-2.32 eV. This effect is related to the wavelength of the laser used, 532 nm (2.33 eV), which nearly resonantly and highly selectively excites these defects. Therefore we will refer to them simply as *green* SPE. Although our MOVPE-grown BN epilayers host numerous point defects of various types, as shown previously in [329], under 532 nm laser illumination, the emitters of the energy below 2.25 eV are observed very rarely. However, the predominance of green emitters cannot be attributed solely to the excitation wavelength. A green laser is commonly used in studies of SPEs in BN, but in most reports, visible SPEs are distributed more uniformly in energy, and the most common emitters are the yellow ones [14, 114, 305, 315–317, 321]. Therefore, our results indicate an exceptionally high green-emitter concentration, which, together with preferential excitation, leads to efficient carrier capture, thereby suppressing the excitation of lower-energy defects. This effect enables us to conduct a detailed study of the properties of green emitters in epitaxial BN. Notably, SPEs emitting in this range have been observed and investigated in BN flakes annealed in carbon-rich or oxygen-rich atmosphere [304, 306]; however, the corresponding results for MOVPE-grown material are missing. Interestingly, as shown in the inset in Figure 4.3a, green centers in the studied BN layer T₁₄₀₀ are not distributed uniformly in energy. Instead, three emitter classes, separated by 20-30 meV, are clearly observed. This behavior might suggest that green emitters involve point defects of various atomic structures, or that their emission energy depends on the local crystal symmetry.

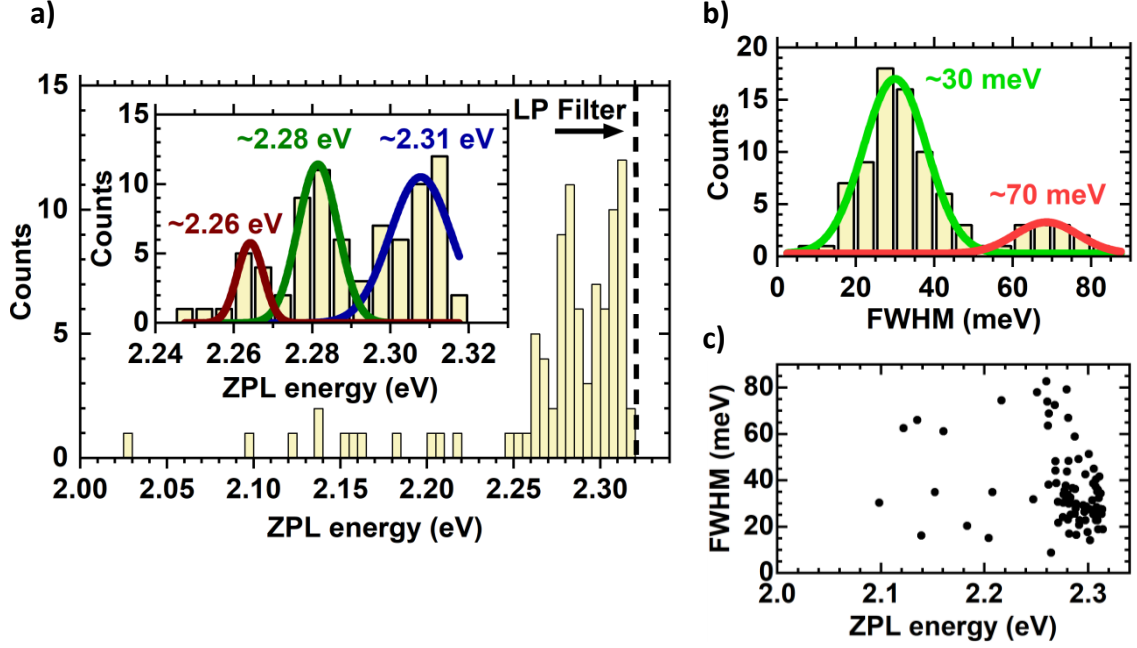


Figure 4.3: Spectral properties of the emitters found in the PL map shown in Figure 4.2c. a) Histogram of ZPL energies in the whole studied range. The vertical dashed line is the 532 nm LP filter edge. Inset is the zoom in the range 2.24-2.33 eV. Dark red, green, and blue curves are Gaussian fits. b) Distribution of FWHM values. Green and red curves are Gaussian fits. c) Direct comparison of FWHM and ZPL energy for 85 emitters.

Ideally, all photons should have the same energy and be indistinguishable, which means that as low FWHM values as possible are desired. As discussed previously in section 2.4.3, the emission linewidth is affected by spectral diffusion, which is crucial at low temperatures, and by phonon-related mechanisms, which lead to dephasing and fluctuations in the transition energy, dominating at higher temperatures [358, 366, 367]. Their impact on the observed emitters will be analyzed later in this work. However, at this stage, we do not focus on these effects since at room temperature the emission linewidth is mostly governed by the acoustic-phonon sideband. Depending on the FWHM, two emitter groups can be distinguished in the investigated BN epilayers, as shown in Figure 4.3b. At some points, emission peaks exhibit a high FWHM of around ~ 70 meV. Such broad emission, occurring in $\sim 15\%$ of cases, might be related to the formation of defect ensembles. However, most emitters might be associated with well-isolated individual point defects with FWHMs in the range of 20-40 meV. While values of around ~ 20 meV and less are considered good for typical room-temperature SPEs [379, 420], FWHM of 30 meV or higher indicates a significant contribution from acoustic phonon-assisted transitions. This result highlights the necessity of integrating the discussed emitters with structures that can effectively narrow the emission. Notably, the room-temperature FWHM reported for green emitters observed in BN flakes annealed in oxygen-rich atmosphere was also close to 40 meV [306]. This indicates that the strong emission broadening observed

in sample T₁₄₀₀ is not related to the quality of our MOVPE-grown material but is rather typical for green emitters. As presented in Figure 4.3c, no direct correlation between FWHM and emission energy is observed.

The distinction between emitter classes shown in Figure 4.3a is based solely on ZPL positions. Now, to extend this analysis, we focus on the shape of emitter spectra. One can distinguish three types of green emitters, characterized by narrow ZPLs and distinct PSB structures. Representative detuning spectra of each type are plotted in Figure 4.4a-c. Spectra of Type 1 and Type 2, shown in Figure 4.4a-b, both exhibit pronounced low-energy PSB associated with acoustic phonons, but they differ significantly in the optical-phonon replica region. In both cases, a strong peak at the detuning energy of ~ 195 meV is observed. Intuitively, it could be attributed to phonon-assisted recombination involving the LO (E_{1u}) mode at Γ , which matches this detuning energy very well [224]. Although this interpretation might be correct, previous studies on 4.1 eV defect emission suggest caution. A similar strong detuning feature observed in the spectra of UV defects was also initially attributed to the LO (E_{1u}) phonon mode. However, recent studies on isotopically purified BN samples have challenged this interpretation and point to a crucial role of a local vibrational mode associated with a carbon dimer, identified as a UV emitter [289].

While both Type 1 and Type 2 emitters exhibit a strong signal detuned by ~ 195 meV, they differ in the spectral region associated with lower-energy optical-phonon-assisted emission. Specifically, Type 2 emitters display a pronounced peak at ~ 165 meV below the ZPL, which is absent in Type 1 spectra. For previously reported visible color centers, such peaks were assigned to LO (E_{1u}) phonon-assisted recombination along the M-K direction [417]. The different coupling of Type 1 and Type 2 green emitters to this phonon mode may arise either from differences in their microscopic structure or from variations in the local symmetry of their environment, even if both originate from the same defect species.

Compared to Type 1 and Type 2 emitters, Type 3 centers exhibit weaker both acoustic- and optical-phonon replicas, as shown in Figure 4.4c. Interestingly, the most prominent feature in the optical phonon replica region appears at a detuning of ~ 165 meV, while the emission at ~ 195 meV below ZPL is barely visible. Type 3 emitters might seem promising for quantum applications, as only a negligible fraction of the emission is lost to PSBs. Unfortunately, as observed in this study, emitters in this class are very rare and typically unstable, exhibiting a strong tendency to bleach under prolonged laser exposure.

As mentioned previously, in addition to the three identified emitter classes, we sometimes observe broad emission bands that may originate from poorly isolated defect ensembles. An exemplary spectrum exhibiting such a broad emission is presented in Figure 4.4d.

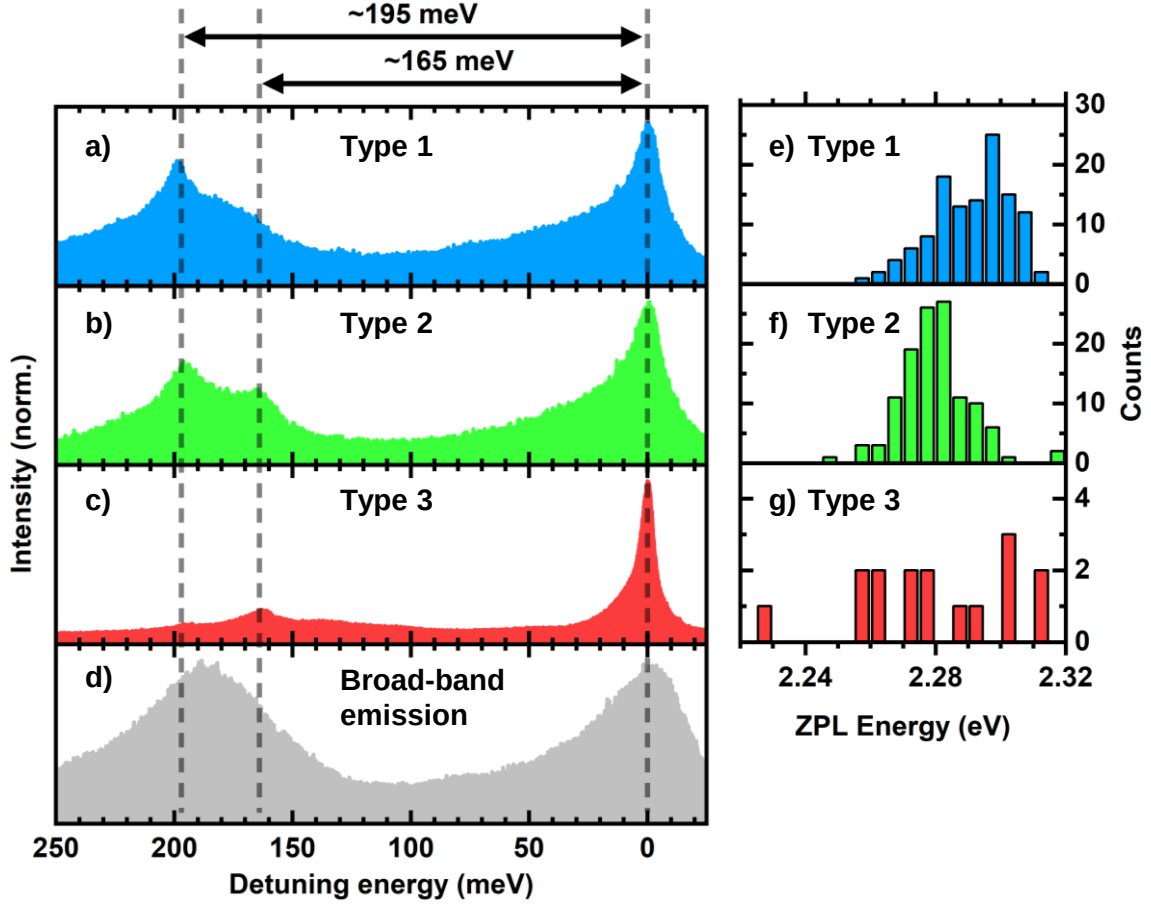


Figure 4.4: (a-c) representative detuning spectra of Type 1-3 green emitters. Dashed vertical lines mark ZPLs shifted to zero and peaks observed in the optical-phonon-replica region at ~ 165 meV and ~ 195 meV. d) Broad emission spectrum related to poor quality defects. (e-g) Histograms of ZPL positions for Type 1-3 emitters.

To investigate the properties of different emitter classes, we performed a statistical analysis of 120 emitters of Type 1 and 120 emitters of Type 2. Notably, only emitters, which can be classified as Type 1 or Type 2 without any doubt, are included. This requirement limits our analysis only to point defects, whose ZPLs are above 2.20 eV, since the classification is based on a phonon-replica shape detuned by ~ 200 meV. To perform a proper classification of emitters below 2.20 eV, the recorded spectral window should be extended below 2.0 eV. However, at energies below this level, PL emission associated with BN-based color centers is hindered by the strong luminescence of the sapphire substrate. The emitters whose ZPL energy is above the edge of the 532nm LP filter are also excluded.

The obtained histograms of ZPL energy are shown in Figure 4.4e-f. Although both types exhibit broad spectral distributions, statistically, Type 1 emitters are clearly blue-shifted relative to Type 2 emitters. This observation supports the interpretation that these emitters either have distinct atomic structures or correspond to the same defect species embedded in different local environments - namely, in different BN polytypes. The distribution maxima found respectively at

~ 2.30 eV ~ 2.28 eV are in good agreement with those found previously in Figure 4.3a. When searching for Type 1 and Type 2 emission spectra, we found only 17 Type 3 emitters across the entire studied spectral range. Therefore, all we can say is that they are extremely rare. Moreover, as noted above, they typically bleach under laser exposure.

4.5 Quantum Properties of Green Emitters

Thanks to the courtesy of Prof. Jan Suffczyński, whose group possesses the necessary equipment, we next performed room-temperature second-order correlation function measurements on 20 green emitters in sample T₁₄₀₀ to statistically analyze their quantum properties. The measurements were conducted in a standard HBT configuration with the assistance of MSc Tomasz Fąs. The excitation scheme was the same as that used for the PL maps discussed above; however, instead of reaching the CCD detector, the emission signal was redirected to the empty output port of the Renishaw inVia spectrometer (see section 3.8). Then, using a 50:50 non-polarizing beamsplitter, the PL signal was directed towards two photomultiplier tubes (Hamamatsu H10721P-110). Photon arrival times from both detectors were recorded using a HydraHarp 400 time-tagging module within a TCSPC scheme, allowing for the measurement of the second-order correlation function $g^{(2)}(\tau)$. The signal was filtered by 532 nm LP and 600 nm shortpass (SP) filters. The results, summarized in Figure 4.5, have been reported in [421].

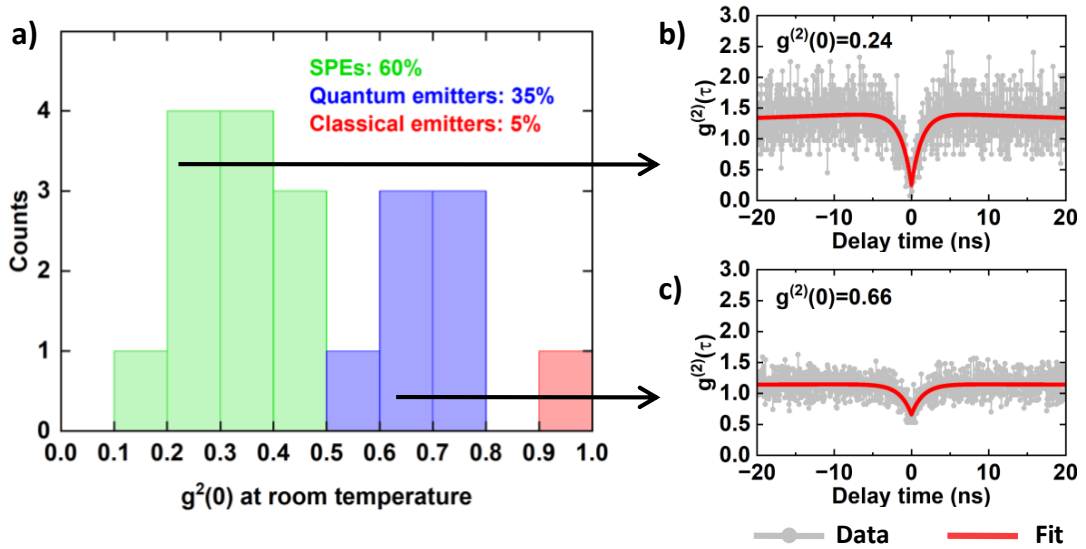


Figure 4.5: Results of room-temperature second-order correlation function measurements on 20 emitters in sample T₁₄₀₀. a) Histogram of $g^{(2)}(0)$. SPEs, exhibiting $g^{(2)}(0) < 0.5$, are marked by green. Quantum emitters, satisfying $0.5 < g^{(2)}(0) < 1$, are marked by blue. The red bar represents one recorded classical emitter. (b-c) Experimental data (gray points) and theoretical $g^{(2)}(\tau)$ curves (red lines) for representative SPE and quantum emitter, respectively. Red curves were fitted with Eq. 1.9. Adapted from [421].

As shown in Figure 4.5a, around 60% of the analyzed point defects (12 out of 20) act as true room-temperature SPEs satisfying the $g^{(2)}(0) < 0.5$ condition. Notably, 7 out of 8 of the remaining emitters exhibit quantum properties ($g^{(2)}(0) < 1$), while only one of the investigated emitters turned out to be a classical emitter. This statistic indicates that green emitters in MOVPE-grown BN are a promising platform for quantum applications, even though further optimization of the growth process is required to enhance their purity. Figure 4.5b-c shows representative $g^{(2)}(\tau)$ data points and fitted curves. Typically, we observe long-timescale bunching behavior, indicating that the quantum light emission does not originate from a simple two-level system, but at least one additional state is involved. Notably, the second-order correlation function measurements presented here were performed not on an as-grown flat epilayer, but on bubbles induced in the sample via e-beam exposure. While the detailed properties of BN bubbles are discussed in chapter 5, at this stage, we note that they enhance the intensity of quantum light emission but do not affect other properties of SPEs [421].

With the assistance of MSc Tomasz Fał, the quantum properties of the observed emitters were also investigated at a low temperature of 1.7 K [421]. As previously, we studied layer T₁₄₀₀ with bubbles, which enhance the defect-related emission. The studied sample was placed inside an Oxford Instruments Spectromag cryostat and excited with a 532 nm CW laser. The laser beam of power around 3 mW was focused using a lens integrated with a piezoelectric nanopositioning system (Attocube), yielding a spot diameter of ~ 1.5 μm . The PL signal was analyzed using a polarization-resolved detection scheme comprising a rotatable half-wave plate followed by a linear polarizer, enabling polarization-dependent measurements. Second-order correlation measurements were carried out in an HBT configuration. The emission split by a beamsplitter was directed to two high-resolution spectrometers, each equipped with a single-photon counting module (PerkinElmer AQR-14). Since the emission of the studied point defects becomes very narrow at low temperature, spectrometers were used to select a desired spectral line and route it to the detectors. TCSPC was performed using a HydraHarp 400 time-tagging module, the same as for room-temperature measurements. The second-order correlation function, $g^{(2)}(\tau)$, was determined with an overall temporal resolution of approximately 400 ps.

Counterintuitively, performing low-temperature second-order correlation function measurements on green emitters was much more challenging than at room temperature. While the emission of quantum emitters becomes narrower and more intense as the temperature decreases, we found the effective recorded signal intensity to be very low due to optical losses introduced by the cryostat window. That is why PerkinElmer AQR-14 photon-counting modules were used

instead of the less-sensitive Hamamatsu H10721P-110 photomultiplier tubes. The low effective detected photon counting rate forces the measurements of $g^{(2)}(\tau)$ to be performed over a long period of time, on the order of several hours. Combined with the fact that only a very narrow spectral line is selected, only ultrastable emitters may be investigated.

Figure 4.6a shows a low-temperature time-evolution spectrum of an exemplary green emitter, which exhibits rapid variations in the emission energy. Spectral jumps observed for BN-based visible SPEs may originate from interactions with local charges [351, 352]. Another possible explanation is the recently proposed mechanism of quantum light emission based on donor-acceptor-pair-like transitions [335, 336]. Within this model, fast variations in the ZPL energy are attributed to transitions between recombination pathways associated with different donor-acceptor pairs. Regardless of their origin, the jumps in emission energy are highly undesired for quantum applications. Therefore, the emission stability is a crucial issue that must be addressed for SPEs in MOVPE-grown BN.

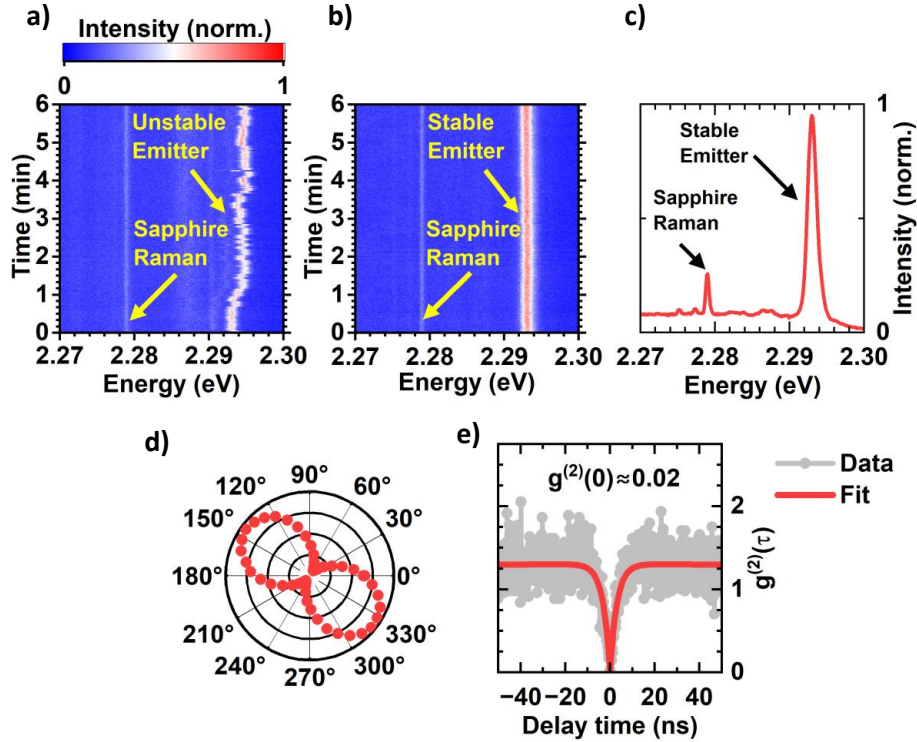


Figure 4.6: Results of low-temperature (1.7 K) optical characterization of green emitters. (a-b) Normalized time-evolution spectra of exemplary unstable and stable emitters, respectively. c) PL spectrum of the stable emitter. d) Angular dependence of ZPL emission intensity for the stable emitter. The angle shown corresponds to twice the half-wave plate's rotation angle. The result indicates a dipole-like emitter symmetry. e) Result of the second-order correlation function measurement for the stable emitter. Gray dots are experimental points. The red curve was fitted with Eq. 1.9. Extremely low $g^{(2)}(0) \approx 0.02$ indicates very pure single-photon emission. Adapted from [421]

While the energy of some color centers varies rapidly, other emitters remain stable over time, as shown in Figure 4.6b. Typically, the linewidth of the studied green emitters ranges from 1 to 2 meV. While these values are in agreement with ~ 2 meV reported for similar emitters in [304], they remain an order of magnitude larger than those found for green emitters in [306], where the FWHM was below 120 μ eV. This indicates that even stable MOVPE-BN-based green emitters, which do not exhibit rapid variations in ZPL energy, still experience significant spectral diffusion. The representative low-temperature spectrum of the stable green emitter is presented in Figure 4.6c, while Figure 4.6d shows a polar plot of its emission intensity versus polarization angle. A typical in-plane dipole-like emission is observed, as previously reported for green and other visible emitters, indicating a linear symmetry of the defect. Finally, Figure 4.6e presents the result of the second-order correlation function measurement conducted for the stable green emitter. The obtained value of $g^{(2)}(0) = 0.02^{+0.05}_{-0.02}$ indicates very pure single-photon emission crucial for applications.

Results from both room- and low-temperature measurements on the green emitters indicate that they act as SPEs. Obviously, although around 60% of emitters satisfy the $g^{(2)}(0) < 0.5$ criterion at 300 K, and values as low as $g^{(2)}(0) = 0.02^{+0.05}_{-0.02}$ can be observed at cryogenic temperatures, the emission purity at this stage remains insufficient for immediate practical applications. However, the obtained results are very promising and suggest that further optimization could enable these systems to achieve the performance requirements for quantum technologies. In particular, other SPEs investigated in BN flakes initially also did not exhibit sufficient purity, but developed post-fabrication protocols and integration with appropriately designed photonic architectures enabled overcoming this issue. Therefore, we believe that similar approaches may be applied for the green emitters discussed here.

4.6 Temperature-Dependent Broadening of Green Emitters

Besides the purity, another crucial aspect for applications is the emission linewidth. Therefore, in this section, we discuss the phonon-mediated broadening of an exemplary green emitter in sample T_{1400} , based on temperature-dependent PL measurements. Similar studies have been reported for color centers in BN flakes exfoliated from bulk crystals [337, 358, 361, 367, 370, 371]. However, SPE linewidth broadening remains unexplored in epitaxially grown BN, which exhibits distinct mechanical properties compared to exfoliated flakes [374]. The temperature-dependent PL measurements and data analysis were performed by BSc Bartosz Kaczmarek with the support and under the supervision of the author

of this dissertation. During the measurements, the sample was mounted in an Oxford Instruments Microstat HiRes helium cryostat. PL emission was excited with a 532 nm laser beam focused on the sample with a 50 $\times$ objective (NA=0.5). The incident laser power before entering the objective was approximately 6 mW. The PL signal was acquired with the Horiba T64000 spectrometer equipped with a Symphony CCD camera. The PL spectra of the investigated emitter collected in the temperature range 4-230 K are plotted in Figure 4.7a. We observe a ZPL, whose intensity decreases when increasing the temperature, and a sapphire Raman mode, which becomes more prominent at higher temperatures. The cryostat window introduces optical losses and prevents us from achieving good focus, making the emitter signal inaccessible above 230 K.

Increasing the temperature T is expected to cause a redshift in emission energy due to electron-phonon coupling. A rise in temperature results in a higher occupation of phonon modes. When phonons scatter electrons, the transition energy becomes lower. The same mechanism governs the temperature dependence of the bandgap in semiconductors [422]. One of many models to describe this mechanism is given by the O'Donnell equation [423], used previously for the analysis of color centers in BN [337]:

$$E(T) = E(0) - S \cdot E_{ph} \cdot \left[\coth \left(\frac{E_{ph}}{2kT} \right) - 1 \right], \quad (4.7)$$

where E_0 is the transition energy at 0 K, E_{ph} is the average energy of phonons affecting ZPL position, and S is a dimensionless exciton-phonon coupling constant. k is the Boltzmann constant. Although increasing the temperature is expected to cause a redshift, at low temperatures, the ZPL position of the studied emitter varies nonmonotonically. We attribute this effect to fluctuations in emission energy, similar to those observed for an unstable emitter shown previously in Figure 4.6a. This effect becomes less important at higher temperatures when electron-phonon coupling becomes a dominant mechanism. The relative shift of the ZPL energy is plotted in Figure 4.7b. The experimental data are fitted with Eq. 4.7. The obtained average phonon energy $E_{ph} = (46 \pm 1)$ meV matches very well the energy of ZA acoustic modes along the M-K direction [224], suggesting that these particular modes prominently govern the electron-phonon coupling in the investigated system.

Figure 4.7c shows ZPLs recorded at 60 K and 110 K. Both lines are fitted with Lorentzian and Gaussian profiles. Based on R-squared values (R^2), we find that at 60 K, the ZPL linewidth is determined primarily by inhomogeneous broadening, arising from spectral diffusion, resulting in a Gaussian lineshape. In contrast, at 110 K, the observed line exhibits a Lorentzian shape, indicating that homogeneous thermal phonon broadening is dominant. The transition from inhomogeneous to

homogeneous broadening regime upon increasing temperature is typically observed for color centers in BN [358].

The dependence of FWHM versus temperature T is plotted in Figure 4.7d. The data are analyzed using two common approaches described previously in section 2.4.3. In the first framework, the linewidth $\Gamma(T)$ might be described as:

$$\Gamma(T) = \Gamma_0 + bT^n, \quad (4.8)$$

where Γ_0 is the FWHM in the limit of inhomogeneous broadening and b quantifies the strength of the coupling between the emitter and phonons. Different values of n characterize various phonon-related mechanisms, which might affect emission linewidth. While Eq. 4.8 assumes a single dominant mechanism, in general, multiple mechanisms may contribute, requiring additional temperature-dependent terms [361, 367, 371]. For the studied emitter, Eq. 4.8 describes the data well for $n = (3.2 \pm 0.1)$ (the red curve in Figure 4.7d). This value fits very well the $\sim T^3$ dependence, attributed to two-phonon elastic scattering processes and observed previously for color centers in BN and other materials [360, 365–367]. Cubic dependence of linewidth on temperature is observed in crystals that exhibit high defect concentration and large inhomogeneous broadening [365]. Sample T_{1400} meets both these conditions. It hosts many carbon-related defects introduced during the growth. Also, the obtained value $\Gamma_0 = (1.39 \pm 0.1)$ meV is much above the reported Fourier-transform limit of 0.2 μ eV [357], suggesting the strong spectral diffusion.

The temperature dependence of the FWHM was also analyzed within the second previously discussed model, assuming that the broadening is mediated by an effective single-frequency phonon, whose occupation follows the Bose-Einstein distribution. The theoretical formula, given by Eq. 2.4, and the corresponding fitted curve (blue) are shown in Figure 4.7d. The found effective average phonon energy $E_{ph} = (44 \pm 2)$ meV corresponds to the ZA acoustic phonon mode along the M-K direction, and is very close to the phonon energy previously extracted from the temperature dependence of the ZPL position. This result indicates the consistency between the two models and clearly demonstrates the crucial impact of ZA acoustic phonons on the properties of green emitters.

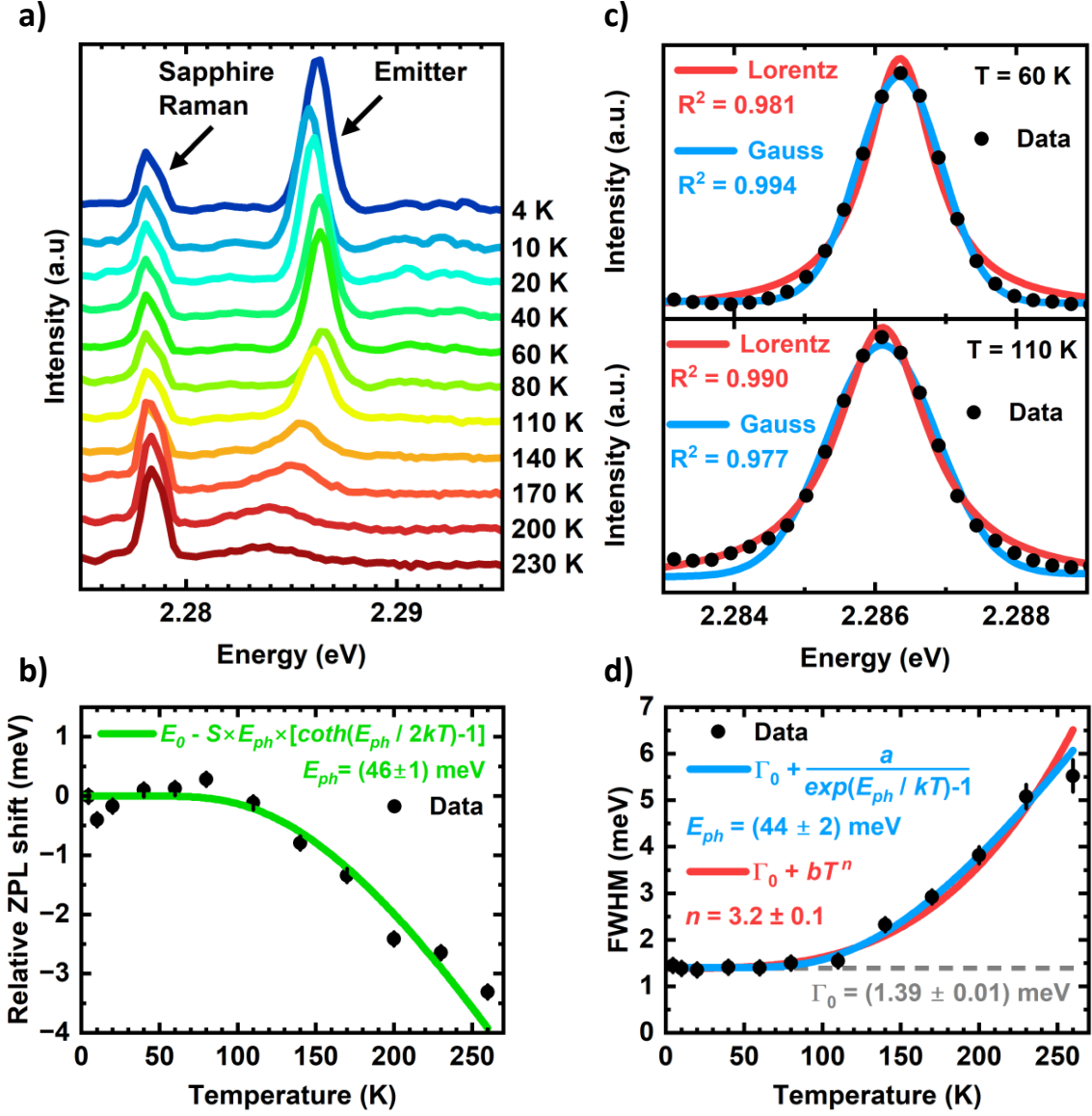


Figure 4.7: Results of temperature-dependent PL studies for an exemplary green emitter. a) Emission spectra acquired in the temperature range 4-230 K. Spectra are vertically shifted for clarity. b) The relative shift of the studied ZPL versus temperature. The green curve was fitted with Eq. 4.7 to black points. The zero-temperature transition energy is found to be $E_0 \approx 2.286 \text{ eV}$. The fitted average phonon energies and coupling constant are $E_{ph} = (46 \pm 1) \text{ meV}$ and $S = (0.29 \pm 0.1)$, respectively. c) Acquired emission lines (black dots) and fitted Lorentzian (red) and Gaussian (blue) curves for the studied emitter at 60 K (top panel) and 110 K (bottom panel). R^2 is given for each fit. The transition from inhomogeneous to homogeneous broadening regime is observed upon increasing the temperature. d) Change of emission linewidth versus temperature. Black dots represent FWHM values. The red curve shows a fit to Eq. 4.8. with $b = (9 \pm 6) \times 10^{-8} \text{ meV K}^{-1}$ and $n = (3.2 \pm 0.1)$. The blue curve is a fit to the Eq. 2.4. The fitted average phonon energy and coupling constant are $E_{ph} = (44 \pm 2) \text{ meV}$ and $a = (29 \pm 5) \text{ meV}$, respectively. For both fits, the zero-temperature emission linewidth was fitted as $\Gamma_0 = (1.39 \pm 0.01) \text{ meV}$.

4.7 Growth-Dependent Structural Properties of BN

Now we move towards studying the influence of TEB flow rate on the properties of visible SPEs in the MOVPE-grown BN sample. To this end, we compare the structural and optical properties of samples belonging to class F that differ in the applied TEB flow rate during growth. The idea behind these studies is that increasing the flow rate of the organic precursor should influence the formation and properties of carbon-related point defects, as well as affect BN's overall quality. To provide a clear distinction between effects caused by changes in TEB flow rate and those related to variations in BN thickness, the properties of samples from series P, which differ only in a number of NH_3 /TEB pulse cycles, are also analyzed. First, we compare the general structural properties of the investigated samples.

Figure 4.8 presents SEM images of all investigated BN layers taken by Dr Aleksandra Dąbrowska and Dr Mateusz Tokarczyk. For samples thicker than approximately 10 nm, we observe wrinkles, similar to those present in layers T_{1300} and T_{1400} . For thinner layers, wrinkles are too small to be observed in this scale. In almost all cases, the BN surface is clean, except for sample P_{1000} , where debris is present. Its appearance is independent of sample thickness, since the debris-free layer F_{20} is thicker. Therefore, we attribute the formation of these 3D objects to increased growth time or other factors, such as the MOVPE system's history.

The structural quality of BN layers was assessed with XRD measurements around the (002) peak position performed by BSc Gabriela Szwed and Dr Mateusz Tokarczyk. The measured XRD curves are presented in Figure 4.9. Depending on the sample, the XRD diffraction signal was fitted with one, two, or three Gaussian peaks. The found peak positions and corresponding BN interlayer spacings are included in Table 4.4. The thinnest samples of the thickness below 6 nm (F_{10} , P_{100} , and P_{200}) can be fitted with only one Gaussian component corresponding to BN with a high interlayer distance above 3.35 Å, which we previously called tBN (filled in red).

The XRD signal of the ~ 10 nm-thick BN layer P_{400} can be fitted with one Gaussian peak corresponding to high-quality, well-ordered sp^2 -bonded BN, with interlayer distance 3.35 Å (filled in light blue). We see that for samples belonging to the series P, interlayer distances are getting smaller upon increasing BN thickness from 3.39 Å found for P_{100} , through 3.38 Å for P_{200} , up to 3.35 Å for P_{400} . This dependence indicates that the material quality improves with layer thickness. This is expected, as the first grown atomic layers experience the strongest lattice mismatch with the substrate, whereas subsequent planes form on the previously deposited BN, providing a better growth template.

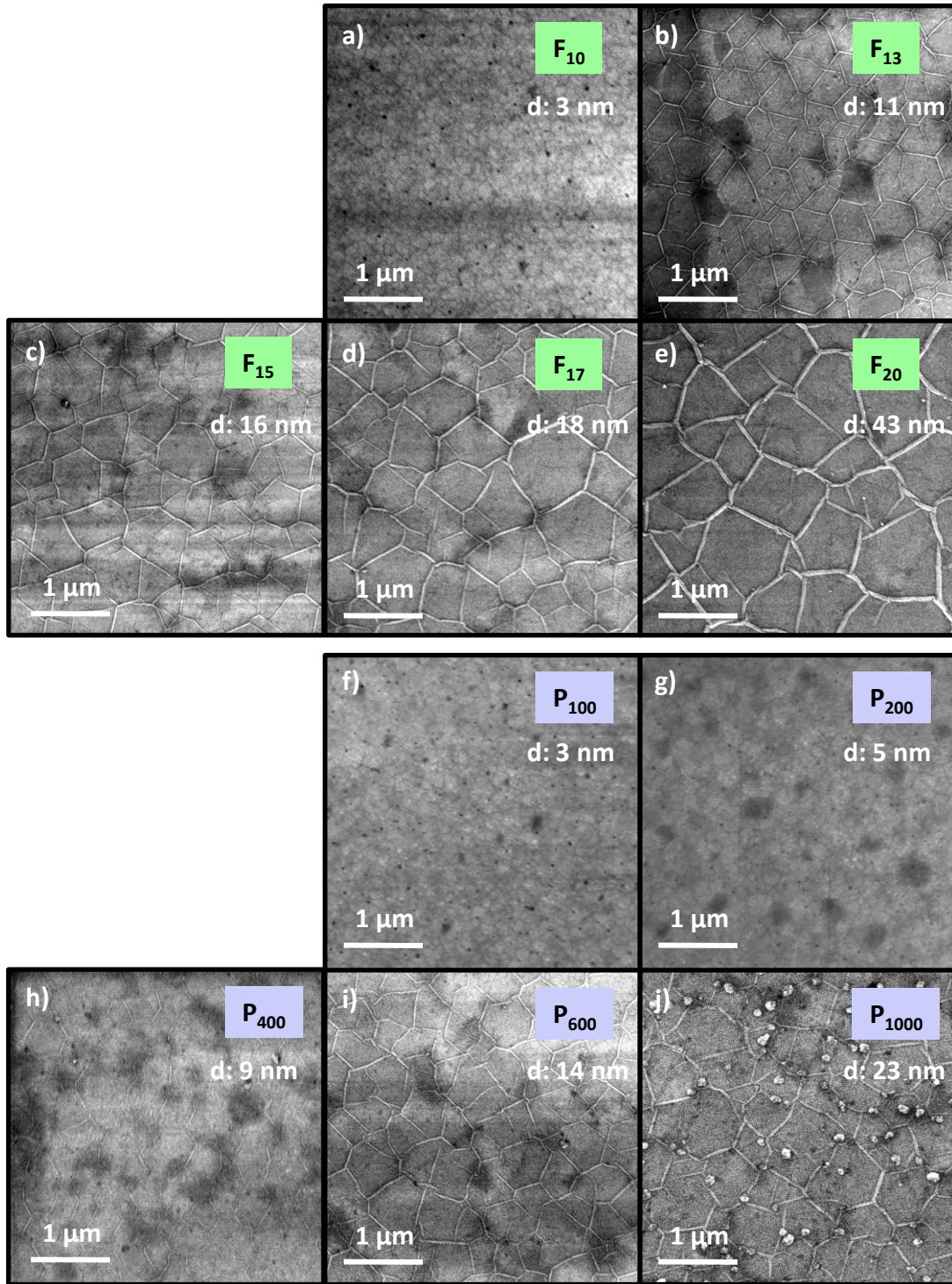


Figure 4.8: SEM images of investigated BN layers belonging to series F (a-e) and P (f-j). In BN layers thicker than around 10 nm, wrinkles are observed. The surfaces of all epilayers are clean, except for sample P₁₀₀₀, where debris is present. Scalebars are 1 μm . Thickness d is provided for each sample.

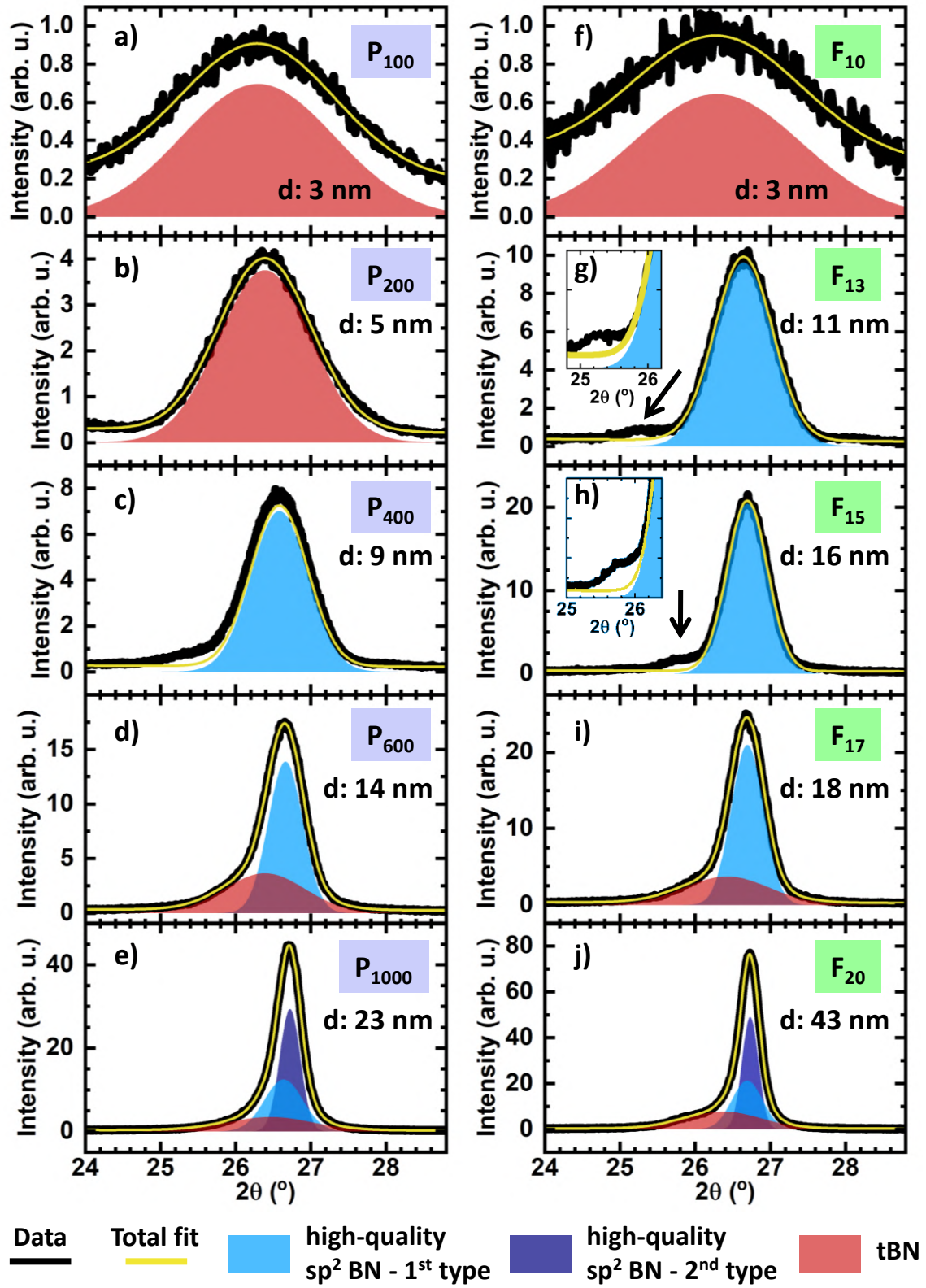


Figure 4.9: Results of XRD measurements close to the (002) peak position for samples P₁₀₀-P₁₀₀₀ and F₁₀-F₂₀, respectively. Experimental data and the total fits are marked by black and yellow lines, respectively. Components corresponding to lower-quality tBN are filled in red, while peaks related to high-quality BN are filled in light-blue or dark-blue. Thickness d is provided for each sample.

Table 4.4: BN (002) XRD peak positions and corresponding interlayer spacings for tBN and high-quality BN components in samples F₁₀-F₂₀ (marked by green) and P₁₀₀-P₁₀₀₀ (marked by blue), following the color coding used in Table 4.1

Sample	tBN		high-quality BN (1 st component)		high-quality BN (2 nd component)	
	2θ (°)	Interlayer spacing (Å)	2θ (°)	Interlayer spacing (Å)	2θ (°)	Interlayer spacing (Å)
F ₁₀	26.29	3.39	-	-	-	-
F ₁₃	-	-	26.64	3.35	-	-
F ₁₅	-	-	26.70	3.34	-	-
F ₁₇	26.42	3.38	26.70	3.34	-	-
F ₂₀	26.38	3.38	26.70	3.34	26.73	3.33
P ₁₀₀	26.30	3.39	-	-	-	-
P ₂₀₀	26.39	3.38	-	-	-	-
P ₄₀₀	-	-	26.58	3.35	-	-
P ₆₀₀	26.39	3.38	26.66	3.34	-	-
P ₁₀₀₀	26.46	3.37	26.64	3.35	26.72	3.34

Consequently, other BN layers, whose thicknesses vary in the range 10-20 nm, also exhibit much superior crystalline quality compared to the thinner ones. Similar to the results obtained for layer P₄₀₀, experimental XRD curves for samples F₁₃ and F₁₅ can be described by single-Gaussian curves corresponding to high-quality BN, with interlayer distances of 3.35 Å and 3.34 Å, respectively. Notably, for these two samples, on the low-angle side of the main peak, we observe a small signal, marked by black arrows and zoomed in insets provided in Figure 4.9g-h. These features are associated with Laue oscillations, which arise from interference between X-rays reflected at the bottom and upper BN interfaces. Typically, Laue oscillations are observed only in high-quality thin layers [424], so their appearance indicates superior crystalline quality. For samples P₆₀₀ and F₁₇, the XRD signal is also dominated by a peak associated with high-quality BN; however, in both cases, we observe a non-negligible component related to lower-quality tBN.

Finally, the XRD signal collected for the thickest samples, P₁₀₀₀ and F₂₀, requires three Gaussian peaks to fit the experimental data well. In both cases, one component corresponds to a low-quality BN, while two peaks might be attributed to a high-quality material (an additional peak is filled in dark blue). The presence of many BN-related components in thick samples indicates structural inhomogeneity and the coexistence of BN regions with different stacking orders. Variations in structural properties within the same sample may arise from several mechanisms,

including strain accumulation, formation of new nucleation sites, or changes in surface chemistry. Also, we cannot exclude the possibility that many sp^2 -bonded BN phases exist in thinner epilayers as well, but are not observed because the reduced thickness yields a weaker XRD signal. The measurements performed clearly demonstrate that the thickness is a crucial property of BN layers, determining their long-range order and stacking along the c -axis. Unfortunately, based on the XRD data obtained, we cannot clearly distinguish the effects of BN thickness and the TEB flow rate used during growth.

In the next step, we performed Raman measurements of all investigated samples. Experimental data were collected and analyzed in the same way as for samples T_{1300} and T_{1400} . Figure 4.10a shows how the $\text{E}_{2g}^{\text{high}}$ phonon mode energy and FWHM change with the BN thickness for samples belonging to the series P. Similar dependencies on TEB flow rate for samples F_{10} - F_{20} are plotted in Figure 4.10b. On both graphs, the Raman shift and FWHM scales are set to the same ranges to enable a clear comparison between the studied layers. The results are summarized in Table 4.5. We observe that all samples P_{100} - P_{1000} , grown under the same TEB flow, exhibit similar vibrational properties. Indeed, the layers thicker than 5 nm exhibit very small dispersion of $\text{E}_{2g}^{\text{high}}$ mode position, which is below 1 cm^{-1} . Also, weighted FWHM values are centered around 17.2 cm^{-1} , with variations smaller than the corresponding uncertainties. Small deviations towards higher Raman shift and FWHM values observed for sample P_{100} of the thickness below 5 nm might be attributed to the influence of the sapphire substrate, which is non-negligible for ultrathin BN layers. The results indicate that although layer thickness governs the long-range order investigated by XRD, the local crystal quality, probed by Raman spectroscopy, remains unaffected over the thickness range 5-25 nm.

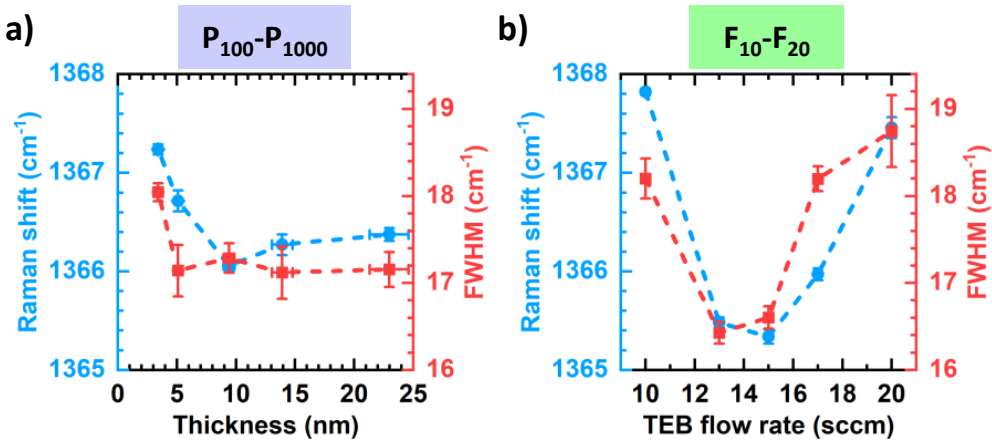


Figure 4.10: Vibrational properties of samples from the P and F series. a) Dependence of the $\text{E}_{2g}^{\text{high}}$ peak position (blue points) and FWHM (red points) on BN thickness for samples P_{100} - P_{1000} . b) Dependence of the $\text{E}_{2g}^{\text{high}}$ peak position (blue points) and FWHM (red points) on the TEB flow rate during growth measured for samples F_{10} - F_{20} . Dashed lines in both panels serve as guides to the eye.

Table 4.5: Energy and FWHM of the E_{2g}^{high} Raman-active phonon mode in samples F₁₀-F₂₀ (marked by green) and P₁₀₀-P₁₀₀₀ (marked by blue), following the color coding used color coding in Table 4.1.

Sample	E_{2g}^{high} Energy (cm ⁻¹)	E_{2g}^{high} FWHM (cm ⁻¹)
F ₁₀	1367.82 ± 0.03	18.20 ± 0.23
F ₁₃	1365.48 ± 0.05	16.43 ± 0.12
F ₁₅	1365.34 ± 0.07	16.60 ± 0.13
F ₁₇	1365.97 ± 0.06	18.20 ± 0.14
F ₂₀	1367.47 ± 0.11	18.75 ± 0.41
P ₁₀₀	1367.24 ± 0.05	18.05 ± 0.10
P ₂₀₀	1366.72 ± 0.11	17.14 ± 0.30
P ₄₀₀	1366.06 ± 0.06	17.29 ± 0.18
P ₆₀₀	1366.27 ± 0.11	17.12 ± 0.30
P ₁₀₀₀	1366.38 ± 0.07	17.16 ± 0.20

In contrast, samples grown under different TEB flow rates exhibit significant variations in their vibrational properties. As expected, sample F₁₀, whose thickness is as low as below 3 nm, experiences compressive strain, resulting in a shift of the E_{2g}^{high} Raman mode toward higher wavenumbers compared to other samples. The high strain in this sample arises from the BN/sapphire thermal expansion mismatch and is generated during cooling to room temperature after growth. As discussed previously, for such a thin layer, wrinkle formation, which causes strain relaxation, does not occur (Figure 4.8a). In contrast, for samples F₁₃-F₁₇, the E_{2g}^{high} mode position falls within the range 1365-1366 cm⁻¹, typical of high-quality BN. For sample F₂₀, which is the thickest studied BN layer, E_{2g}^{high} mode is blueshifted to around 1367.5 cm⁻¹. This increase in phonon frequency may originate from strain accumulation. Such an explanation is consistent with XRD results, which indicate the coexistence of at least three BN-related components. Indeed, the strain may accumulate at interfaces between different BN polytypes.

While the differences in phonon mode energy observed for samples F₁₀-F₂₀ can be explained by referring to their thicknesses only, TEB flow is found to affect the local structural quality of BN, thereby determining the Raman peak FWHM. In particular, the linewidth of E_{2g}^{high} mode in sample F₁₇ appears to be over 1.5 cm⁻¹ larger than those found in layers F₁₃ and F₁₅ (see Table 4.5). Notably, this increase in E_{2g}^{high} phonon FWHM cannot be attributed to BN thickness, which varies from ~11 nm for F₁₃, through ~16 nm found for F₁₅, up to ~18 nm for F₁₇. Indeed, as found in the analysis of Raman spectroscopy results for samples P₁₀₀-P₁₀₀₀, within this thickness range the FWHM of the Raman mode should remain constant.

Moreover, if the BN thickness played a role, we should observe a significant difference between samples F_{13} and F_{15} , which is not found. This result indicates that increasing the TEB flow rate from 15 sccm to 17 sccm significantly degrades BN quality, probed locally by Raman spectroscopy. This feature, which might seem insignificant at this stage, appears important when discussing the results of PL measurements performed in the next step. The deterioration of local quality caused by a high TEB flow rate is also observed in sample F_{20} , which exhibits a broad Raman peak. In contrast, the bad quality of sample F_{10} originates from its low thickness, as first-grown BN atomic planes experience the strongest lattice mismatch with the substrate.

4.8 Growth-Controlled Formation of Green Emitters

In the next step, we investigate how the formation of green emitters depends on the BN thickness. Unfortunately, we cannot assess the incorporated carbon concentration because it is below the detection limits of commonly used techniques such as secondary ion mass spectrometry, X-ray photoelectron spectroscopy, or energy-dispersive X-ray spectroscopy. Therefore, we discuss defect formation based on the results of optical measurements. To this end, we performed PL mapping measurements of samples P_{100} - P_{1000} . Measurements were performed in the same manner as those discussed previously for samples T_{1300} and T_{1400} . Room-temperature PL spectra were acquired in the spectral range 2.01-2.32 eV from the area $34 \times 34 \text{ } \mu\text{m}^2$ with a step of $0.4 \text{ } \mu\text{m}$. Maps of the total integrated PL intensity are presented in Figure 4.11a-e. In all maps, we observe many bright spots. As expected, their spatial concentration increases along with sample thickness, since carbon, which is responsible for defect formation, can be incorporated into each atomic plane. Notably, within the investigated range of BN thickness, bright spots remain well isolated. Representative spectra acquired at exemplary bright spots, marked by blue circles, diamonds, and squares, are presented in Figure 4.11f-j. The gray-filled spectra represent the average emission from 7396 pixels for each map. The obtained PL spectra associated with green emitters are similar in shape and intensity to those observed previously for sample T_{1400} , suggesting that the spectral properties of the visible color centers formed in MOVPE-grown BN do not depend on sample thickness.

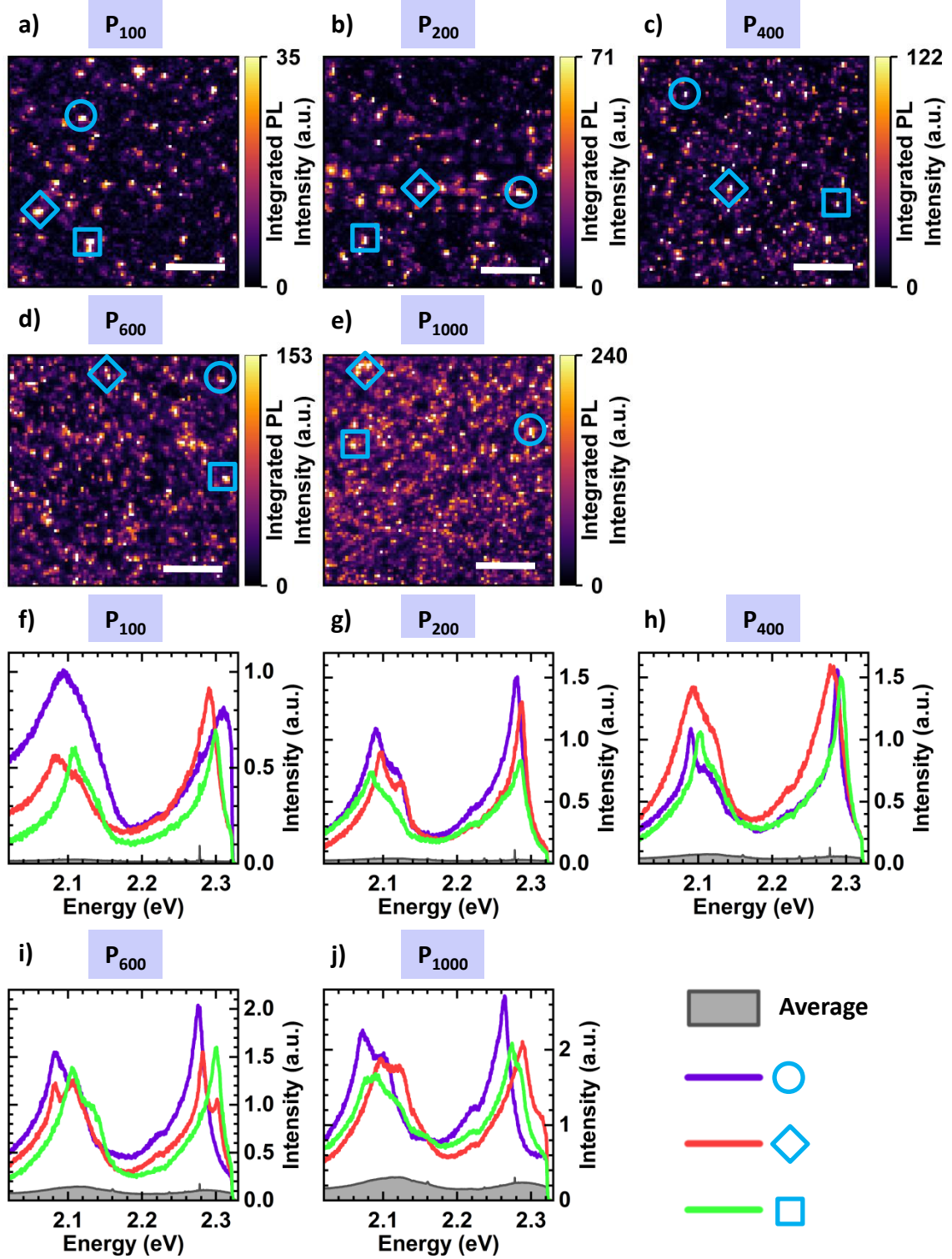


Figure 4.11: Results of PL mapping measurements for samples P₁₀₀–P₁₀₀₀. (a–e) 34×34 μm² maps of the total integrated emission intensity in the range 2.01–2.32 eV. Step size is 0.4 μm. Scalebars are 10 μm. Intensity color scales can be directly compared. For clarity, they were limited such that the brightest 1% of points lie outside the displayed range. (f–j) PL spectra acquired at bright spots marked by blue circles, diamonds, and squares in a–e. The gray-filled spectra are the averaged PL signals from the whole maps (7396 pixels). Intensity scales can be directly compared.

The investigated spectral region lies well below the band-edge emission, so the entire measured signal originates from carbon-related defects introduced during the growth. Therefore, the mean integrated PL intensity J (integrated over gray-filled spectra) is an indicator of the incorporated carbon concentration. If we assume that the chance for carbon incorporation is the same for each BN atomic plane, then J should increase linearly with sample thickness d . However, as shown in Figure 4.12, the observed growth is $\sim d^{1.4 \pm 0.1}$. The superlinear dependence may suggest that the probability of carbon incorporation increases with BN thickness. Such a behavior could originate from modifications in BN morphology or changes in surface chemistry during growth. On the other hand, this subtle effect may also be related to thickness-dependent nanophotonic effects similar to those observed for V_B^- created in BN flakes [425].

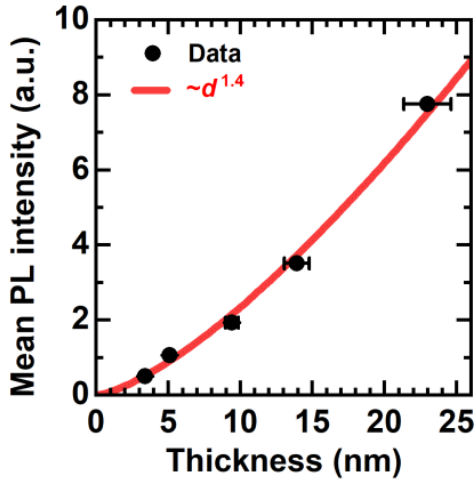


Figure 4.12: Dependence of the mean integrated total visible PL emission J as a function of BN thickness for samples P₁₀₀-P₁₀₀₀. Black points - data points. The fitted red curve indicates a $J \sim d^{1.4}$ relation.

To address this issue, we consider thickness-dependent variations in BN morphology. Figure 4.13a-e show AFM images of samples P₁₀₀-P₁₀₀₀ acquired by MSc Rafał Bożek. Figure 4.13f presents the root mean square roughness, extracted from the AFM images by the author, as a function of epilayer thickness. The observed increase in RMS for thicker BN samples indicates an evolution of the surface topography during the growth. Importantly, this trend is not related to the formation of wrinkles, which are excluded from the analysis. The RMS values are derived only from flat regions within wrinkle cells, indicating a progressive increase in surface roughness during the growth. Such modification of sample morphology is expected to influence the formation of subsequent layers and, consequently, the probability of carbon incorporation. Therefore, we assume that the observed superlinear growth of total emission intensity J with BN thickness originates from increasing probability of point-defect formation.

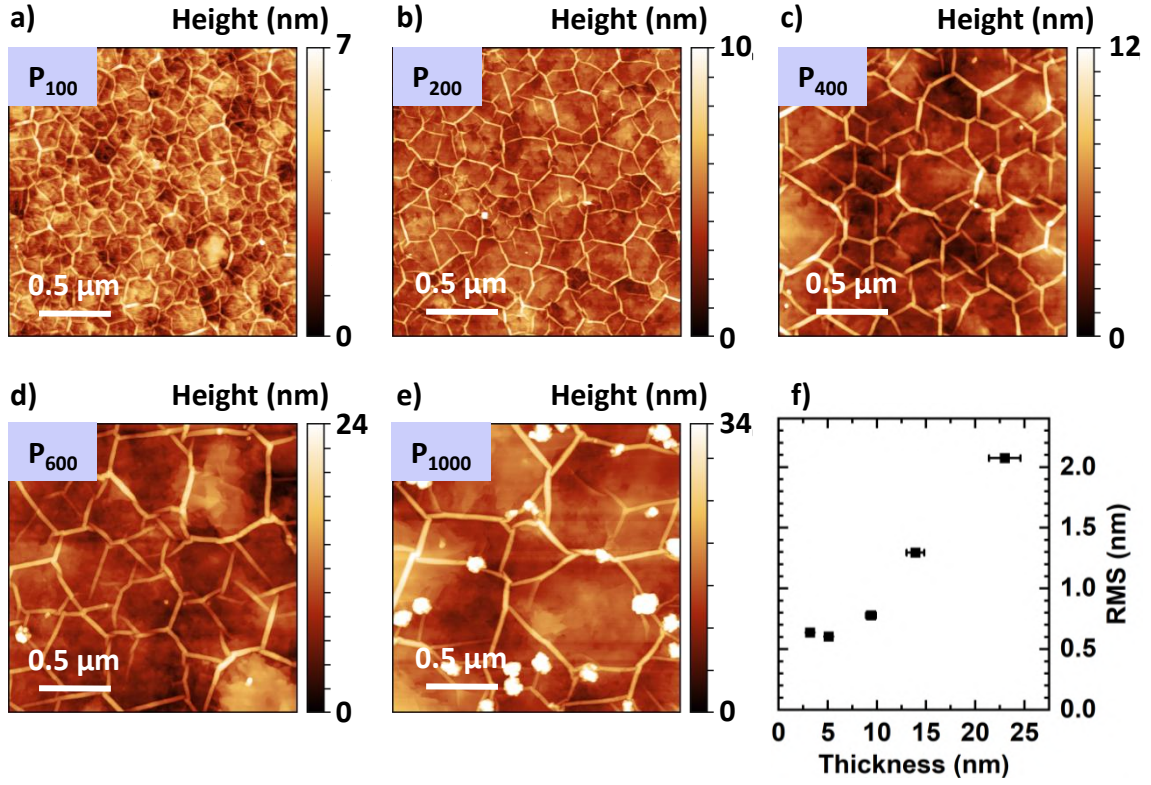


Figure 4.13: Thickness-dependent changes in BN morphology. (a-e) $2 \times 2 \mu\text{m}^2$ AFM images of samples P₁₀₀-P₁₀₀₀. Scalebars are 0.5 μm . f) Change of surface RMS versus BN thickness.

Our final goal is to provide a model that links emitter density to growth conditions, thereby enabling SPE engineering. A key parameter for such a model is the probability of defect formation in successive atomic planes. Since the mean observed emission intensity J is expected to be proportional to the total number of generated point defects, it should depend on both BN thickness d and the probability p of introducing carbon-related defects into subsequent atomic planes. Therefore, we can write:

$$J \sim \int_0^d p(D) dD, \quad (4.9)$$

where D is the distance from the substrate and d is the total sample thickness. Let's assume that the probability p scales as $p(D) \sim D^\beta$. Then, using Eq. 4.9 we obtain:

$$J \sim \frac{d^{\beta+1}}{\beta+1}, \quad (4.10)$$

From Eq. 4.10 we see that if the $J \sim d^{1.4}$ dependence fitted to experimental data truly comes from the enhanced probability for carbon incorporation for thicker BN, then this probability should scale as $p \sim D^{0.4}$. Notably, this relation appears to be crucial for further analysis of emitter generation in MOVPE-grown BN.

Now, based on the analysis of overall defect-related emission J , we develop a simple mathematical model that describes the emitter concentration as a function of BN thickness. It is important to note that the number of emitters is not determined by the number of bright pixels, but it is obtained using the previously-introduced procedure described by Eq. 4.1 - 4.6 regarding spatial separation and ZPL intensity. Another important aspect is that PL mapping projects the entire BN volume onto a 2D map. In simple terms, if two point defects exist in BN at different depths but are spatially so close that the optical setup cannot resolve them, we observe only one bright spot in the PL map.

Intuitively, in the thin-layer regime, the emitter concentration increases with sample thickness. However, in the limit of a very thick material, all analyzed pixels are expected to be bright, since at each spatial position, a point defect would form in at least one atomic plane. In such a situation, the criterion of spatial separation is not met, and the number of well-resolved emitters drops to zero. In the regime of intermediate thicknesses, a maximum concentration of resolvable emitters is achieved. Keeping this in mind, we propose a very simple model to describe the obtained results.

We consider a material consisting of N ideally stacked planes, with discrete points defined on them. We assume that the probability of generating a point defect in a given plane labeled as n at a specific spatial position is equal to $p(n)$ and is constant for the whole plane. The last assumption is crucial to the proposed model, as it implies that point defects form independently of one another.

It is important to note that we do not specify the exact relationship between the theoretical points introduced above and the atomic sites in the BN lattice. Instead, these theoretical points correspond rather to the regions occupied by defects, which can cover one, two, or more atomic sites, depending on the atomic nature of green emitters. This simplification does not alter the final conclusions, as during PL mapping, we do not have access to atomic sites, but are rather limited by the spatial resolution of the setup.

Since the introduced defects are responsible for visible light emission, in our model, any spatial point where at least one defect exists in any of N layers is called bright. Notably, in the further discussion, we distinguish between bright points, as defined above, and bright spots observed in PL maps. The point is called dark if no defect is formed in any of the N layers. The probability of such an event is equal to:

$$P_{dark} = \prod_{n=1}^N (1 - p(n)), \quad (4.11)$$

so the probability that a given point is bright is given by:

$$P_{bright} = 1 - \prod_{n=1}^N (1 - p(n)), \quad (4.12)$$

which can be rewritten as:

$$P_{bright} = 1 - \prod_{n=1}^N \exp[\ln(1 - p(n))] \quad (4.13)$$

To make the next step, we assume that for each n , the value of $p(n)$ is very low and satisfies $p(n) \ll 1$. This assumption seems reasonable, since across all samples P₁₀₀-P₁₀₀₀ we observe well-isolated emitters, indicating a low probability of defect formation. Then, P_{bright} can be approximated by:

$$P_{bright} \approx 1 - \prod_{n=1}^N \exp(-p(n)) \quad (4.14)$$

and rewritten as:

$$P_{bright} \approx 1 - \exp\left(-\sum_{n=1}^N p(n)\right) \quad (4.15)$$

Now, we transition from a description based on summation over layers to one based on integration through the epilayer thickness:

$$P_{bright} \approx 1 - \exp\left(-\int_0^d p(D) dD\right), \quad (4.16)$$

where $p(D)$ is the probability of defect generation at distance D from the substrate. We assume that $p(D)$ governs both the formation of individual defects and the average PL emission discussed previously. Therefore, based on the analysis of the dependence of the total emission intensity J on sample thickness (Eq. 4.9 and Eq. 4.10), we assume that within the investigated range of BN thickness:

$$p(D) = aD^\beta, \quad (4.17)$$

where $\beta = 0.4$ and a is an unknown constant. Under this assumption, the final probability that a given point is bright may be approximated as:

$$P_{bright} \approx 1 - \exp\left(-\frac{a}{\beta + 1} d^{\beta+1}\right), \quad (4.18)$$

The PL maps shown in Figure 4.11a-e suggest that samples P₁₀₀-P₁₀₀₀ belong to the thickness regime in which almost all emitters are well-isolated, and we do not observe merging of experimentally-observed bright spots. Interpreted within our model, this observation indicates that bright points are typically separated and that

the probability of neighboring points being bright is low. In this regime, almost all bright points satisfy the separation condition for being an emitter. Therefore, we assume that the total number of found emitters, and thereby their density $\rho_{low}(d)$, is directly proportional to the number of bright points formed within the BN layer, which depends on the probability P_{bright} . In consequence, the spatial density of found emitters satisfies

$$\rho_{low}(d) \sim \left[1 - \exp\left(-\frac{a}{\beta+1}d^{\beta+1}\right) \right], \quad (4.19)$$

Finally, by putting $\beta = 0.4$ and introducing two fitting parameters ρ_0 and d_{15} , we obtain the final expression for the emitter density in the low-concentration regime

$$\rho_{low}(d) = \rho_0 \left[1 - \exp\left(-\left(\frac{d}{d_{15}}\right)^{1.4}\right) \right], \quad (4.20)$$

As we assumed, Eq. 4.20 is valid only in the regime of low emitter concentration. Indeed, in the regime of very thick BN layers, it predicts asymptotic behavior, while a drop to zero is expected, as discussed previously. In the above expression, ρ_0 is the asymptotic value of the emitter concentration, while d_{15} may be interpreted as a characteristic thickness for emitter formation for a TEB flow rate equal to 15 sccm.

Figure 4.14 shows the dependence of the emitter density on BN thickness for samples P₁₀₀-P₁₀₀₀, fitted with the model given by Eq. 4.20. We see that the theoretical curve reconstructs the data; however, we are approaching the limits of the model's validity, as the sample P₁₀₀₀ is in the plateau range. We note that our model considers only two types of points - bright and dark, while some carbon-related emission is observed throughout the whole studied layers. Therefore, the probability p , introduced in the model formulation, should be interpreted only in terms of generating sufficiently bright emitters.

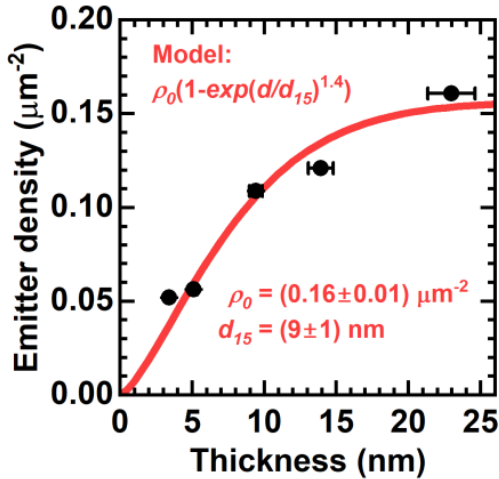


Figure 4.14: Density of identified emitters as a function of BN thickness for samples P₁₀₀-P₁₀₀₀. Black data are data points. The red curve is fitted with Eq. 4.20. The obtained fitting parameters are: $\rho_0 = (0.16 \pm 0.01) \mu\text{m}^{-2}$ and $d_{15} = (9 \pm 1) \text{ nm}$

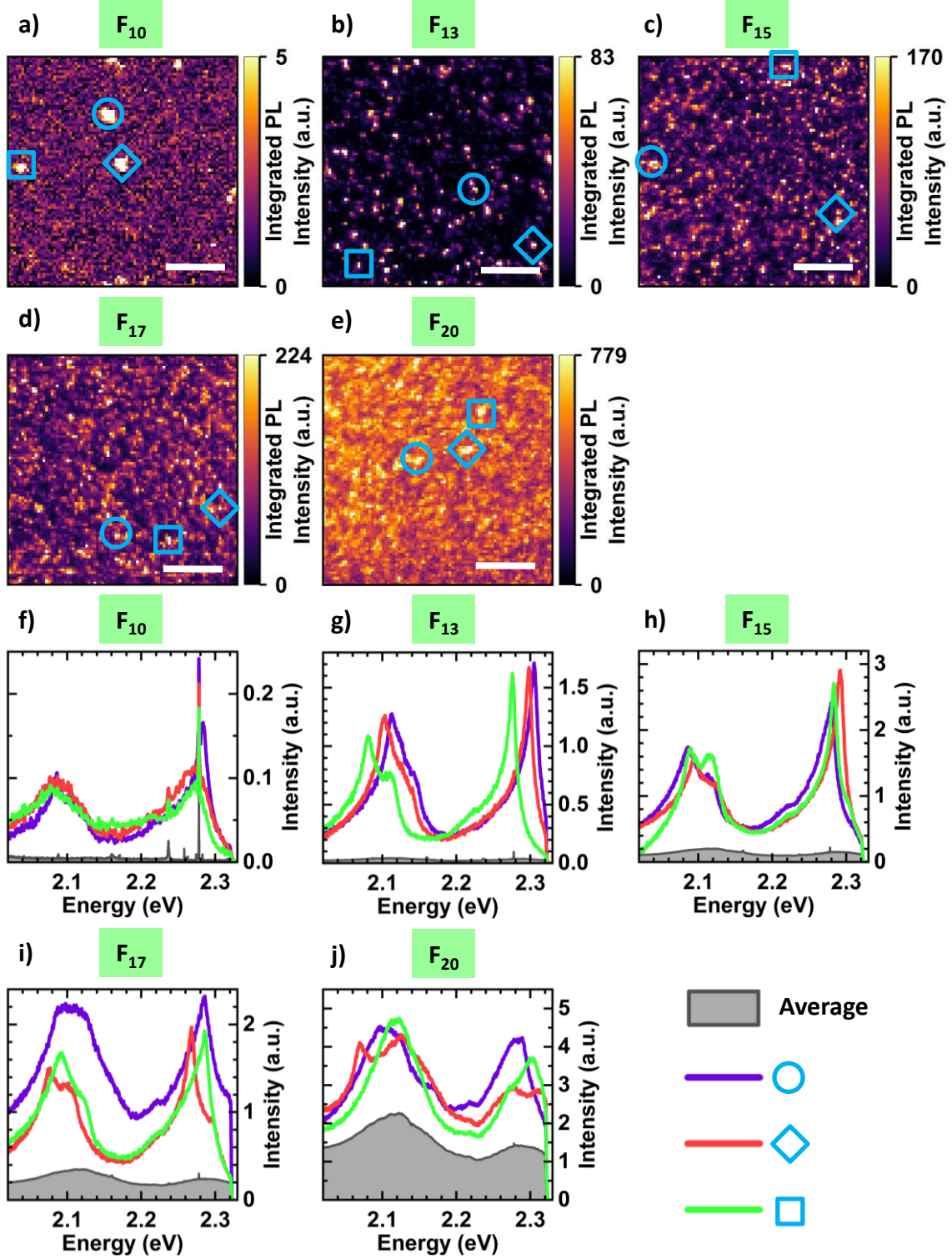


Figure 4.15: Results of PL mapping measurements for samples F₁₀-F₂₀. (a-e) 34 × 34 μm² maps of the total integrated emission intensity in the range 2.01-2.32 eV. Step size is 0.4 μm. Scalebars are 10 μm. Intensity color scales can be directly compared. For clarity, they were limited such that the brightest 1% of points lie outside the displayed range. (f-j) PL spectra acquired at bright spots marked by blue circles, diamonds, and squares in a-e. The gray-filled spectra are the averaged PL signals from the whole maps (7396 pixels). Intensity scales can be directly compared.

To investigate the dependence of emitter formation on TEB flow rate, for samples F_{10} - F_{20} , we performed PL mapping measurements analogous to those acquired for samples in series T and P. Figure 4.15a-e present maps of the total integrated PL intensity within the measured range 2.01-2.32 eV, while spectra acquired at some representative bright spots are shown in Figure 4.15f-j. The gray-filled spectra represent the average emission from 7396 pixels for each map. In contrast to the series P, the defect-related emission varies significantly between samples F_{10} - F_{20} . First, we see that in sample F_{10} bright spots are extremely rare (Figure 4.15a) and the found ZPLs are about 1 order of magnitude less intense than those found in other samples. Clearly, for this particular sample, the formation of visible color centers during the growth was ineffective. In contrast, in samples F_{13} - F_{17} , we observe well-isolated green emitters. Typically, the found emitter spectra are similar in shape and ZPL intensity to those acquired for samples T_{1400} and P_{100} - P_{1000} . In sample F_{20} , intense emission is observed across the entire investigated area. In particular, the average broad emission reaches intensities comparable to those of the brightest narrow emitters found in other BN layers. Furthermore, spectra collected at the brightest locations show no qualitative differences from the average PL spectrum, differing only in overall intensity. It indicates that, for this sample, we are beyond the limit for generating a well-isolated emitter, and instead defect ensembles form.

The discussion of the influence of growth conditions on green emitter formation in BN layers F_{10} - F_{20} is not as straightforward as for samples P_{100} - P_{1000} , since now we have to consider two varying parameters - BN thickness d and TEB flow rate F . As discussed previously, the total PL emission intensity, J , serves as an indicator of the incorporated carbon concentration. For samples P_{100} - P_{1000} , J scales with BN thickness as $d^{1.4 \pm 0.1}$. To analyze carbon incorporation into the BN lattice as a function of the TEB flow rate, F , we therefore use the thickness-normalized integrated emission $\tilde{J}$, shown in Figure 4.16, obtained via normalizing J by $d^{1.4}$.

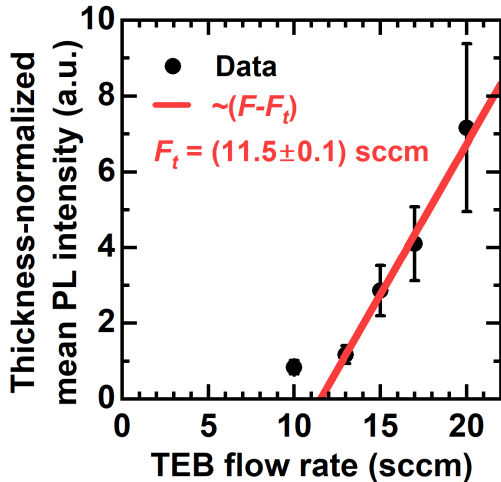


Figure 4.16: Thickness-normalized mean integrated total PL emission $\tilde{J}$ as a function of TEB flow rate F used during the growth for samples F_{10} - F_{20} . Values are normalized by $d^{1.4}$. Black points mark data. The red curve is fitted with Eq. 4.21. The extracted threshold TEB flow rate for effective formation of carbon-related defects is $F_t = (11.5 \pm 0.1)$ sccm

While the growth in thickness-normalized mean total emission intensity $\tilde{J}$ is very low for small TEB flow rates, for F in the range 13-20 sccm, we observe a much more rapid, nearly linear increase. Therefore, we clearly observe two regimes. First, at low TEB flow rates, the total integrated emission intensity increases slowly, suggesting ineffective formation of carbon-related defects. When the TEB flow rate reaches a threshold value, carbon incorporation becomes much more effective, leading to a rapid, linear increase in $\tilde{J}$. This result is of key importance, as it confirms that the formation of green-emitting centers is directly related to the presence of carbon originating from TEB molecules, as previously hypothesized. Although we do not know the exact mechanism leading to the activation, in the regime of effective carbon incorporation, $\tilde{J}$ versus F dependence can be fitted by a simple empirical linear function:

$$\tilde{J}(F) = m(F - F_t), \quad (4.21)$$

indicating that above the threshold TEB flow rate $F_t = (11.5 \pm 0.1)$ sccm, the thickness-normalized total emission intensity increases linearly with slope m . In the following steps, we assume that the probability p for carbon incorporation follows a similar linear trend, with the same threshold TEB flow rate F_t .

To analyze how TEB flow rate affects formation of isolated green emitters, we propose a simple model that follows the same idea as that applied for samples P₁₀₀-P₁₀₀₀. First, we consider the regime of low emitter density. We start with Eq. 4.16, as all steps leading to it also apply here.

Based on the results obtained for samples P₁₀₀-P₁₀₀₀, we assume that the probability p of defect generation at a distance D from the substrate scales as $p \sim D^{0.4}$. In addition, based on Eq. 4.21, we assume its linear dependence on F , namely $p \sim (F - F_t)$. Therefore, we can write:

$$P_{\text{bright}} \approx 1 - \exp\left(-\int_0^d k_0(F - F_t)D^{0.4} dD\right), \quad (4.22)$$

where we put $F_t = (11.5 \pm 0.1)$ and k_0 is an unknown constant describing how the probability of emitter formation increases with F and D . Upon integration, we obtain:

$$P_{\text{bright}} \approx 1 - \exp\left(-k(F - F_t)d^{1.4}\right), \quad (4.23)$$

where $k = k_0/1.4$. Therefore, following the same argumentation as for Eq. 4.20, in the regime of low emitter concentration, we can approximate emitter density as:

$$\rho_{\text{low}}(d, F) \sim \left[1 - \exp\left(-k(F - F_t)d^{1.4}\right)\right] \quad (4.24)$$

We note that Eq. 4.20 is a special case of Eq. 4.24 for $F = F_{15} = 15$ sccm. Therefore, by comparison of these two, to avoid the overparametrization of the final model, we assume that:

$$k = \left((F_{15} - F_t) \cdot (d_{15})^{1.4} \right)^{-1}, \quad (4.25)$$

where $F_{15} = 15$ sccm and $d_{15} = (9 \pm 1)$ nm are fixed based on previous results obtained for samples P₁₀₀-P₁₀₀₀. Substituting k into Eq. 4.23, we obtain:

$$P_{bright} \approx 1 - \exp \left(- \left(\frac{F - F_t}{F_{15} - F_t} \right) \cdot \left(\frac{d}{d_{15}} \right)^{1.4} \right) \quad (4.26)$$

To simplify further analysis, we note that instead of describing the probability P_{bright} in a 2D space of parameters (d, F) , we can express it as:

$$P_{bright} \approx 1 - \exp(-w) \quad (4.27)$$

where w is a single effective parameter defined as:

$$w = \left(\frac{F - F_t}{F_{15} - F_t} \right) \cdot \left(\frac{d}{d_{15}} \right)^{1.4} \quad (4.28)$$

As observed for sample F₂₀, for high TEB flows, the observed emitter density decreases, as newly formed point defects are sufficiently close that the spatial separation criterion is no longer satisfied. To incorporate this effect into our model, and extend its applicability to the regime of high defect concentrations, we note that, if a bright point is isolated, its neighboring sites must remain dark. The probability $P_{isolated}$ of such a situation is also governed by the probability P_{dark} of adjacent sites being dark.

$$P_{isolated} = P_{bright} (P_{dark})^\gamma \quad (4.29)$$

In a simple idealized model of theoretical points arranged into a lattice, a spatial separation condition for being an emitter requires that all nearest-neighboring points, whose number is given by γ , are dark. However, in our experiment, we cannot assess individual atomic sites; we observe the optical response of a material excited by a finite-size laser spot using an optical setup with limited spatial resolution. Moreover, we do not know how many point defects must be located in proximity to an emitter to disturb their properties. Therefore, in our model, γ is treated as a fitting parameter that encompasses all the above-mentioned effects. It is worth noting that γ may account for effects associated with increasing background luminescence, which also increases linearly with F . Finally, we propose the formula for the approximated

emitter density, including the high-concentration regime, as:

$$\rho(w) = \rho_0 \cdot \left[1 - \exp(-w) \right] \cdot \exp(-\gamma w), \quad (4.30)$$

where ρ_0 and γ are fitting parameters.

Emitter densities for samples F₁₃-F₂₀, P₂₀₀-P₁₀₀₀ and T₁₄₀₀ versus effective parameter w , are plotted in Figure 4.17. Sample F₁₀ is excluded from the analysis because it was grown at a TEB flow rate below F_t and therefore cannot be considered within the proposed model. The obtained points are fitted with Eq. 4.30. Keeping in mind all assumptions made, the proposed model reconstructs experimental results very well. Notably, the uncertainties of fitted parameters $\rho_0 = (0.21 \pm 0.02) \mu\text{m}^{-1}$ and $\gamma = (0.11 \pm 0.04)$ are reasonably small. The highest emitter density is expected to occur for the effective parameter $w_{max} = (2.3 \pm 0.3)$. To achieve the highest concentration of well-isolated emitters, growth conditions should be adjusted to meet this value (Figure 4.18).

While the proposed model reproduces the experimental data, its limitations, previously discussed and restated below, should be borne in mind. First, it distinguishes only 2 types of points - bright and dark. In the experiment, many studied points exhibit broad, visible emission but are not classified as emitters because of their low intensity. This background luminescence also originates from lattice imperfections, which are not included directly in the proposed model. Therefore, the density given by Eq. 4.30 should be understood in terms of the density of emitters of a particular type rather than all possible point defects. Also, defect ensembles can sometimes be classified as emitters, especially in the regime of intermediate concentration, where the spatial resolution of the optical setup is key. Consequently, although the proposed model describes the number of intense emitters well, it does not provide any information on their properties, such as purity, which are affected by other unconsidered defects. It suggests that the density of true high-quality SPEs is lower than predicted, especially for higher w values.

Notably, our model does not account for the BN buffer layer grown by the CFG method, which does not introduce emitters. Indeed, if bright defects were present in this layer, they would be visible in the PL map of sample F₁₀. Therefore, its only impact on our model is a slight artificial increase in the effective thickness of the BN hosting the emitters, by approximately 1.5 nm, which does not affect the final conclusions significantly.

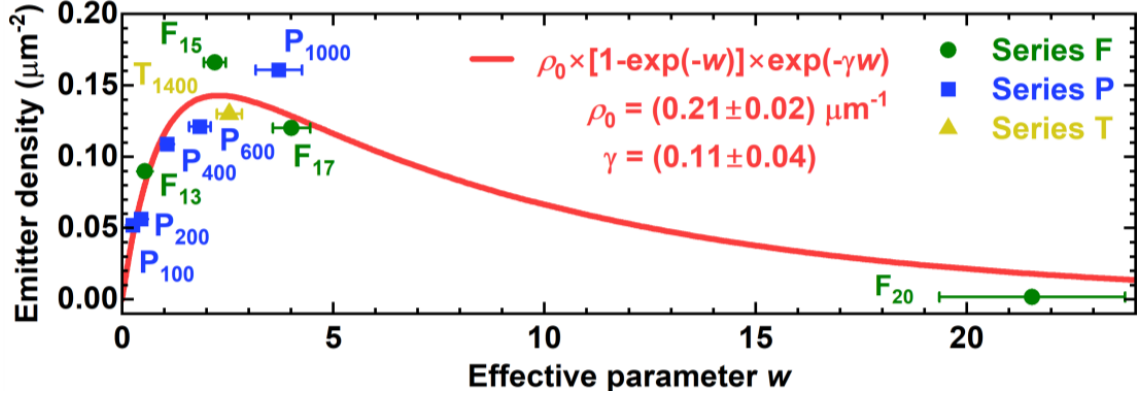


Figure 4.17: Spatial density of identified emitters as a function of the effective parameter w . Green circles are data for samples F₁₃-F₂₀. Blue squares are data for samples P₁₀₀-P₁₀₀₀. The yellow triangle corresponds to the sample T₁₄₀₀. The red curve is fitted to all data points with Eq. 4.30.

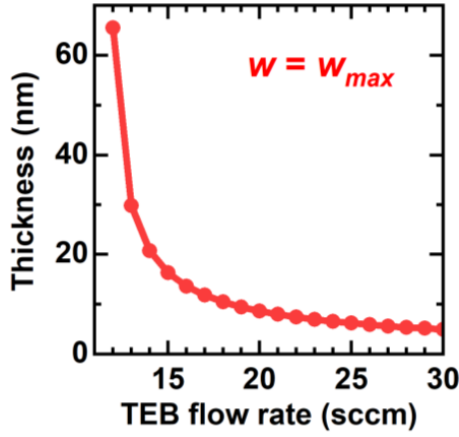


Figure 4.18: Combinations of BN thickness and TEB flow rate for which the model given by Eq. 4.30 predicts the maximum emitter concentration.

In conclusion, both the TEB flow rate F and the sample thickness d influence the formation of visible emitters and should therefore be optimized for MOVPE growth of BN. However, for the investigated samples, the spatial emitter density can be effectively described by a single parameter w , defined in Eq. 4.28. This behavior significantly simplifies the optimization of growth conditions, as it reduces the problem to tuning a single parameter w , rather than independently adjusting F and d . In our case, the highest emitter concentration is expected for the effective parameter value of $w_{max} = (2.3 \pm 0.3)$. Naturally, the presented results were obtained for samples grown at specific pressure and temperature, and using TEB as the boron precursor. Therefore, the conclusions cannot be directly generalized to BN layers grown under different conditions. Nevertheless, the approach presented in this work provides a general strategy for optimizing emitter formation in MOVPE-grown BN.

4.9 Engineering of Quantum Emitter Properties

In the next step, we investigated how the TEB flow rate and BN thickness affect the purity of green SPEs. To this end, with the assistance of MSc Tomasz Fąs, we performed room-temperature second-order correlation function measurements for color centers in samples F₁₃-F₁₇ and P₁₀₀₀. The measurements were carried out in the same manner as those performed for sample T₁₄₀₀. For statistical analysis, we recorded $g^{(2)}(\tau)$ curves for approximately 10 emitters for each sample. The distributions of obtained $g^{(2)}(0)$ values for the investigated epilayers are shown in Figure 4.19a-d. Since $g^{(2)}(0)$ is expected to lie in the range 0-1, the histograms are fitted with a beta distribution. Finally, Figure 4.19e-h show representative $g^{(2)}(\tau)$ curves with $g^{(2)}(0)$ values closest to the average value obtained for each BN layer.

For samples F₁₃ and F₁₅, most green emitters (8 out of 10 and 10 out of 11, respectively) act as room-temperature SPEs (Figure 4.19a-b) with the mean $g^{(2)}(0)$ values close to 0.4. In contrast, F₁₇ shows a dramatic drop in emission purity with the expected $g^{(2)}(0)$ reaching ~ 0.6 , and only 4 out of 12 studied emitters exhibiting single-photon emission (Figure 4.19c). F₁₇ was grown at higher TEB flow rates than F₁₃ and F₁₅, but it is also thicker. Therefore, a comparison of these three epilayers alone does not allow us to identify the origin of the reduced emission purity. However, green emitters in sample P₁₀₀₀ show an expected $g^{(2)}(0)$ of around 0.4, similar to SPEs in F₁₃ and F₁₅ (Figure 4.19d). Since P₁₀₀₀ is thicker than F₁₇ yet still exhibits high emission purity, we conclude that the TEB flow rate, rather than layer thickness, primarily governs the formation of high-purity SPEs. Increasing the TEB flow from 15 sccm to 17 sccm triggers a transition from the growth regime favoring formation of high-quality room-temperature SPEs to one that promotes the formation of defects that do not satisfy $g^{(2)}(0) < 0.5$.

Sample F₁₇ maintains a high concentration of green emitters, comparable to those found in F₁₃ and F₁₅. However, its local structural quality is significantly poorer, as confirmed by the Raman spectroscopy results discussed in section 4.7. This degradation is associated with more efficient carbon incorporation, leading to the formation of additional lattice imperfections that affect green emitters. Consequently, despite their density, the observed emitters exhibit reduced quantum performance. The obtained results indicate that the successful growth of green SPEs requires TEB flow rates only slightly above the threshold necessary for their formation. Excessively high organic precursor flow disrupts the structural quality of BN, thereby degrading the quantum properties of the hosted SPEs. The results also highlight the limitations of the model regarding bright and dark points introduced in the previous section, as the deterioration of emission purity is not accounted for.

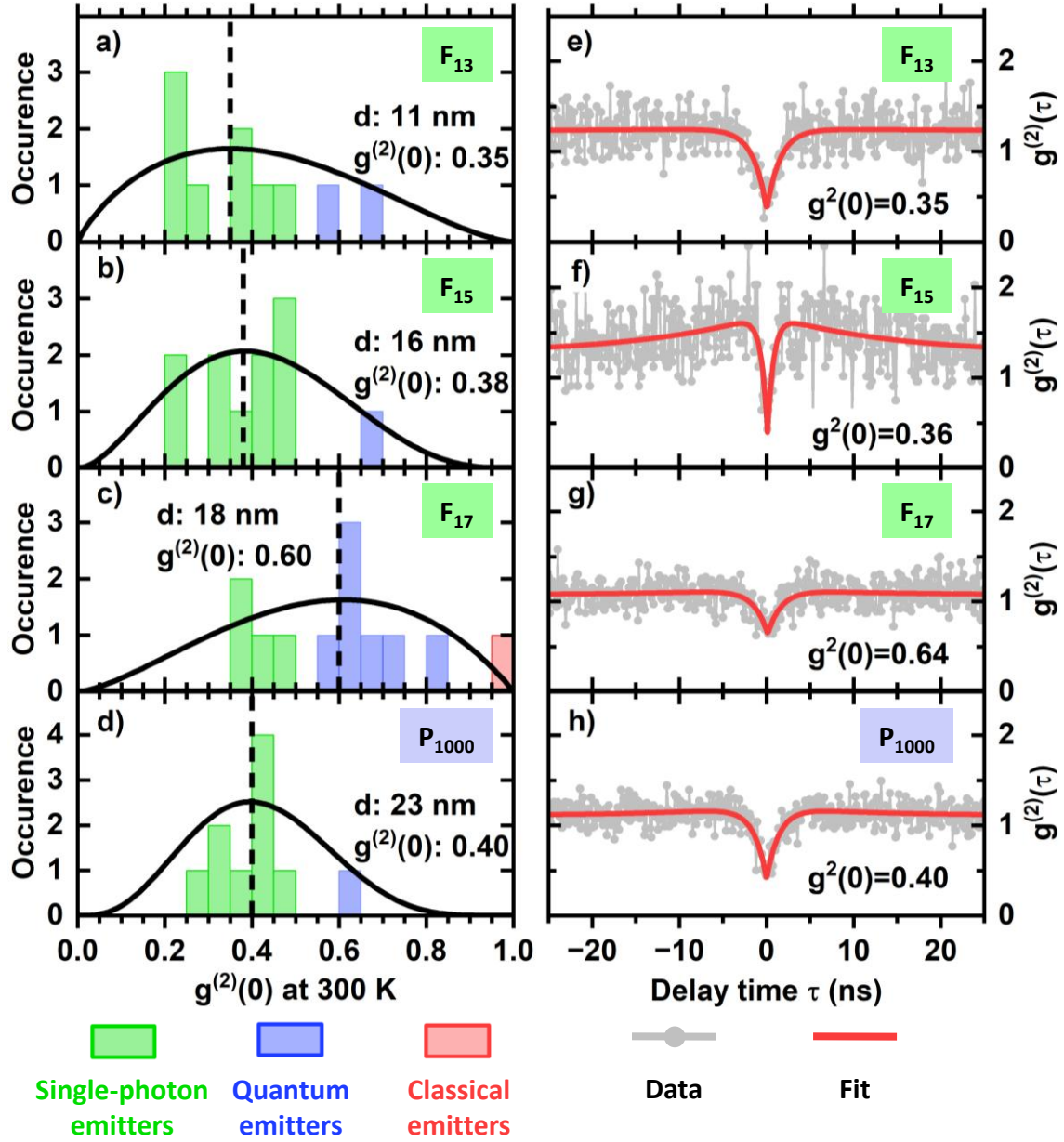


Figure 4.19: Results of room-temperature second-order correlation function measurements for samples F₁₃-F₁₇ and P₁₀₀₀. (a-d) Histograms of found $g^{(2)}(0)$. True SPEs, exhibiting $g^{(2)}(0) < 0.5$, are marked by green. Quantum emitters, satisfying $0.5 < g^{(2)}(0) < 1$, are marked by blue. The red bar represents one recorded classical emitter. Solid black curves are the fitted beta distributions. Black vertical dashed lines mark the expected $g^{(2)}(0)$ values. Expected $g^{(2)}(0)$ and BN thickness d are given for each studied sample. (e-h) Experimental (gray points) and fitted (red lines) $g^{(2)}(\tau)$ curves for representative emitters found in each sample. $g^{(2)}(0)$ values found for chosen emitters are close to the expected values found within particular samples.

4.10 Photostability of Green Emitters

In the final part, we discuss how emitter photostability, a crucial property for applications, varies across our BN epilayers. The analysis is limited to samples F₁₃-F₁₇ and P₂₀₀-P₁₀₀₀. Using the same excitation scheme as for PL maps, we recorded the time-evolution PL spectra of 20 emitters for each studied BN layer. If an emitter becomes dark within 5 minutes, it is classified as unstable. Conversely, emitters that remain optically active after this period are considered stable.

As shown in Figure 4.20, within the investigated range, the fraction of photostable emitters increases linearly with BN thickness, exhibiting a slope of $(3.1 \pm 0.2) \text{ \%}/\text{nm}$. Although this trend is expected to saturate for thicker layers, since perfect (100 %) photostability cannot be achieved, no indication of saturation was observed so far. We attribute this increase in emitter photostability to the shielding of the inner BN layers from the environment by the topmost BN planes. As the grown epilayer thickens, more atomic planes are protected, thereby isolating more embedded SPEs from environmental fluctuations. A similar effect of increasing emitter photostability in BN flakes upon increasing the number of stacked layers has been previously reported [354].

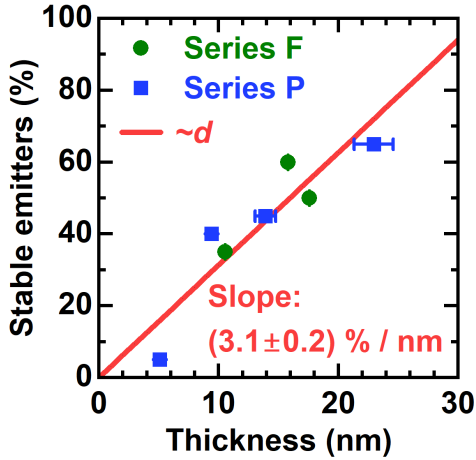


Figure 4.20: Fraction of stable emitters as a function of BN thickness. Green circles and blue squares represent experimental data for samples from the F and P series, respectively. Red curve is a linear fit with the slope of $(3.1 \pm 0.2) \text{ \%}/\text{nm}$.

4.11 Conclusions

We have shown that BN epilayers grown by MOVPE at 1400 °C host carbon-related green color centers that act as room-temperature SPEs. A detailed statistical analysis of their spectral properties revealed three classes of green emitters. ZPLs of Type 1 and Type 2 emitters are accompanied by strong acoustic- and optical-phonon replicas. Type 2 SPEs are statistically redshifted relative to Type 1 emitters and exhibit more pronounced features associated with LO (E_{1u}) phonon-assisted recombination along the M–K direction. Type 3 emitters show very weak phonon replicas, with emission dominated by the ZPL. Unfortunately, they are rare and

tend to become optically inactive under prolonged laser exposure. In addition, at some points we observe broad emission bands, suggesting a significant influence of neighboring defects or the formation of defect ensembles. Phonon-induced broadening of green emitters has been investigated using temperature-dependent PL measurements. The results indicate a crucial influence of the acoustic ZA phonon along the M-K direction.

Next, we investigated how BN thickness and the TEB flow rate used during the growth influence the formation and properties of green emitters. To this end, we studied changes in overall BN quality and defect-related emission in two series of MOVPE-grown epilayers differing either in BN thickness or in the TEB flow rate used during growth. Our results suggest that the probability of carbon incorporation does not vary significantly with BN thickness. In contrast, it increases linearly with TEB flow rate above a threshold of approximately (11.5 ± 0.1) sccm. We propose a simple model describing the spatial density of isolated bright emitters in terms of a single effective parameter, w , which depends on sample thickness and TEB flow rate. Such an approach significantly facilitates optimization of emitter concentration since only one parameter is modified. Unfortunately, the proposed model does not account for the effects of other lattice imperfections that disrupt the quantum properties of emitters.

Finally, we investigated how the TEB flow rate and BN thickness affect the purity and stability of SPEs. We found that increasing the TEB flow rate from 15 sccm to 17 sccm results in a significant increase in the expected room-temperature $g^{(2)}(0)$ value, from around 0.4 to 0.6, indicating a strong impact of this parameter on the quantum properties of the resulting emitters. Namely, an increase in TEB flow rate shifts the growth regime from one that favors SPE generation to one that promotes the formation of low-quality emitters and defect ensembles. In the explored range, the photostability of the investigated SPEs increases linearly with BN thickness. This effect is attributed to the shielding of the inner BN layers from the environment by the outer BN planes.

The obtained results indicate that the range of TEB flow rates that can be used for generating pure green SPEs is approximately 11.5-15 sccm. To improve photostability, the BN layer should be as thick as possible; however, a usable thickness is limited by the deterioration in structural quality observed in excessively thick epilayers. To provide high emitter concentration, the BN thickness and TEB flow rate should be carefully balanced to keep the parameter w near $w_{max} \approx 2.3$ or slightly below. Naturally, precise values of optimal parameters vary for different MOVPE systems or other growth regimes. However, the approach demonstrated in this work provides a general strategy for optimizing MOVPE growth for SPE generation.

Chapter 5

Boron Nitride Bubbles for Single-Photon Emitters

5.1 Introduction

As discussed in section 2.5.1, bubbles, which form when gas molecules or organic residues become trapped between a thin film and a substrate, are a promising platform for engineering the properties of 2D materials, also in terms of quantum applications. Interferences occurring in a resonator-like substrate-bubble system have been reported to enhance UV defect emission in BN [389], while high strain of the order of a few %, present in bubbles, has been shown to induce light emitters in TMDCs, [15, 385, 391]. This second phenomenon is of particular interest for BN, because high strain is known to induce quantum emitters in this material [18, 141], although not yet demonstrated in BN bubbles.

Conventional bubble formation relies on the transfer of small 2D material flakes or their treatment with protons or plasma. While these methods are limited to small areas, in 2023, our group reported e-beam-induced bubble formation in large-area, non-transferred MOVPE-grown BN [17]. As described in section 2.5.2, such an approach works only for as-grown material that hosts wrinkles, which provide channels for water intercalation from the ambient. Under electron treatment, interfacial water undergoes radiolysis, and the molecular hydrogen produced in this process detaches BN from the substrate and lifts it, resulting in bubble formation. In this chapter, we extend these studies and propose e-beam-induced bubbles in epitaxial BN as a deterministic, universal platform for investigating visible SPEs. All the results presented in this chapter were published in the article P. Tatarczak, et al. “Deterministic hBN Bubbles as a Versatile Platform for Studies on Single-Photon Emitters.” *Adv. Funct. Mater.* 36, no. 24 (2026): e26312 [421], in which the author of this dissertation is the first author.

First, we demonstrate that, due to the specific formation mechanism, bubbles in MOVPE-grown BN exhibit markedly different mechanical properties from those in other similar systems reported in the literature. These extraordinary properties are related to the presence of wrinkles, unique to as-grown epitaxial material. Interestingly, the geometry of the investigated bubbles cannot be fully understood within existing theoretical frameworks.

In the next part, we demonstrate that the domes enhance the emission from green SPEs several times. By comparing defect-related emission in non-irradiated and e-beam-exposed BN, we prove that the observed enhancement originates truly from bubble formation, not from electron irradiation. Then, by combining PL and Raman mapping measurements, we explain the origin of this phenomenon and attribute it to interference-like effects.

In the last part, we address the problem of bubble reproducibility. Using a mask-assisted approach, we demonstrate that e-beam-induced bubbles can be formed deterministically in selected areas. Since the proposed strategy does not disturb the quantum properties of the emitters, the results indicate that the investigated bubbles are an interesting platform for studying SPEs in epitaxial BN.

5.2 Mechanical Properties of Bubbles

We start with a discussion of the mechanical properties of e-beam-induced bubbles generated in the sample T₁₄₀₀ introduced in the previous chapter. For electron exposure, we employed an FEI Helios 600 Dual Beam system equipped with a RaithElphy electron lithography setup. The experiment was performed using an electron beam with a typical current of 1 nA and an incident electron energy of 5 keV. At this stage, we did not focus on precise control of the total delivered dose, which depends on the irradiation time; rather, we intended to obtain bubbles of various sizes.

Bubble formation in as-grown MOVPE BN under electron irradiation is possible due to the material's characteristic morphology, namely the presence of wrinkles. In particular, it is not observed in wrinkle-free BN, which can be obtained by transferring delaminated BN layers onto a new substrate. Consequently, the geometrical characteristics and mechanical properties of the bubbles are strongly governed by the wrinkle arrangement. In particular, bubble dimensions are not arbitrary; the minimum achievable bubble size corresponds to a single mesh unit in the wrinkle pattern. Figure 5.1 shows AFM images of the smallest possible one-cell-sized bubble taken by Dr Jan Pawłowski. Interestingly, the observed structure does not resemble a typical bubble, but rather a hexagonal prism with nearly vertical walls. Notably, its height is approximately twice that of the

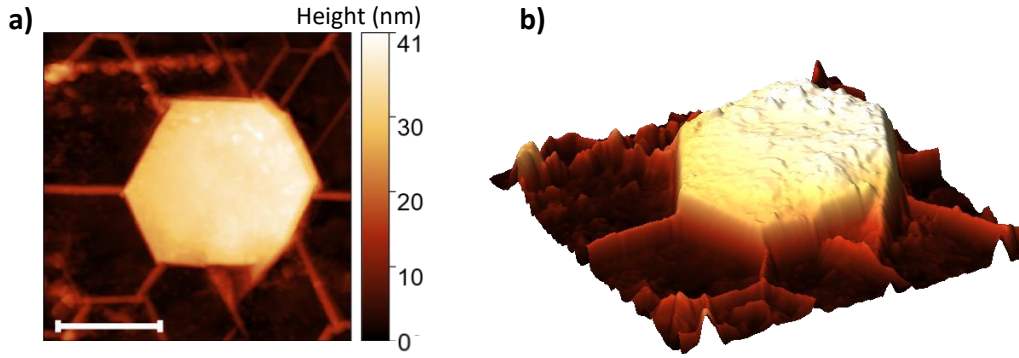


Figure 5.1: AFM images of a one-cell-sized bubble. a) top view, b) side view. The scalebar in a) is 500 nm. The total area is $1.5 \times 1.5 \mu\text{m}^2$. Adapted from [421]

surrounding wrinkles, indicating that the formation mechanism involves the rapid delamination of entire mesh units. The absence of significant bending in the lifted BN layer and the lack of a hemispherical shape indicate the exceptionally high stiffness of the BN detached from the sapphire. Further bubble expansion occurs through the sequential detachment of neighboring BN mesh regions, along with the associated wrinkles, and via the coalescence of small bubbles, which can form larger domes. As a consequence of this discrete growth mechanism, large bubbles spanning multiple wrinkle mesh units also exhibit geometries that deviate from the circular symmetry characteristic of conventional bubbles. Instead, their shape is governed by the wrinkle network [421].

The principle of e-beam-induced bubble formation in MOVPE-grown BN differs fundamentally from the mechanism underlying conventional bubble generation in 2D materials [421]. Typical bubbles emerge spontaneously when gas molecules or organic residues become trapped between a flake and a substrate [384, 385, 389]. An alternative approach employs plasma or ion exposure of exfoliated flakes. Ions and atoms penetrating a few layers of a 2D crystal trigger the formation of trapped molecules that cannot diffuse out through the overlying layers, thereby leading to bubble formation. In particular, hydrogen atoms and ions, which form H_2 molecules, are considered [390–392]. In such a case, the material initially occupies a flat circular region, but bubble formation forces it to expand over a larger, nonplanar area. Therefore, to maintain the stability of such a system, the pressure of the confined gas must be as high as hundreds of MPa or a few GPa [384] and consequently, bubbles may experience high strain. Notably, when the temperature drops below the confined-gas liquefaction point, bubbles formed by these methods immediately lose stability and deflate, as no internal gas can sustain them [390].

In contrast, the properties of e-beam-induced bubbles in MOVPE-grown BN are not determined by the stored gas [421]. While molecular hydrogen produced during water radiolysis initiates the formation of bubbles, their mechanical behavior is

governed primarily by the rigidity of BN itself. The wrinkles act as a reservoir of extra BN available for bubble formation, eliminating the need for extensive stretching of the original material, as is typical for conventional bubbles. Indeed, the formation of the structure shown in Figure 5.1 did not require material bending; only detaching BN and moving it up was necessary. Due to the material excess, the resulting structures behave more like rigid domes than inflated membranes and exhibit high mechanical stability. In particular, unlike previously reported plasma-induced hydrogen-filled bubbles in BN flakes [390], the e-beam-induced domes investigated here remain stable even below the hydrogen liquefaction temperature of 33.18 K, demonstrating that the enclosed gas contributes negligibly to their structural integrity. Therefore, they might be considered for cryogenic applications. Unfortunately, the pressure of the confined hydrogen is not readily accessible. Since it does not govern the mechanical properties of bubbles, it cannot be estimated from their geometry.

Figure 5.2a-d show AFM images of four representative bubbles, labeled B1-B4, induced in sample T₁₄₀₀. The AFM measurements were performed by Dr Jan Pawłowski, while the subsequent analysis of the bubble geometry was carried out by the author. From left to right, the bubble diameters are ~ 2.6 μm , ~ 4.3 μm , ~ 7.1 μm , and ~ 9.4 μm , respectively. Due to the specific formation mechanism, which involves merging adjacent mesh units, all observed structures exhibit irregular boundaries that reflect the wrinkle pattern. Additional bubbles spanning one or a few cells are also observed. To compare the properties of bubbles B1–B4 with those of conventional bubbles in 2D material flakes, we analyze their cross-sectional profiles $y(x)$ using two models introduced previously in section 2.5.1 (Eqs. 2.7 and 2.8), hereafter referred to as models M1 and M2, respectively. In these models, H and R denote the bubble height and radius, respectively, while α and q describe the profile shape. For clarity, both models are reproduced in Figure 5.2.

As discussed in section 2.5.1, model M1 predicts $\alpha = 1$ in the membrane limit and $\alpha = 2$ in the nonlinear plate regime [393]. Since the deflection of bubbles B1-B4 exceeds several times the BN thickness, the membrane limit could be expected. On the other hand, the significant rigidity observed for e-beam-induced domes may also suggest the plate-like behavior. However, as shown in Figure 5.2e-h, the model fails to reproduce the experimental data, in either the membrane regime ($\alpha=1$) or the nonlinear plate limit ($\alpha=2$). A similar discrepancy was reported for multilayer BN bubbles [389], where $\alpha = 1.5$ was found to describe bubble profiles. In that system, finite bending rigidity led to a deviation from the membrane limit, while the fully plate-like regime was not reached due to weak interlayer van der Waals interactions. Following the approach presented in [389], we treated α as a fitting parameter. Surprisingly, as shown in Figure 5.2e-h, a good agreement with

the experimental data is obtained only for $\alpha < 1$, which is not predicted by the existing theory. Similarly, model M2 reproduces the bubble cross-sectional profiles only for q values within the range 2.5-3.5 (Figure 5.2i-l), whereas $q \approx 2.2$ was reported for typical 2D material bubbles [394]. These results demonstrate that the bubbles induced in MOVPE-grown BN by electron exposure exhibit highly unusual mechanical properties that cannot be described within the framework of well-established theories [421].

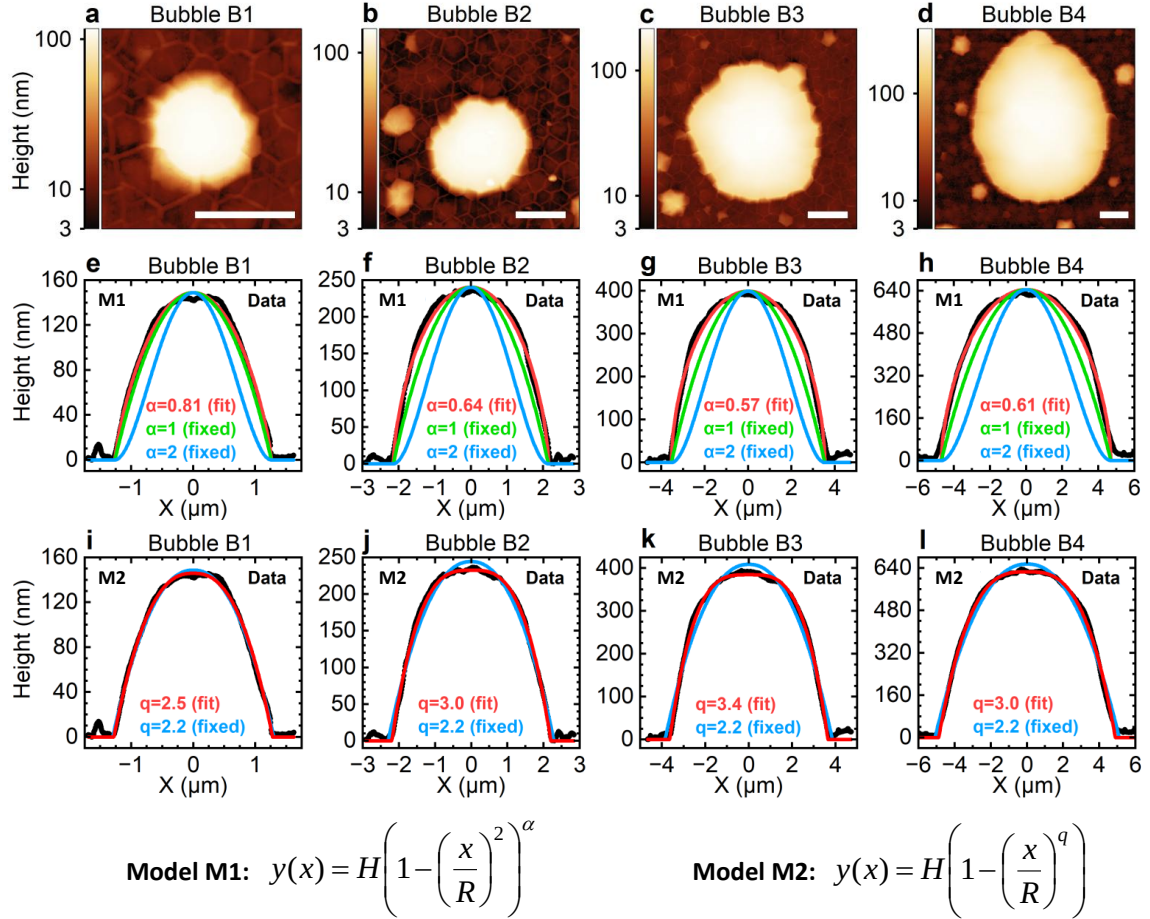


Figure 5.2: (a-d) AFM topography images of bubbles B1-B4. All scale bars are 2 μm . A logarithmic color scale was applied to enhance the visibility of the wrinkle network and of smaller bubbles. (e-h) AFM cross-sectional profiles of bubbles B1-B4, along with theoretical curves given by model M1 (Eq. 2.7). Black points represent the experimental data. Green and blue curves correspond to fits obtained with fixed values of $\alpha = 1$ and $\alpha = 2$, respectively, while red curves show fits with α treated as a free parameter. (i-l) AFM cross-sectional profiles of bubbles B1-B4, along with theoretical curves given by model M2 (Eq. 2.8). Black points represent the experimental data. Blue curves correspond to fits obtained with fixed $q = 2.2$ (following Ref. [394]), whereas red curves show fits with q as a fitting parameter. The analytical expressions for bubble profiles in models M1 and M2, primarily introduced in section 2.5 as Eq. 2.7 and Eq. 2.8, are provided at the bottom of the Figure, for the reader's convenience. Adapted from [421]

A comparison between the experimental cross-sectional profiles and the theoretical curves expected for typical bubbles (green and blue curves in Figure 5.2e-l indicates that the e-beam-induced domes in MOVPE-grown BN are slightly flattened in their upper regions. At first glance, the observed geometry could be attributed to atmospheric pressure, which may compress a bubble, thereby reducing its height and increasing its lateral dimensions, resulting in flattening. However, this interpretation cannot be considered valid when analyzing one of the most robust descriptors of bubble geometry, H/R aspect ratio. As discussed in section 2.5.1, it should remain nearly constant between bubbles obtained in a given 2D material, with only small substrate-dependent deviations. For monolayer BN, the reported H/R aspect ratio is approximately ~ 0.11 , while thicker bubbles generally exhibit slightly smaller values [384, 389, 398]. The e-beam-induced bubbles analyzed in this work exhibit an H/R ratio of 0.11-0.12, consistent with previous reports. Consequently, the disagreement between the experimental cross-sectional profiles and the analytical descriptions provided by models M1 and M2 cannot be attributed primarily to atmospheric pressure effects. Instead, we relate the observed discrepancy to BN wrinkles. Importantly, both models M1 and M2 assume clamped bubble boundaries. However, for the e-beam-induced BN bubbles investigated here, this assumption is not valid, as wrinkles act as efficient strain-relaxation channels and, consequently, the edges are not clamped. This fundamental difference in boundary conditions likely underlies the unusual geometries of bubbles B1-B4 and explains the deviations from the conventional analytical models. Due to the non-clamped character of the edges, the bubbles resemble mechanically rigid domes in which the generated strain relaxes via wrinkles rather than through significant modification of the dome geometry. This mechanism appears to be responsible for bubble stability both under ambient pressure and at cryogenic temperatures below the hydrogen liquefaction point. At this point, we have to note that for sufficiently large BN bubbles (with diameters of the order of ~ 20 μm or greater), the material rigidity plays a less important role and the influence of atmospheric pressure becomes significant. Consequently, after reaching a critical size that varies across different BN layers, bubbles collapse. However, the stability of smaller bubbles investigated here is maintained by the intrinsic BN stiffness, while the presence of molecular hydrogen inside them is of minor importance [421].

5.3 Bubble-Mediated Single-Photon Emission Enhancement

In the next step, we investigated how bubble formation affects the optical properties of MOVPE-grown BN epilayers. To this end, we performed room-temperature PL mapping measurements of bubbles B1-B4 in the range 2.0-2.33 eV. Spectra were acquired using a Renishaw inVia spectrometer. The sample was excited with a 532 nm CW laser beam of the power of 20 mW, focused by a 100 $\times$ objective (NA=0.9). A high excitation power was employed to simultaneously assess changes in the properties of the E_{2g}^{high} Raman mode across the bubbles, which are discussed later. Maps for bubbles B1-B4 were collected with a step size of 0.3 μ m, 0.3 μ m, 0.35 μ m, and 0.5 μ m, respectively. Figure 5.3a-d show optical images

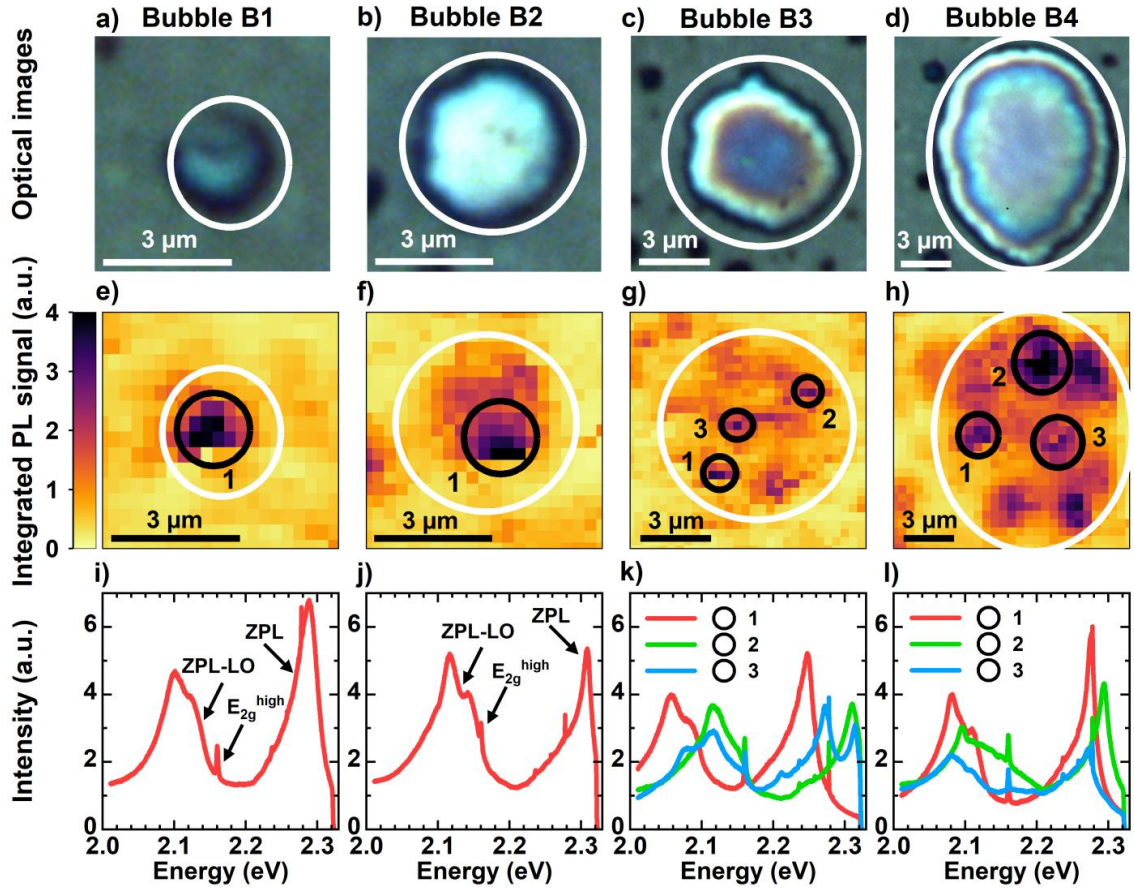


Figure 5.3: Results of PL mapping measurements performed on bubbles B1-B4 (each column corresponds to a single bubble). (a–d) Optical microscopy images of the investigated bubbles. (e–h) Spatial maps of the total integrated PL intensity in the energy range 2.0–2.33 eV. In panels a–h, the white circles mark the positions of the bubbles. Notably, the presented bubbles are rotated with respect to the AFM images shown in Figure 5.2a–d. Scalebars are 3 μ m. (i–l) PL spectra of defects highlighted by black circles in panels e–h. The very sharp peak near 2.28 eV is the sapphire Raman mode. Adapted from [421]

of the investigated bubbles, while Figure 5.3e-h present the total integrated PL intensity maps. On each bubble, we observe bright spots, which do not occur in the flat material. The PL spectra acquired at these bright points, which are plotted in Figure 5.3i-l, reveal the presence of green emitters investigated in the previous Chapter. The origin of such high intensity might have three plausible explanations. In the first scenario, electron exposure, which induces bubble formation, simultaneously triggers the generation of bright green emitters. If that was the case, emitter formation would not be associated with material bending, although the two processes would have the same origin. The second possible explanation is that due to their geometry, the bubbles behave similarly to cavity-like structures, thereby enhancing the emission of color centers present in the material before irradiation. Finally, the strong green emission may be related to strain within the bubbles.

To verify the two above-mentioned hypotheses, we have performed the following experiment. First, we conducted PL mapping measurements of $30 \times 30 \text{ }\mu\text{m}^2$ flat BN area with a step size of $0.4 \text{ }\mu\text{m}$. Experimental conditions were the same as in the previously described experiment, except for the laser power, which was set to 2 mW this time, since the focus was solely on the emitters, which are expected to saturate above a certain incident power threshold. Figure 5.4a shows the acquired map of the total integrated PL emission intensity within the range 2.2-2.32 eV corresponding to green emitters. In the next step, we irradiated the same area with electrons to induce bubble formation and repeated the PL mapping measurement. The repeated PL intensity map is provided in Figure 5.4b. Black circles mark the positions of 7 induced bubbles, whose optical image is presented in Figure 5.4c. In both PL maps, we identified 47 emitters, marked by blue circles, whose properties before and after e-beam exposure can be directly compared. Notably, we find that the PL maps are reproducible, which means that no emitter vanished and no new emitters were formed. This result indicates that neither e-beam exposure nor BN bending generates new emitters. It also demonstrates the high stability of green SPEs over time and under electron irradiation.

Next, we compared the spectral properties of all 47 identified emitters before and after electron irradiation. Figure 5.4d shows representative spectra of an emitter located in an area that remained flat after e-beam exposure. In this case, the observed color center emission remains unchanged. Figure 5.4e provides spectra of a typical emitter, which, after the whole procedure, is placed on a bubble. Here, the final emitter intensity is a few times larger than the initial one. Figure 5.4f presents the enhancement factor, defined as the ratio of final to initial emitter intensity, for all 47 identified point defects. The results clearly demonstrate that the electron treatment itself does not alter the properties of pre-existing green emitters,

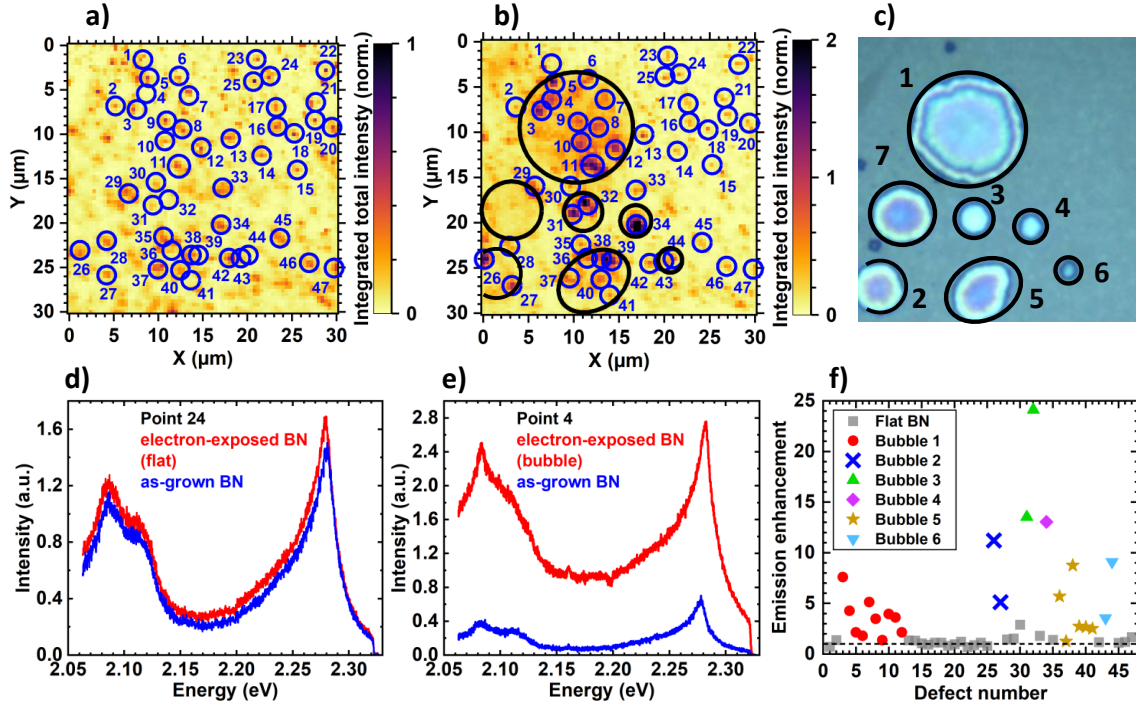


Figure 5.4: (a,b) Confocal PL intensity maps acquired from a $30 \times 30 \mu\text{m}^2$ BN area before and after e-beam irradiation, respectively. The color scale represents the total integrated PL intensity over the energy range 2.2–2.32 eV corresponding to green emitters. A total of 47 point defects, analyzed in both datasets, are marked with blue circles. (c) Optical image of the mapped region after e-beam exposure. Black circles in panels b) and c) indicate the positions of bubbles. (d,e) Representative PL spectra of green emitters acquired before and after electron irradiation at point 24 (flat hBN) and point 4 (bubble), respectively. (f) Emission enhancement factors (PL emission after vs before irradiation) for all 47 identified color centers. Various point shapes and colors correspond to flat hBN and different bubbles. The black dashed line marks the enhancement factor equal to one (no enhancement). Adapted from [421]

as the intensity of color centers in the flat material typically remains unaffected. In contrast, bubble formation, understood only as a change in BN geometry, leads to a significant enhancement of SPE emission by factors ranging from a few to even tens. Notably, the enhancement factor is not constant for a given bubble, suggesting a dependence on the spatial position.

Our observations demonstrate that e-beam-induced bubbles are an interesting platform that facilitates observation of color centers in BN. Notably, in contrast to other emission-enhancing systems developed in 2D material flakes, the generation of bubbles in MOVPE-grown BN does not require material transfer. Therefore, the risk of material damage or the introduction of unintentional defects is reduced. Moreover, in addition to enhancing SPE emission, bubbles act as markers, facilitating studies of the same emitter across different setups. Notably, the second-order correlation function measurements of green emitters in sample T₁₄₀₀, whose results were discussed in the previous chapter in section 4.5, were conducted for SPEs located in

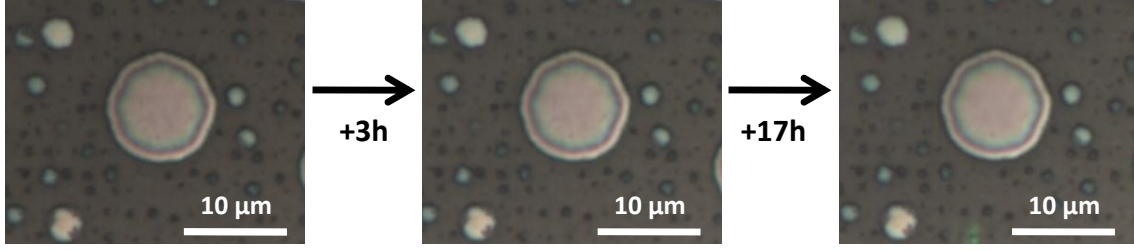


Figure 5.5: Optical microscopy images of a representative bubble recorded during continuous illumination with a 532 nm laser focused using a 100 $\times$ objective (NA = 0.9) at an excitation power of 5 mW. a) Before laser exposure. b) After 3 h of illumination. c) After a total illumination time of 20 h. The white scalebars are 10 μ m. Prolonged laser exposure does not affect bubble geometry. Adapted from [421]

bubbles. The fact that 12 out of 20 investigated emitters act as room-temperature SPEs indicates that bubble formation does not disrupt the quantum properties of green centers. Importantly, as shown in Figure 5.5, bubbles do not degrade under prolonged laser exposure, which is a key property for potential future applications.

To fully exploit the bubble-mediated enhancement of single-photon emission, it is crucial to understand its origin. We consider two options - the influence of strain or interference-like effects similar to those previously reported for UV-defect emission from bubbles in BN flakes [389]. To distinguish between these two effects, we analyze the properties of the Raman active E_{2g}^{high} phonon mode across bubbles B1-B4. The Raman peaks were acquired during PL mapping measurements presented in Figure 5.3; therefore, changes in E_{2g}^{high} mode properties can be analyzed with respect to PL emission. The results, summarized in Figure 5.6, reveal that bubble formation strongly affects vibrational properties of epitaxial BN. First, spatially across the bubbles, the Raman peak intensity oscillates, reaching several-fold amplification. Similar oscillations in Raman signal intensity have been previously reported in various 2D material bubbles and have been attributed to interference effects and the formation of standing waves between the bubbled material and the substrate [386, 387, 395]. Intuitively, this interpretation seems to be reasonable also for the bubbles investigated here. In particular, the Raman intensity maxima observed for bubble B3 (Figure 5.6c) correlate with the Newton’s rings observed in the optical image (Figure 5.3c). On the other hand, the maximum height of bubble B1 is less than half the wavelength corresponding to the Raman peak position (~ 574 nm), so the interference-based explanation is less straightforward. The Raman response of the bubbles can be explained by means of 3D finite-difference time-domain simulations performed by Dr Piotr Wróbel. To simulate Raman intensity variations, we consider the electromagnetic enhancement factor defined as:

$$E_F = |E/E_0|^4, \quad (5.1)$$

where E_0 is the electric field of the incident wave and E is the local electric field, which is governed by bubble geometry. Theoretical fits to the AFM cross-sectional profiles of bubbles B1–B4 were used as input geometries for the simulations. A linearly polarized plane-wave excitation was employed, while perfectly matched layer boundary conditions were applied to suppress artificial reflections. Figure 5.6e-h present the simulated spatial variations in E_F in the bubble-forming BN layer. The E_F values were normalized relative to the flat

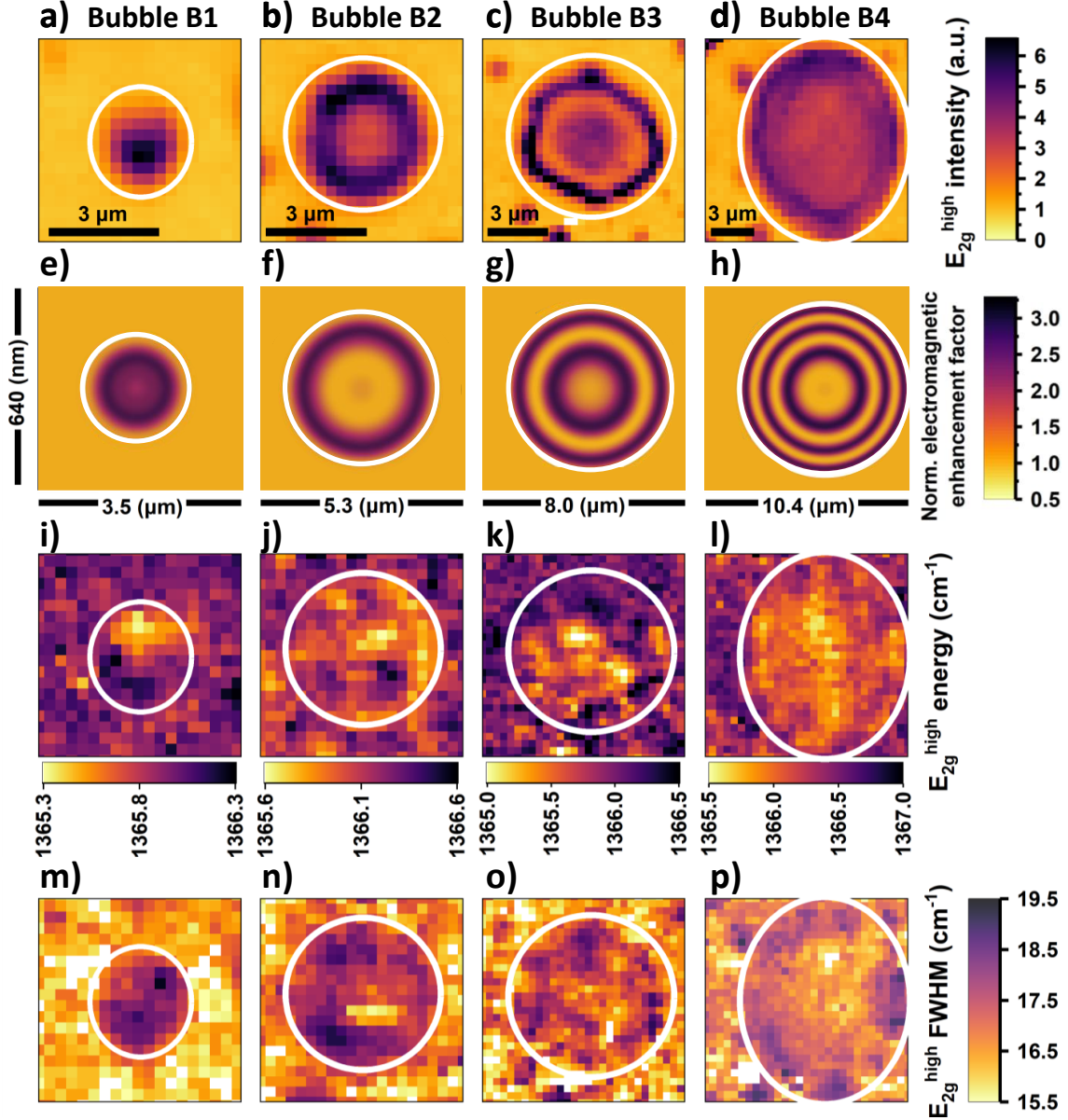


Figure 5.6: Raman mapping results and corresponding optical simulations for BN bubbles B1–B4, with each column representing a different bubble. (a–d) Spatial maps of the E_{2g}^{high} Raman mode intensity. Scalebars are 3 μm . The presented bubbles are rotated with respect to the AFM images shown in Figure 5.2a–d. White circles indicate the bubble locations. (e–h) Simulated spatial maps of the normalized electromagnetic enhancement factor E_F within bubble-forming BN layer. (i–l) Spatial variations of the phonon energy. (m–p) Maps of the Raman peak FWHM. Adapted from [421]

BN regions surrounding the bubbles, and thus correspond to the Raman intensity enhancement at a given point with respect to flat BN. The maxima of the calculated E_F correlate very well with the Raman intensity maxima observed experimentally. In particular, simulations reproduce the Raman signal enhancement across the entire bubble B1. The good agreement between experiment and simulations indicates the crucial role of interference-like effects.

Figure 5.6i-l present variations in E_{2g}^{high} phonon energy throughout investigated areas. In general, on bubbles, the Raman peak is redshifted by around $1\text{-}2\text{ cm}^{-1}$ compared to the surrounding flat BN. This result is in agreement with previous reports on multilayer BN bubbles [389, 390]. The shift of $1\text{-}2\text{ cm}^{-1}$ may indicate the presence of a small strain of the order of $\sim 0.1\%$ [426, 427]. However, its origin may also be different. As discussed in section 2.5.2, the as-grown epilayer is slightly compressed due to the thermal expansion mismatch between BN and sapphire. Thus, the slight redshift observed in bubbles may also arise from the relaxation of material that detaches from the substrate. At this stage, it is difficult to determine which option is realized. What we can say for sure is that no significant stress is observed in the generated bubbles. 2D material bubbles generated via hydrogen irradiation have been reported to display a strain of the order of $\sim 1\%$ [392]. However, reaching such a high strain in the e-beam-induced bubbles investigated here is not possible due to non-clamped edges and strain relaxation through wrinkles.

Figure 5.6m-p show spatial variations in E_{2g}^{high} Raman mode linewidth. In central regions of bubbles B2-B4, the found FWHM values are comparable to those measured for flat BN on sapphire. Such a behavior is expected, as the biaxial strain at the top of a bubble should not favor any direction, so it preserves the in-plane symmetry. Consequently, the E_{2g}^{high} mode is not split, and its FWHM remains unchanged. In contrast, near the bubble edges, the measured FWHM increases to around 19 cm^{-1} because the E_{2g}^{high} mode degeneracy is lifted by the presence of uniaxial strain. Phonon mode splitting leads to an effective increase in FWHM.

Unlike the Raman intensity maps, the E_{2g}^{high} mode energy and FWHM distributions do not exhibit the circular symmetry expected for ideal bubbles. This behavior is likely related to the specific bubble formation mechanism, the accumulation of excess material in wrinkles, and the finite thickness of the BN epilayer. During the coalescence of smaller bubbles into larger structures, rapid variations in BN curvature may arise at the merging regions, leading to the formation of localized residual strain. Although wrinkles act as efficient strain-relaxation channels, the BN layer also remains partially anchored by the wrinkle network, which constrains the bubble geometry and prevents complete mechanical relaxation. As a result, residual strain inhomogeneities prevent the Raman peak position and linewidth distributions from maintaining ideal circular symmetry.

Next, we investigated correlations between the total integrated PL intensity and both the intensity and energy of the E_{2g}^{high} Raman mode in PL/Raman maps acquired for bubbles B1-B4. An additional $25 \times 25 \mu\text{m}^2$ map obtained in a partially e-beam-exposed region with the step $0.5 \mu\text{m}$ (Figure 5.7) was included in the analysis. Since Raman intensity variations are primarily associated with interference-like effects, whereas the E_{2g}^{high} mode energy is sensitive to local strain, this comparison may help identify the mechanism responsible for the observed enhancement in single-photon emission. For each analyzed map, Pearson correlation coefficients (PCCs) were calculated between the total integrated PL intensity and both the E_{2g}^{high} mode intensity and peak position. To focus on regions containing point defects and reduce the influence of background fluctuations, only the 25 % of the pixels with the highest green-emitter intensity were included in the analysis. The obtained PCC values are summarized in Table 5.1. On average, a positive correlation between PL and Raman intensities is observed, with a mean PCC of 0.33. In contrast, no significant correlation occurs between PL intensity and the E_{2g}^{high} mode position. These results suggest that the enhancement of SPE emission is primarily associated with interference-related effects, whereas the influence of strain appears negligible. The obtained mean PCC describing the correlation between the green emission and the Raman signal intensities is, as expected, below unity. This reflects the lack of a strict spatial correlation between interference maxima and color center positions. In particular, interference maxima do not necessarily coincide with green SPEs, while color centers may also be present in regions without interference enhancement [421].

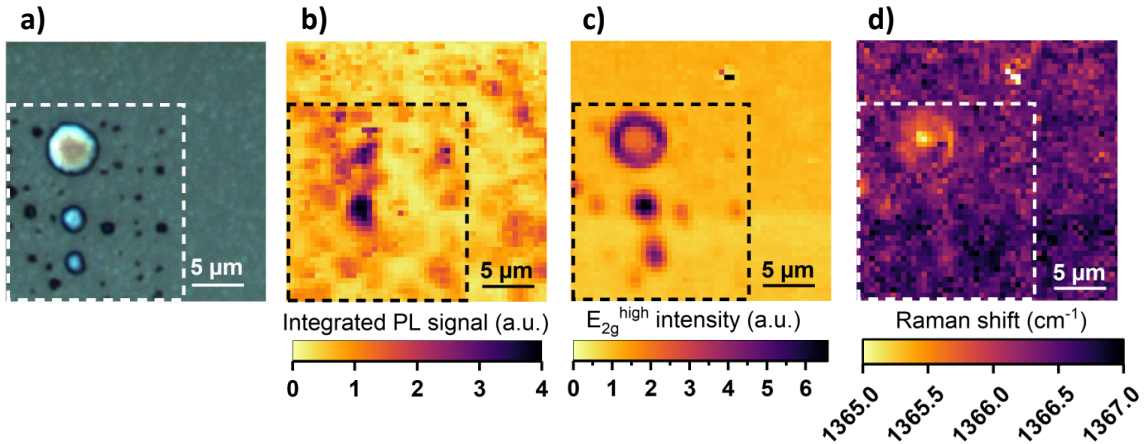


Figure 5.7: PL/Raman mapping results for a $25 \times 25 \mu\text{m}^2$ partially irradiated BN area. The region marked by dashed squares was irradiated with an electron beam. Scalebars are 5 μm . a) Optical image of the mapped area. b) map of the total integrated PL emission in the range 2.0 eV-2.33 eV. c) Map of the E_{2g}^{high} Raman peak intensity. d) Map of the E_{2g}^{high} Raman peak position. a) and b) are adapted from [421]

Table 5.1: Correlations of the total integrated visible PL intensity with the position and intensity of the E_{2g}^{high} Raman mode. Adapted from [421]

Area	Pearson correlation coefficient (PCC)	
	Total PL intensity vs Raman shift	Total PL intensity vs Raman intensity
Bubble B1	-0.12	0.53
Bubble B2	0.06	0.47
Bubble B3	0.03	0.3
Bubble B4	0.17	0.15
Partially irradiated area shown in Figure 5.7	-0.09	0.35
Average	-0.01	0.33

5.4 Deterministic Formation of Bubble Arrays

To fulfill the potential of e-beam-induced bubbles for single-photon emission enhancement in MOVPE-grown BN, precise control of bubble position and scalable bubble formation are required. To address this issue, we next investigated how irradiation parameters affect bubble formation [421]. To this end, using the setup dedicated to the e-beam lithography, we irradiated two $200 \times 200 \mu\text{m}^2$ regular matrices of circular features into the BN layer. In matrix 1 (matrix 2), the diameters of the exposed circles were $1 \mu\text{m}$ ($2 \mu\text{m}$), while the center-to-center spacing was set to $2 \mu\text{m}$ ($5 \mu\text{m}$), respectively. All circles within a given column were exposed to the same dose. The exposure dose assigned to successive columns increased progressively from 1 mC cm^{-2} to 100 mC cm^{-2} . The increment between adjacent columns was 1 mC cm^{-2} for matrix 1 and 2.5 mC cm^{-2} for matrix 2. The beam current was 1 nA , and the incident electron energy was 5 keV . Variations in the applied dose were achieved by adjusting the exposure time.

Despite both matrices being irradiated at doses ranging from 1 to 100 mC cm^{-2} , optical microscopy images of the BN layer after irradiation, shown in Figure 5.8, reveal noticeable differences between the two matrices. In the first exposed area, the generated bubbles are distributed rather irregularly across the e-beam-irradiated region. Their diameters reach approximately $10 \mu\text{m}$, even though the irradiated pattern consisted of $1 \mu\text{m}$ -diameter circles. In contrast, the bubbles formed in the second area are considerably smaller. This region exhibits a more ordered bubble arrangement, although the predefined pattern is still not reproduced perfectly.

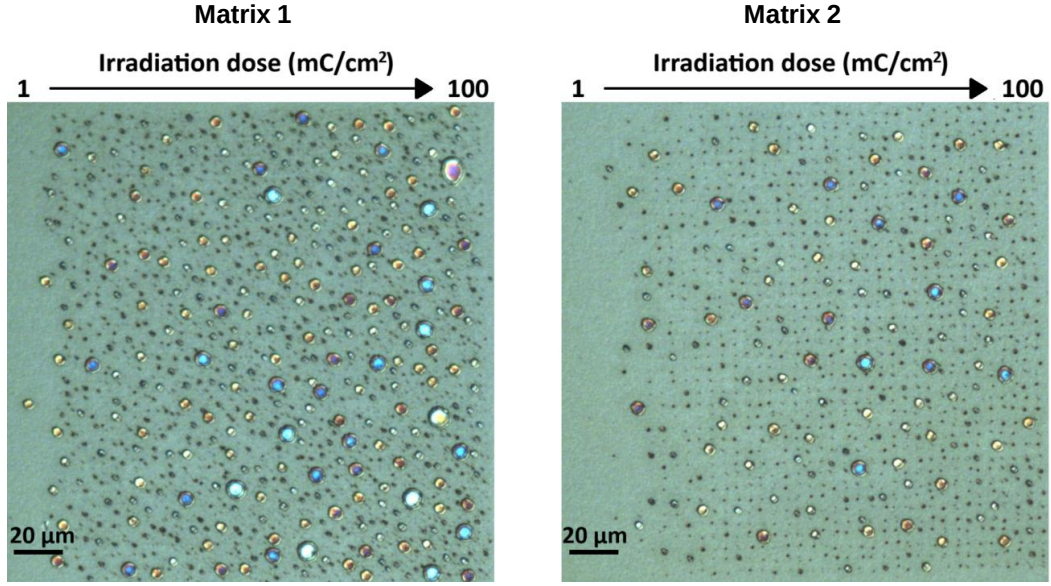


Figure 5.8: Optical images of e-beam exposed $200 \times 200 \mu\text{m}^2$ BN bubble matrices 1 and 2. Scalebars are $20 \mu\text{m}$. In matrix 1 (matrix 2), the irradiated pattern consisted of circles with a diameter of $1 \mu\text{m}$ ($2 \mu\text{m}$) separated by $2 \mu\text{m}$ ($5 \mu\text{m}$). The applied irradiation dose varies across the matrices, increasing from 1 mC cm^{-2} on the left to 100 mC cm^{-2} on the right (within every single column, the applied dose was constant). Adapted from [421].

The observed differences between the two matrices are associated with the bubble formation mechanism, which involves the detachment of neighboring mesh units within the wrinkle network, followed by the coalescence of smaller bubbles. The variation in bubble size is primarily due to differences in the spacing between irradiated circles in the two matrices. For the $2 \mu\text{m}$ spacing applied in matrix 1, neighboring bubbles induced in predesigned areas can readily merge, leading to the formation of irregularly distributed larger structures, which do not follow the predesigned pattern. In contrast, the $5 \mu\text{m}$ separation used in matrix 2 is sufficiently large to prevent bubbles from merging. Therefore, the final array consists of smaller, more regularly distributed bubbles. Additionally, local variations in the wrinkle pattern on the BN surface influence the shape and size of bubbles. Consequently, bubbles within the same column, fabricated with the same applied dose and spacing, may exhibit substantial differences in geometry. Moreover, when performing similar experiments on various BN samples, we found that the formation of new bubbles and the enlargement of existing ones stop after a certain irradiation time, dependent on the specific BN layer. This observation is consistent with previous reports on UV-induced bubble formation in MOVPE-grown BN [398]. This behavior may be associated with the finite amount of intercalated water beneath the BN epilayer. Once the available water in a given region undergoes complete radiolysis, molecular hydrogen, which detaches BN from the sapphire substrate, can no longer be generated. This effect constitutes a strict limitation that must be considered for the deterministic fabrication of BN bubbles.

To address the reproducibility problem, a mask-assisted approach was implemented to restrict bubble formation to predefined regions. For this purpose, the BN layer was coated with a resist layer, in which a matrix of circular openings was patterned using optical lithography (see section 3.11). The BN layer covered with the patterned mask was then exposed to the electron beam. The proposed concept for fabricating deterministic bubble arrays is inspired by the strategy reported in [391, 396], in which e-beam lithography was employed to design the mask. However, because electron-beam irradiation induces bubble formation in MOVPE-grown BN, we fabricated an array of circular openings using optical lithography.

Figure 5.9 presents AFM characterization of an exemplary 4×4 bubble matrix with designed bubble diameters of $3 \mu\text{m}$ and center-to-center spacings of $12 \mu\text{m}$. The fabricated bubbles are lower than the spin-coated resist layer thickness ($\sim 440 \text{ nm}$) and do not extend above the mask surface. The AFM measurements confirm that the proposed fabrication strategy enables the formation of spatially separated bubbles localized within predefined resist-free circular areas. Although some deviations in bubble geometry are still present, indicating that further optimization is required, the results demonstrate a substantial improvement in the regularity of bubble arrays compared with the mask-free approach.

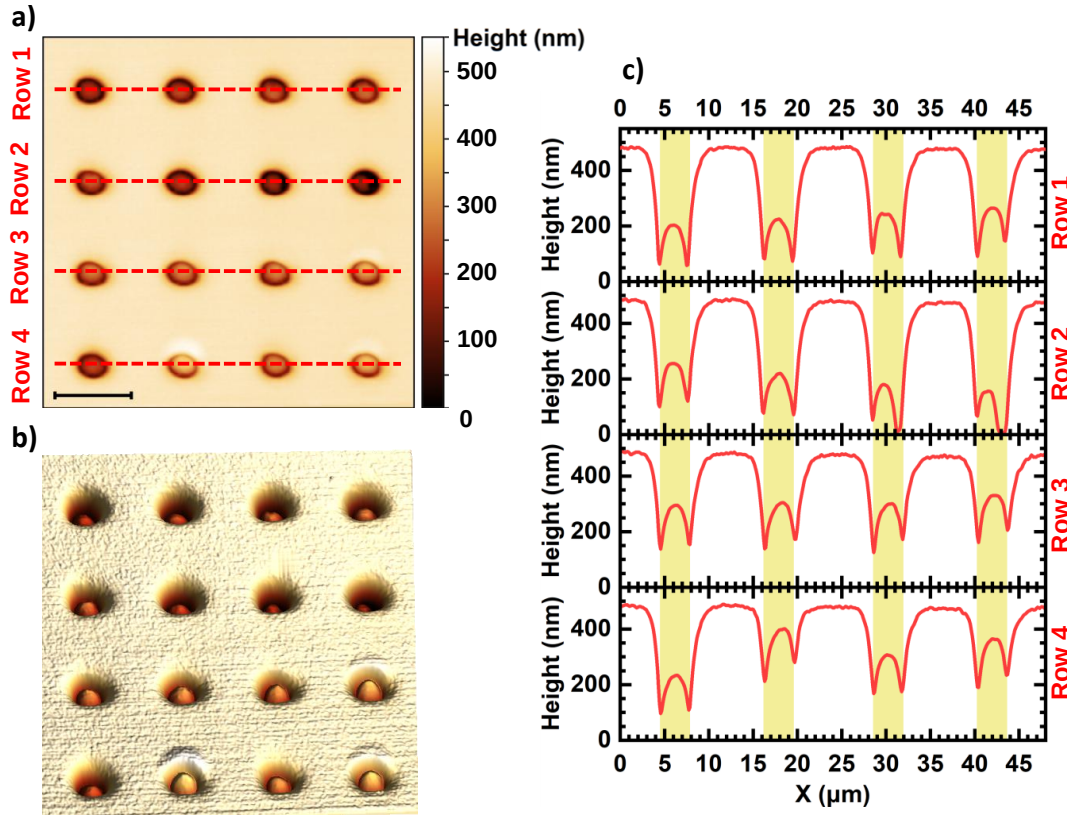


Figure 5.9: AFM characterization of a representative deterministic 4×4 regular array of $3 \mu\text{m}$ -diameter bubbles separated by $12 \mu\text{m}$, obtained via mask-assisted method. a) Top view. Scalebar is $10 \mu\text{m}$. b) 3D AFM image of the area shown in a). c) Cross-sectional profiles along red dashed lines in a). Bubbles are shadowed in yellow. Adapted from [421]

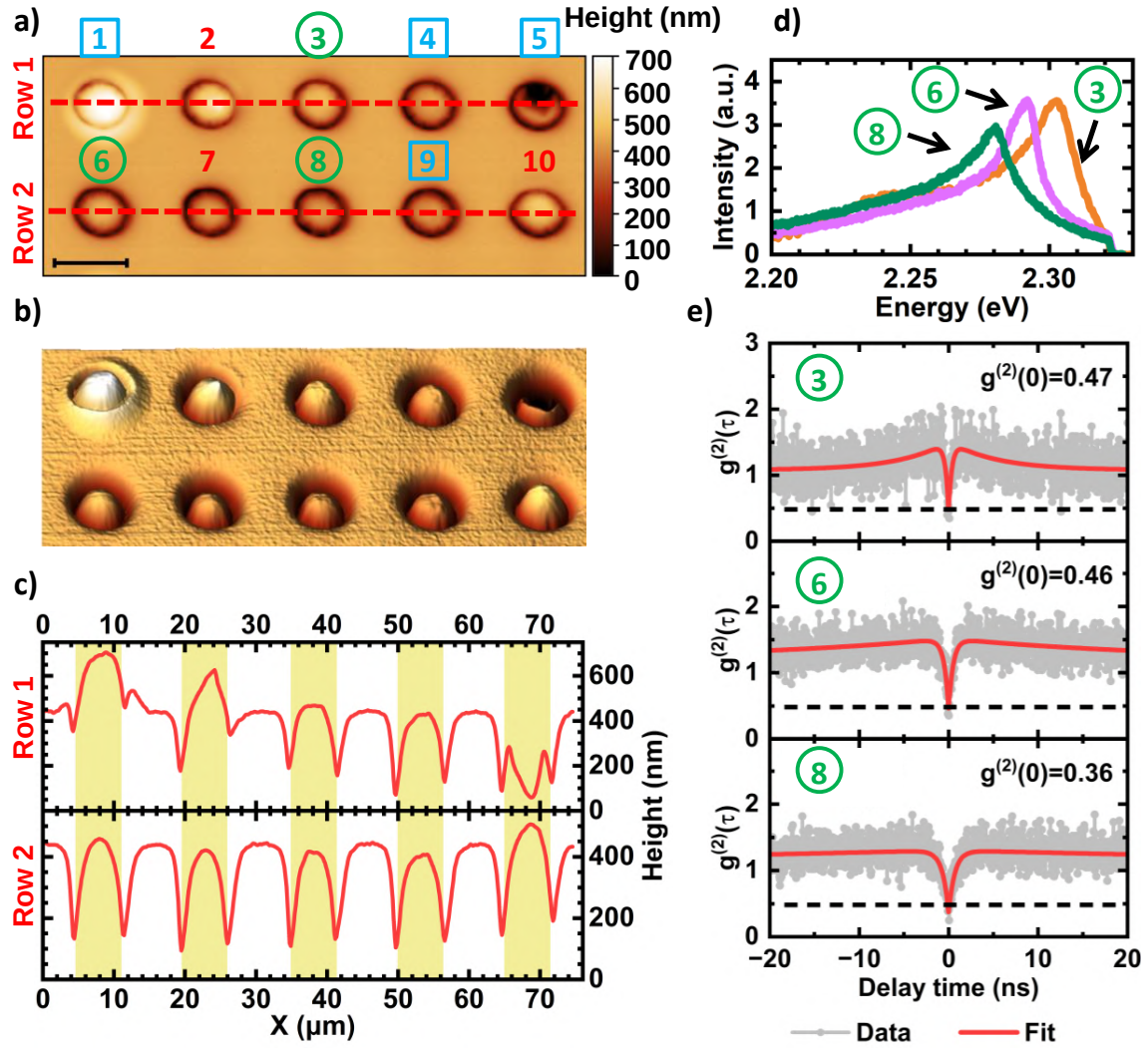


Figure 5.10: (a-c) AFM characterization of a representative deterministic 2×5 regular array of $6 \mu\text{m}$ -diameter bubbles separated by $15 \mu\text{m}$, obtained via mask-assisted method. a) Top-view AFM image of the matrix. Scalebar is $10 \mu\text{m}$. Bubbles marked by green circles and blue squares host SPEs ($g^{(2)}(0) < 0.5$) and quantum emitters ($0.5 < g^{(2)}(0) < 1$), respectively. Bubbles marked in red do not host quantum emitters. b) 3D AFM image of the area shown in a). c) Cross-sectional profiles along red dashed lines in a). Bubble positions are shadowed in yellow. d) ZPL-range PL spectra of green SPEs found in bubbles labeled as 3, 6, and 8. e) Room-temperature experimental (gray points) and theoretical (red lines) $g^{(2)}(\tau)$ curves acquired for emitters shown in d), confirming single-photon emission from color centers located at deterministic bubbles. Adapted from [421]

Similarly, Figure 5.10a-c shows AFM characterization of a deterministic 2×5 matrix of larger bubbles designed to be $6 \mu\text{m}$ in diameter and separated by $15 \mu\text{m}$. As in the previous bubble array, bubble formation occurs exclusively within the predefined openings; however, we note that the bubbles labeled 1 and 2 reached larger sizes than expected, indicating that prolonged e-beam exposure can induce detachment of BN from the substrate even beneath a resist layer. Next, by combining room-temperature PL and second-order correlation function measurements, we investigated green-center emission in the fabricated structures. The measurements

were performed in the same manner as room-temperature second-order correlation measurements discussed in the previous chapter. Among 10 bubbles in the array, 3 were found to host true room-temperature green SPEs satisfying $g^{(2)}(0) < 0.5$, while 4 were found to host quantum emitters ($0.5 < g^{(2)}(0) < 1$). ZPLs of found SPEs are shown in Figure 5.10d. Related $g^{(2)}(\tau)$ curves are provided in Figure 5.10e.

To confirm that deterministically fabricated bubbles provide emission enhancement similar to that observed for randomly distributed bubbles, we statistically analyzed the emission intensity of green emitters in 6 μm -diameter mask-assisted bubbles and in flat, unexposed BN. To provide sufficient statistics, in both cases, we analyzed the 73 most intense emitters. The distributions of ZPL intensity are provided in Figure 5.11. Nearly 30 % of the emitters observed on the bubbles (21 out of 73) are brighter than the most intense color centers found in flat BN, proving that bubbles obtained via a mask-based approach also provide interference-mediated emission enhancement. As discussed previously, a single, well-defined enhancement factor for an entire bubble cannot be determined, as interference maxima, which govern the enhancement, occur only at specific positions on the bubble surface.

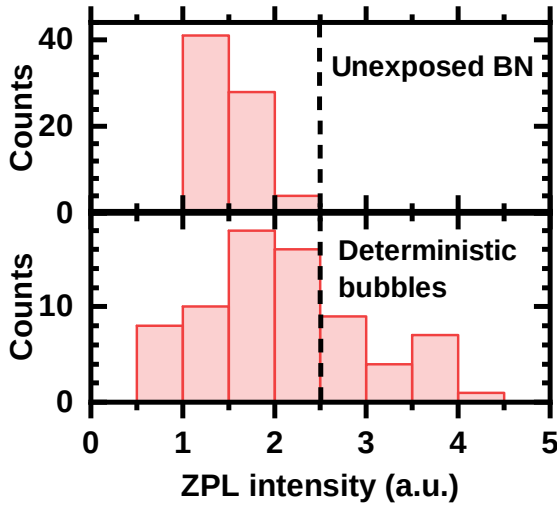


Figure 5.11: Distributions of ZPL intensity for color centers in flat unexposed BN and in 6 μm -diameter bubbles fabricated via mask-assisted approach. In both cases, the 73 most intense found emitters are analyzed. A black dashed vertical line marks the highest ZPL intensity observed in flat BN. Nearly 30 % of emitters registered on bubbles (21 out of 73) are brighter than the most intense color centers in flat BN. Adapted from [421]

The obtained results confirm that the mask-assisted fabrication process used to generate deterministic bubble arrays neither degrades the quantum properties of emitters nor suppresses the emission enhancement effect. This demonstrates that it is possible to simultaneously achieve spatial localization of bubbles in predefined positions and benefit from the bubble-mediated enhancement of single-photon emission. Therefore, despite the remaining deviations in bubble shape, which indicate the need for further optimization of both the mask geometry and the e-beam exposure conditions, the presented results constitute an important step toward the deterministic and reproducible fabrication of uniform BN bubbles that may serve as a versatile platform for investigating SPEs in MOVPE-grown material [421].

5.5 Conclusions

We have demonstrated that bubbles formed in MOVPE-grown BN under electron irradiation exhibit very unusual mechanical properties. They are associated with a specific formation mechanism that involves the detachment and merging of adjacent mesh units within the wrinkle pattern. In particular, the bubble size is not arbitrary, but quantized in units of the mesh cell area. Due to the material’s significant stiffness, the bubbles remain stable even below the liquefaction point of enclosed molecular hydrogen, which induces bubble formation but does not govern their mechanical properties. BN wrinkles provide non-clamped bubble edges, serving as strain-relaxation pathways. As a result, the investigated bubbles exhibit a geometry that is not well described by commonly used theoretical frameworks.

E-beam-induced bubbles provide a few-fold enhancement of BN-hosted visible SPEs. PL mapping of the electron-irradiated and unexposed BN area has shown that the electron treatment itself does not affect the pre-existing emitters, and that the increase in their intensity is attributable solely to changes in the BN layer geometry. Results from PL and Raman mapping, combined with optical simulations, have shown that the observed color-center enhancement originates from interference-like effects in bubbles rather than from strain, which does not exceed ~ 0.1 %.

To investigate bubble reproducibility and scalability, we induced bubble formation by irradiating two regular arrays of circular features. However, merging smaller bubbles into bigger structures prevented us from obtaining the designed pattern. Also, local variation in the wrinkle pattern causes bubbles obtained under the same conditions to display different geometries. To address this issue, we proposed a mask-assisted bubble formation strategy. In this approach, we use optical lithography to define a pattern of circular features in a resist layer spin-coated on the BN surface. Subsequent e-beam exposure induces bubble formation only in the predefined openings. Although mask design and irradiation parameters require further optimization, we demonstrated that the proposed method provides a significant improvement in controlling bubble sizes and position. Importantly, as proven by second-order correlation function measurements, this procedure does not disrupt the quantum properties of the emitters.

Our results show that e-beam-induced bubbles in MOVPE-grown BN provide a versatile platform to study SPEs in BN by enhancing their emission. The proposed mask-assisted procedure of bubble formation constitutes a first step toward their possible implementation into practical applications [421].

Chapter 6

Modifying Quantum Emitters via Thermal Neutron Irradiation

6.1 Introduction

As discussed in section 2.4.4, V_B^- defects possess spin and act as quantum sensors of the magnetic field, strain, temperature, and pressure [20, 142, 143, 253]. A common method for their fabrication is thermal-neutron irradiation of BN [7]. In addition to existing as individual defects, boron vacancies can also be part of more complex vacancy-related centers. Therefore, neutron irradiation should not be considered only in terms of generation V_B^- , but the formation of other color centers also needs to be considered. However, to date, there is a lack of systematic studies on how neutron irradiation affects BN PL emission in spectral ranges other than that of V_B^- centers.

In this chapter, we address this issue by comparing defect-related emission in neutron-irradiated and unexposed thick MOVPE-grown rBN. As the investigated material hosts carbon defects introduced during growth, our samples provide an ideal platform for studying vacancy-carbon complexes.

First, we demonstrate that the grown material is indeed ABC-stacked BN and discuss its overall properties. Then we show that neutron irradiation of our MOVPE-grown BN results in the formation of V_B^- centers. In addition, we analyze temperature-induced changes in their emission. The obtained results may contribute to modeling V_B^- emission governed by interactions with phonons. Finally, using various excitation wavelengths, we investigate changes in visible and UV defect-related emission caused by neutron irradiation of rBN. Our results clearly show that neutron treatment generates various color centers that likely involve carbon atoms and boron vacancies.

6.2 MOVPE-Grown Rhombohedral Boron Nitride

The studied sample was grown via MOVPE by Dr. Aleksandra Dąbrowska on a 2-inch sapphire substrate. In contrast to the BN layers investigated in chapter 4, this sample was grown solely using the CFG method. The growth was carried out at 1050 °C under the pressure of 600 mbar with TEB and NH₃ flow rates of 38 sccm and 2000 sccm, respectively. Such growth conditions result in the formation of a thick ($\sim 1.2 \mu\text{m}$) BN layer. The SEM image, taken by Dr. Mateusz Tokarczyk and shown in Figure 6.1a, clearly demonstrates that the investigated sample exhibits a polycrystalline structure. In terms of XRD measurements, the grown material resembles a powder sample, providing access to asymmetric reflection peaks, which allow distinguishing between different BN polytypes, as described in section 2.2.1. XRD scans, collected by Dr. Mateusz Tokarczyk for the investigated sample and commercially available hBN crystals (HQ Graphene), in the range corresponding to those asymmetric reflections, are presented in Figure 6.1b. For the MOVPE-grown sample, we observe peaks related to (101) and (102) reflections characteristic of rBN, while those associated with (100) and (101) reflections in hBN are not present [402, 403]. This result confirms that the grown material is indeed rBN. The optical signature of a non-centrosymmetric structure of rBN is the possibility of second-harmonic generation (SHG) [200, 201]. Figure 6.1c-e present SHG mapping results obtained over a $25 \times 25 \mu\text{m}^2$ area covering the rBN sample edge and the bare sapphire substrate (top left area). The sample was excited with a 1064 nm CW laser beam of the power of 20 mW, and the response at 532 nm was detected using a Horiba T64000 spectrometer. Although a CW laser was used instead of the pulsed excitation typically employed in such measurements, we observe an SHG signal that correlates with the sample morphology, confirming the non-centrosymmetric nature of the material. Notably, 532 nm emission is not observed in the sapphire not covered with rBN, indicating that the substrate does not affect SHG generation and that the SHG is originating solely from the rBN layer.

The obtained results prove that the investigated material is thick, polycrystalline rBN. Since the organic precursor TEB was used during growth, the sample constitutes an ideal platform for investigating carbon-related defects in ABC-stacked BN.

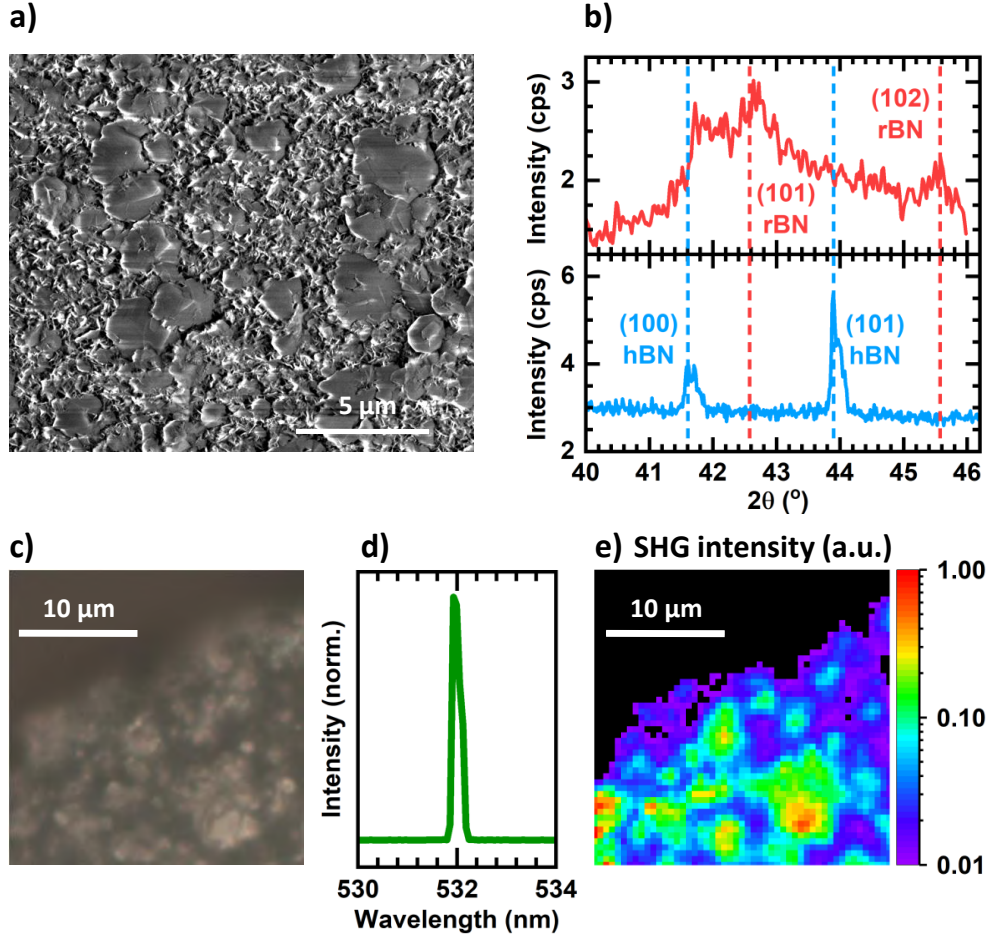


Figure 6.1: Characterization of MOVPE-grown rBN. a) SEM image showing the polycrystalline structure of the sample. Scalebar is 5 μm . b) Results of XRD measurements performed on the rBN sample (top panel) and commercial hBN (bottom panel) in the range corresponding to asymmetric reflection peaks. Dashed lines mark peak positions characteristic of particular BN polytypes. (c-e) Results of SHG mapping over $25 \times 25 \mu\text{m}^2$ rBN area. Scalebars are 10 μm . c) Optical image of the mapped region. d) SHG response of rBN under 1064 nm CW laser excitation. e) Map of the SHG intensity.

6.3 Formation and Properties of Boron Vacancies

In further experiments, we focus on two $1 \times 1 \text{ cm}^2$ rBN samples cut from the same 2-inch wafer. One of them was irradiated by thermal neutrons with a total dose of $2.6 \times 10^{16} \text{ cm}^{-2}$ to induce formation of V_{B}^- . The irradiation was performed in the MARIA reactor (National Centre for Nuclear Research, Świerk, Poland) with the courtesy of M.Eng. Grzegorz Wojtania and Dr. Rafał Prokopowicz. The second sample remained unexposed and acts as a reference. Figure 6.2 shows a photo of the two samples. We observe that after neutron treatment, rBN, which originally is transparent, becomes reddish-brown. A similar effect was previously reported in hBN flakes, which also change their color under neutron exposure. Such a behavior was attributed to the formation of V_{B}^- [428].



Figure 6.2: Photo of two $1 \times 1 \text{ cm}^2$ rBN samples. Left: as-grown, unexposed material. Right: sample irradiated with thermal neutrons.

To verify whether the neutron exposure resulted in the formation of V_B^- centers, we performed optical studies on both as-grown and irradiated samples. Figure 6.3a shows their PL emission spectra acquired in the spectral range characteristic of V_B^- emission. The measurements were performed using a Horiba T64000 spectrometer. The rBN sample was excited with a 532 nm laser beam with a power of around 5 mW, focused with a $100\times$ objective (NA=0.9). The irradiated sample exhibits strong defect-related emission that is absent in the as-grown material. As discussed in section 2.4.4, the presence of V_B^- can be confirmed by ODMR measurements, which reveal the spin-splitting of the ground and excited states. Therefore, we employed this technique to verify that the strong PL emission observed in the exposed sample indeed arises from the formation of V_B^- centers. Figure 6.3b presents the ODMR spectrum acquired from neutron-irradiated BN at 10 K in the 736-1010 nm spectral range by BSc Tomasz Łopion and Dr. Mateusz Goryca (see section 3.9). The obtained result proves that the neutron-exposed sample hosts V_B^- . The two observed dips in ODMR contrast correspond to transitions between $|0\rangle$ and $|\pm 1\rangle$ ground states. The extracted zero-field splitting value, $\nu_0 \approx 3.62 \text{ GHz}$, is consistent with previous reports for measurements performed at cryogenic temperatures [20]

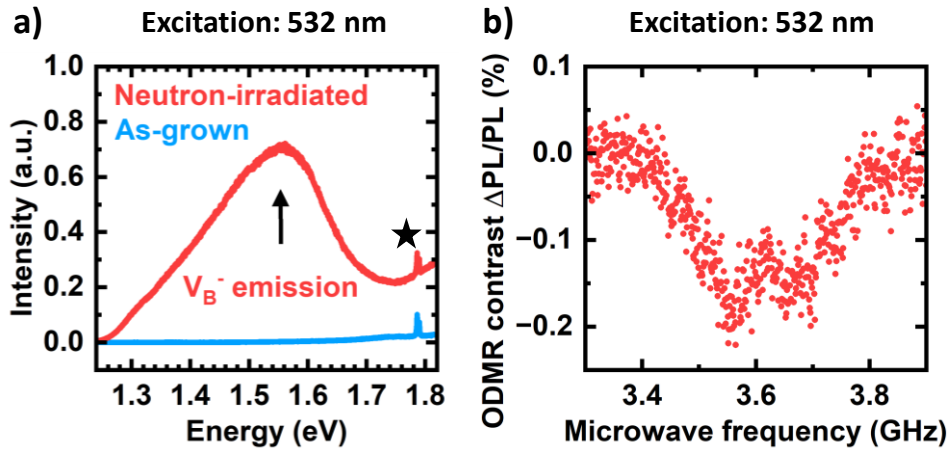


Figure 6.3: a) PL spectra of as-grown (blue) and neutron-irradiated (red) rBN acquired in the spectral range typical for V_B^- under 532 nm laser excitation. Clearly, neutron treatment induces strong defect-related emission. The peak marked by a star originates from Cr dopants in the sapphire substrate. b) ODMR spectrum recorded for the neutron-exposed sample in the spectral range 736-1010 nm at 10 K. The result confirms that generated defects are V_B^- .

In the next step, we performed temperature-dependent studies of V_B^- PL emission in neutron-irradiated MOVPE-grown rBN. While many studies focus on temperature-dependent spin properties of V_B^- , there is a lack of systematic studies of its emission shape, particularly in rBN. The defect-related spectra were acquired using a Horiba T64000 spectrometer. The emission was excited with a 532 nm laser beam focused with a $50\times$ objective (NA=0.5). During the measurements, the sample was mounted in an Oxford Instruments Microstat HiRes helium cryostat. PL spectra of V_B^- were collected in the temperature range 4-360 K. At higher temperatures, V_B^- -related emission becomes undetectable due to its lower intensity and an increase in the background luminescence.

Figure 6.4a provides V_B^- background-corrected PL spectra recorded at 10 K and 300 K. As the temperature increases, the maximum emission energy shifts to higher values. Such a behavior is the opposite of the commonly observed temperature dependences for emitters in various semiconductors [429–431]. However, it has been previously reported for V_B^- in hBN flakes [432, 433].

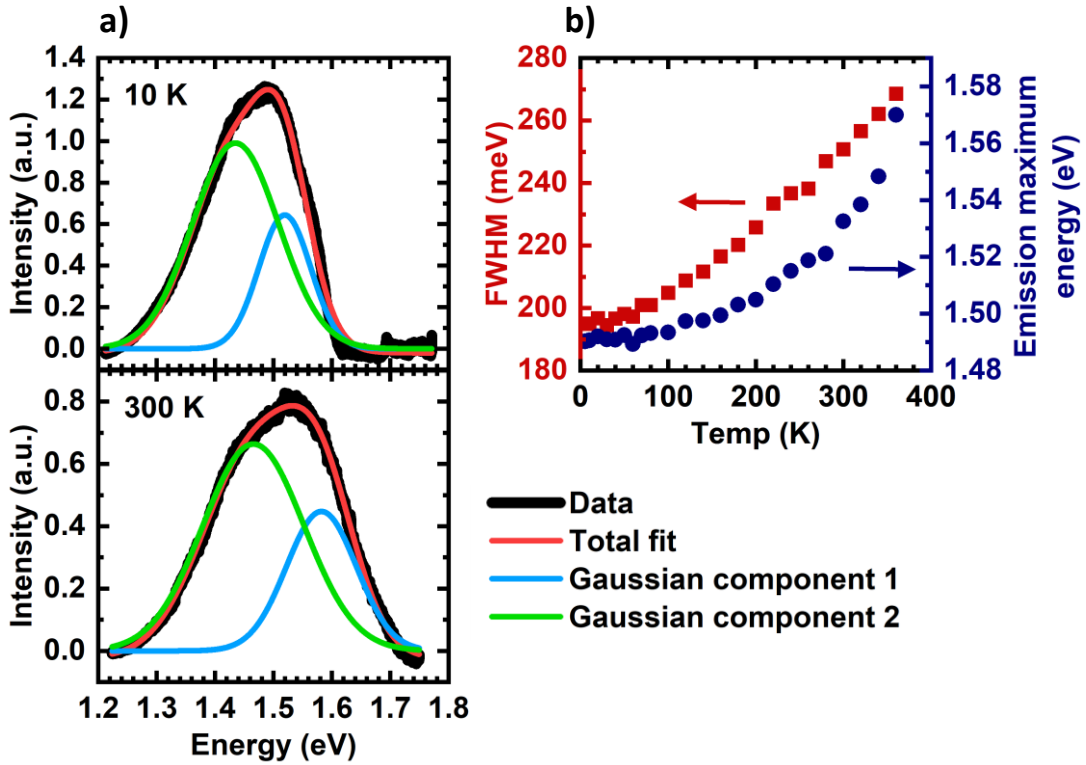


Figure 6.4: Temperature-dependent PL studies of V_B^- centers in the neutron-irradiated rBN. a) PL spectra acquired at 10 K (top panel) and 300 K (bottom panel), together with the fitted double-Gaussian profiles. Black curves are experimental data, while Red curves are total fits. Two fitted Gaussian profiles are plotted in green and blue. b) Dependences of PL emission FWHM (dark red squares) and maximum emission energy (dark blue circles) on temperature.

This unusual blueshift with increasing temperature is related to a specific emission mechanism. As discussed in section 2.4.4, due to symmetry reasons, phonon-free ZPL emission of the V_B^- defect is dark. The entire observed signal originates from phonon-induced symmetry breaking. Notably, as demonstrated theoretically in [375], the phonon-assisted emission of V_B^- is not well-described by a common Huang-Rhys theory (described in further part); instead, many-body perturbation theory should be employed. In this framework, V_B^- emission is described to originate from the strong exciton-phonon coupling between two excitons and lattice vibration. As these two excitonic states are of different symmetries, a particular phonon couples to each of them in a different way. Also, the contributions of various phonon modes to the PL spectrum are expected to change with temperature. Therefore, a proper theoretical description of the observed emission shape is non-trivial and requires advanced theoretical formalism.

Here, as shown in Figure 6.4a, we fit the entire spectrum as a sum of two Gaussian peaks and then numerically find the emission energy maximum and FWHM, which are plotted as a function of temperature in Figure 6.4b. Although the obtained curves reproduce the experimental spectra well, the interpretation of the two Gaussian components is not straightforward. Therefore, the fitted procedure provides only numerical access to the maximum emission energy and FWHM. Since we do not observe ZPL of V_B^- , but rather a broad emission arising from phonon-induced symmetry breaking, the obtained data cannot be analyzed using the same framework as that employed in section 4.6 to interpret the results of temperature-dependent PL studies of green emitters. Based on theoretical calculations considering hBN structure, in the temperature range 0-200 K, the authors of [375] predict a linear increase of emission FWHM from ~ 270 meV to ~ 320 meV. At higher temperatures, they expect the drop in FWHM caused by the strong influence of lower-energy phonons. In our case, we do not observe such an extraordinary drop in FWHM up to 360 K; however, we note that, due to different symmetries of hBN and rBN resulting in different vibrational modes, our results cannot be directly compared with the theoretical calculations discussed in [375]. The results obtained may provide important data for modeling the exciton-phonon interactions that governs the emission of V_B^- in rBN.

6.4 Modification of Visible and UV Emitters

Finally, we investigate how neutron irradiation affects defect-related emission across spectral ranges other than that corresponding to V_B^- centers. To this end, we analyze the PL emission of both as-grown and neutron-exposed samples under various excitation wavelengths: 532 nm (~ 2.33 eV), 442 nm (~ 2.81 eV), 405 nm (~ 3.06 eV), and 288 nm (~ 5.44 eV). Notably, regardless of the excitation energy, both the reference and irradiated samples exhibit very intense defect-related emission across the entire area, rather than only at specific spots. Such behavior contrasts with that observed in BN layers investigated in chapter 4 and is related to a completely different growth regime. Within each sample, the spectra collected under a particular excitation wavelength show very little variation. Therefore, the spectra presented in this section are representative of each sample.

We start the analysis with the spectral range corresponding to green emitters. Room-temperature PL spectra of both samples, excited with a 532 nm laser, are provided in Figure 6.5a. The emission was recorded using a Horiba T64000 spectrometer. A beam of the power of around 5 mW was focused via a 100 $\times$ objective (NA=0.9). The spectra acquired from as-grown and neutron-exposed rBN differ significantly. The first sample hosts green emitters whose ZPL is centered at ~ 2.283 eV, and the intensity is comparable to that of E_{2g}^{high} Raman peak. The neutron-irradiated sample also hosts green emitters, but they are blueshifted by around 23 meV. Moreover, the observed emission intensity is approximately one order of magnitude higher. The presence of two different green emitters is not surprising, as various types have been analyzed in chapter 4. However, we now observe a strong dominance of a single type within one sample. This result provides some suggestions on the nature of green emitters. First, as two distinct emitter types are observed in rBN, they are not related to different stacking orders but rather to different atomic structures. As the investigated rBN layer was grown via MOVPE, and based on the results discussed in the chapter 4, we suppose that both ZPLs observed in as-grown and neutron-exposed rBN originate from carbon-related defects. Indeed, the spectrum recorded from hBN flakes (HQ graphene), which were irradiated with neutrons in the same manner as the MOVPE-grown BN, does not reveal the presence of any green emitters, indicating that carbon is necessary for their formation (Figure 6.5b). However, the very strong emission at ~ 2.306 eV is observed only in the sample treated with thermal neutrons, suggesting that this particular emitter involves both carbon atoms and boron vacancies (in an unknown charge state). This result may be of key importance for future identification of green emitters in BN.

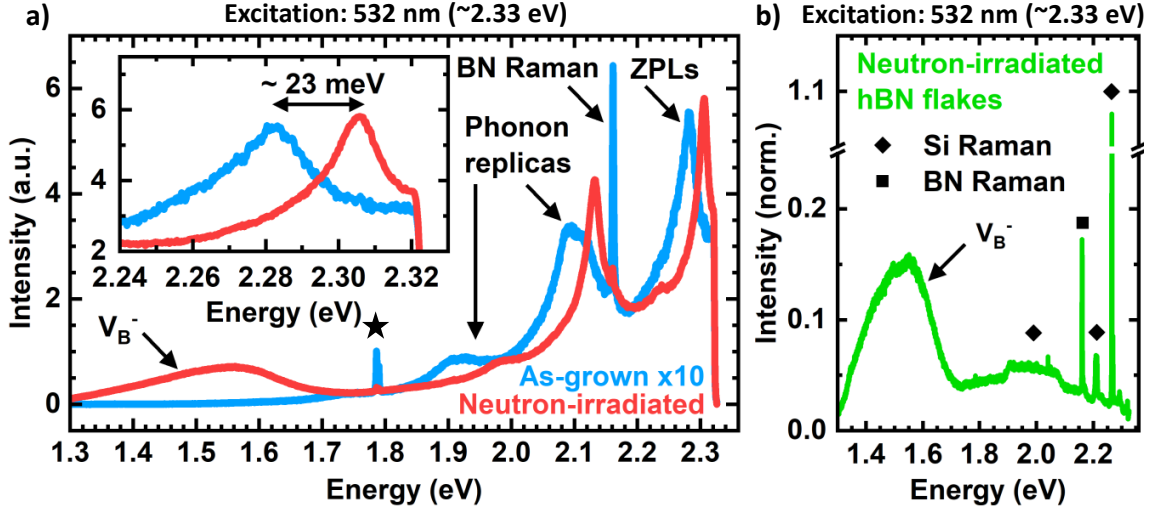


Figure 6.5: PL spectra acquired in a wide range under 532 nm laser excitation. a) As-grown (blue) and neutron-irradiated (red) rBN. The signal of the as-grown sample was multiplied by $\times 10$ for clarity. The peak marked by a star originates from Cr dopants in the sapphire substrate. Inset is a zoom on the region corresponding to green-emitter ZPLs. b) Neutron-irradiated hBN flakes transferred onto Si. Black diamonds and square mark Si and BN Raman peaks.

Next, we move to the analysis of room-temperature defect-related emission excited by a 442 nm laser beam with a power of around 10 mW. The optical setup used in the experiment was the same as for measuring green emitters. The PL spectrum recorded from as-grown rBN is presented in Figure 6.6a. The observed PL emission exhibits a characteristic multiphonon structure related to strong electron-phonon coupling. Typically, spectra that show such a behavior are well described by Huang-Rhys theory [434, 435]. This model assumes that intracenter transitions can lead to vibronic excitations, resulting in phonon replicas in the acquired spectrum. In this framework, the spectrum consists of a Gaussian-like ZPL with intensity I_{ZPL} centered at an energy E_{ZPL} . It is followed by a series of phonon replicas, separated by a constant phonon energy E_{ph} . Amplitudes of the next phonon replicas change as:

$$A_K = I_{ZPL} \cdot \frac{S^K}{K!} \cdot \exp(-S), \quad (6.1)$$

where A_K is the amplitude of the K phonon replica and S is so-called Huang-Rhys factor describing the coupling strength. Additionally, all peaks (ZPL and phonon replicas) are assumed to exhibit the same constant FWHM. Consequently, the complex spectra can be well reproduced with just 5 fitting parameters.

The acquired spectrum of the as-grown sample is well reproduced by one broad Gaussian peak centered at ~ 2.27 eV and a Huang-Rhys curve with $E_{ZPL} \approx 2.66$ eV and $E_{ph} \approx 183$ meV. The characteristic Huang-Rhys emission has been observed previously in our MOVPE-grown BN layers under 473 nm excitation and has been

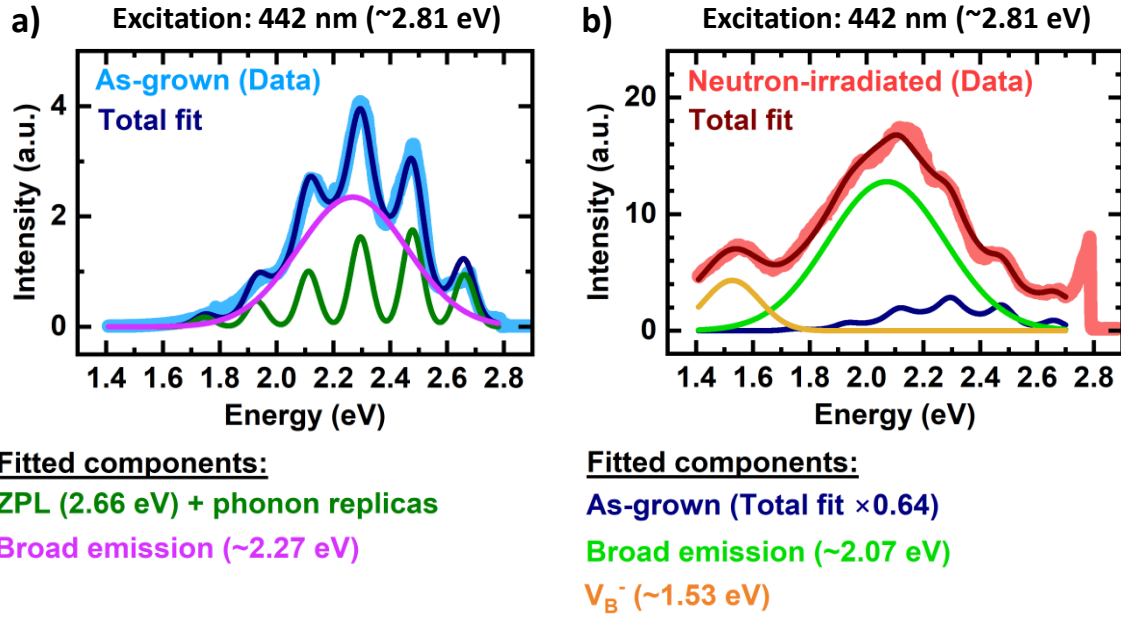


Figure 6.6: PL measurements under 442 nm laser excitation. a) Spectrum acquired from the as-grown rBN. Experimental data (light blue) are well-reproduced by a Gaussian-like broad-emission centered at ~ 2.27 eV (violet) and a Huang-Rhys structure (dark green) with fitted values of $E_{ZPL} \approx 2.66$ eV, $E_{ph} \approx 183$ meV, $S \approx 1.84$, and FWHM ≈ 80 meV. The dark blue curve is the total fit. Errors of the fitted parameters are smaller than the quoted significant digits. b) The spectrum acquired from the neutron-irradiated rBN. Below 2.7 eV, the experimental data (light red) are well reproduced by a sum of three components. The dark blue component is the total fit from a), multiplied by a factor of 0.64. The orange curve is a Gaussian centered at ≈ 1.53 eV, corresponding to V_B^- . Finally, the light-green component is a broad, Gaussian-like emission, centered at ~ 2.07 eV, attributed to DAP transitions. The dark red curve is the total fit. Errors of the fitted parameters are smaller than the quoted significant digits. Above 2.7 eV, one observes an additional emission that is not present in the as-grown material.

attributed to the presence of C_B , C_N , carbon dimers, or trimers [329]. Such an interpretation also seems reasonable for the investigated sample, which is expected to contain many carbon dopants incorporated during MOVPE growth. The broad Gaussian component may originate from structural disorder, such as rotational misalignment between adjacent layers, which spectrally broadens the emission. In particular, in our work on UV-defect related emission, Gaussian background components were also required to fully reconstruct the collected spectra [197].

The spectrum of the neutron-irradiated sample is presented in Figure 6.6b. Similar to the case of green color centers, the observed emission is a few times more intense than that recorded from the as-grown rBN. After neutron treatment, the spectrum is dominated by a strong emission fitted with a Gaussian centered at ~ 2.07 eV. According to the previous work of our group [329], in this spectral range C_B/V_B -related DAP transitions are expected. The rise of a strong PL emission after generating boron vacancies in the material that hosts carbon impurities is

consistent with this interpretation. At ~ 1.53 eV, we observe an emission associated with the presence of V_B^- centers. Here, for simplicity, it is fitted with one Gaussian. Additionally, the recorded spectrum displays Huang-Rhys-like features originating from defects formed during growth and pre-existing in the sample before neutron treatment. Therefore, the last spectral component considered is the fitted spectrum of the as-grown sample, scaled by a fitting coefficient. These three components reconstruct the acquired emission spectrum at energies below 2.7 eV. Notably, above this energy, we observe the emergence of an additional emission, which is not included in the fit. The origin of this emission is still unclear.

To study it further, in the next step, we focus on the room-temperature emission excited with a 405 nm laser beam of the power of around 50 μ W focused with a $100\times$ objective (NA=0.55). The spectra were collected using a Princeton Instruments SpectraPro HRS 750-mm spectrometer available in the laboratory of Prof. Maciej Molas. Measurements were assisted by MSc Łucja Kipczak. The spectrum acquired from the as-grown rBN is presented in Figure 6.7a. The observed emission is strikingly similar in shape to that acquired under 442 nm laser excitation; the only difference is the different energy range. Indeed, the spectrum is well reconstructed by one broad Gaussian peak centered at ~ 2.66 eV and a Huang-Rhys curve with $E_{ZPL} \approx 3.05$ eV and $E_{ph} \approx 188$ meV. As before, we associate the broad peak with the structural disorder that leads to the emission broadening. Interestingly, as shown in Figure 6.7b, when comparing the normalized Huang-Rhys components fitted for 442 nm and 405 nm excitations, we see that although the two fits yield different ZPL positions, the resulting phonon sideband structures overlap remarkably well. This result may suggest that, in both cases, we observe the same defect, while different excitation wavelengths selectively address particular phonon-assisted transitions.

As shown in Figure 6.7c, after neutron-irradiation, the intensity of the Huang-Rhys vibronic structure observed in the as-grown material decreases significantly. Instead, the spectrum is dominated by two new spectral components. First, we observe strong and broad emission that can be described as a Gaussian peak centered at ~ 2.37 eV. Similarly as for 442 nm excited spectra, this emission also appears in the range in which C_B/V_B -related DAP transitions are expected [329].

When subtracting this broad signal from the entire spectrum, we observe the appearance of a new defect with a sharp ZPL at ~ 2.88 eV, which is zoomed in Figure 6.7d. The found ZPL energy matches very well with that of B-centers in rBN flakes (~ 2.87 eV) [292] (see section 2.4.2). The spectrum of the newly formed defect reveals a series of phonon replicas accompanying the ZPL. In [292], the authors observed similar phonon sidebands at ~ 186 meV (LO), ~ 154 meV (TO), ~ 70 meV (ZO), and ~ 40 meV (ZA) below the ZPL. We marked these energies in our spectra

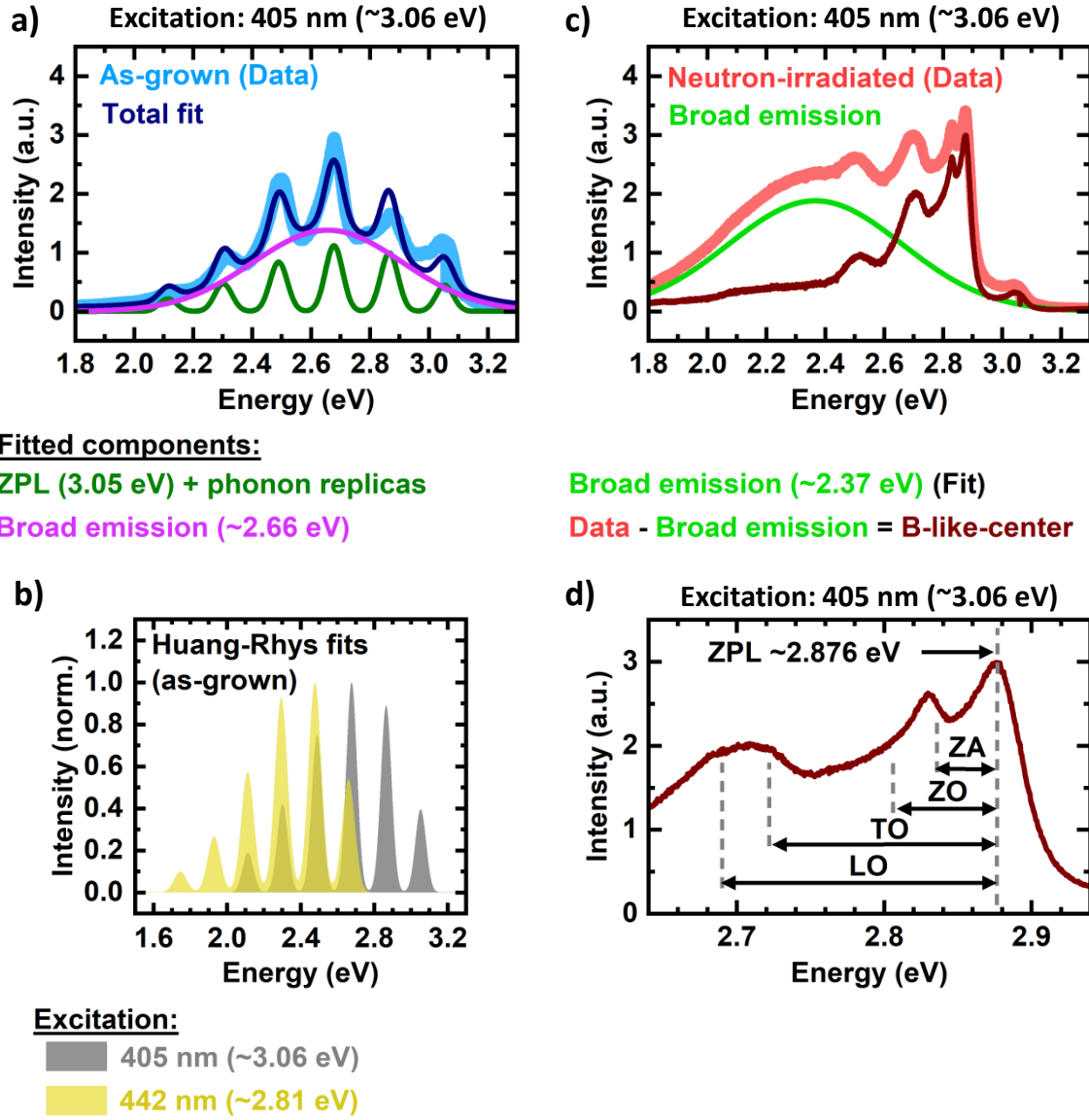


Figure 6.7: PL measurements under 405 nm laser excitation. a) Spectrum acquired from the as-grown rBN. Experimental data (light blue) are well-reproduced by a Gaussian-like broad-emission centered at ~ 2.66 eV (violet) and a Huang-Rhys structure (dark green) with fitted values of $E_{ZPL} \approx 3.05$ eV, $E_{ph} \approx 188$ meV, $S \approx 2.25$, and FWHM ≈ 70 meV. The dark blue curve is the total fit. Errors of the fitted parameters are smaller than the quoted significant digits. b) Huang-Rhys components fitted to 442 nm (yellow) and 405 nm (gray) excited spectra of the as-grown sample. c) The spectrum acquired from the neutron-irradiated rBN. The experimental data (light red) can be decomposed into a broad Gaussian centered at ~ 2.37 eV (light green) and a defect-related emission similar to that of B-centers in rBN (dark red). d) Zoom on ZPL and phonon replicas of the B-like-center. Vertical dashed lines, from right to left, mark the positions of ZPL and the expected ZA (~ 40 meV), ZO (~ 70 meV), TO (~ 154 meV), and LO (~ 186 meV) phonon replicas.

and found a very good agreement with the replicas visible in our measurements, except for the ZO phonon replica, which is absent in our case. However, it should be noted that our measurements were performed at room temperature, whereas in [292] the ZO-phonon related peak was observed at 4 K and appeared only as a very weak signal. Conversely, our spectra show a very strong peak at the position corresponding to the ZA replica, while in [292] it was relatively weak. This discrepancy may originate from the difference in the experiment geometry. The authors of [292] investigated rBN flakes, for which the excitation beam was always incident parallel to the c -axis. In contrast, our rBN is a polycrystalline material with randomly oriented crystallites. Therefore, during the measurements, we simultaneously probe the sample response under various excitation geometries, which may lead to different transition probabilities for individual phonon-assisted channels. Interestingly, the energy of this particular peak also coincides with the ZPL energy reported for the B-center in hBN (~ 2.83 eV). Nevertheless, such an interpretation appears unlikely in our case, since the investigated material is primarily rBN.

As discussed in section 2.4.2, the formation of B-centers is accompanied by a decrease in UV emitter concentration [293, 294, 297]. Therefore, to assess whether the hypothesis of B-center formation in neutron-exposed rBN is plausible, we conducted PL measurements in the UV range. The PL spectra of as-grown and neutron-irradiated rBN were acquired by Prof. Krzysztof Korona using a Princeton Instruments Acton SP2300 spectrometer. PL emission was excited using the 3rd harmonic of a Ti:sapphire laser (288 nm) generated with two β -BaB₂O₄ crystals and focused with a Schwarzschild objective. During the measurements, the samples were mounted in a Cryovac Konti cryostat and cooled down to 8 K. The acquired spectra are shown in Figure 6.8. We observe that the neutron treatment of rBN results in a drop in 4.1 eV defect emission intensity by a factor of ~ 5 . This observation supports the hypothesis of neutron-induced B-center formation, which, notably, is in direct conflict with the current understanding of how these emitters are formed. Up to now, the only reported procedure of B-center formation is BN electron-exposure. According to the current model, B-center formation is believed to result from the restructuring of UV defects (carbon dimers) through bond breaking induced by electron–electron collisions and the subsequent migration of ionized atoms in the electric field of the electron beam [293, 294]. Further studies are required to determine if the observed emission at ~ 2.88 eV indeed originates from B-centers. If so, the current model of their formation would need to be reconsidered, as neutrons do not generate the electric field required to drive the migration of ionized species. Additionally, this would offer a completely new perspective on BN-based quantum devices, as neutron irradiation could potentially enable the simultaneous generation of quantum sensors (V_B^-) and blue SPEs in the same material in a single process.

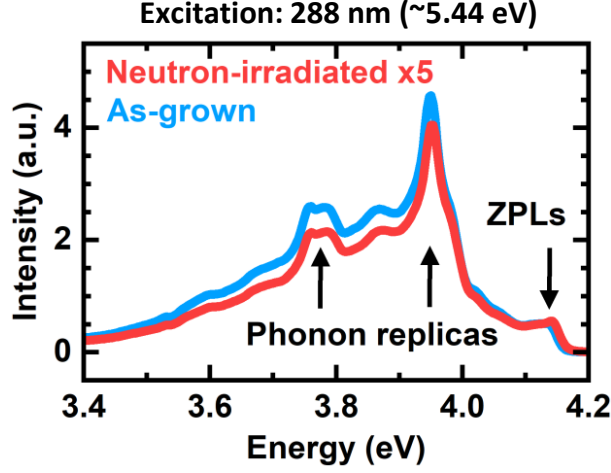


Figure 6.8: UV-range PL spectra of as-grown (blue) and neutron-irradiated (red) rBN acquired at 8 K under 288 nm laser excitation. The signal of the neutron-exposed sample was multiplied by $\times 5$ for clarity.

6.5 Conclusions

In summary, we have investigated color centers that form in MOVPE-grown rBN under neutron irradiation. First, we have shown that neutron treatment of our material leads to the formation of V_B^- centers, as previously reported for hBN flakes. We have also performed temperature-dependent studies of their emission. The results may contribute to the development of an accurate theoretical description of the V_B^- center emission in ABC-stacked BN, where lattice vibrations play a crucial role.

Next, using various excitation wavelengths, we investigated the influence of rBN neutron treatment on defect-related emission in the visible-UV range. The results clearly demonstrate that, except for V_B^- generation, neutron irradiation may also significantly affect other BN-based quantum emitters. First, neutron treatment has been shown to induce the formation of new green emitters not present in the as-grown material, suggesting a crucial role of complexes containing both carbon dopants and boron vacancies. It offers an interesting perspective on BN-based devices that could host both V_B^- centers for quantum sensing and green emitters formed via a single process. Additionally, neutron exposure led to the emergence of broad emission peaks within the range 2.0-2.4 eV, which, according to the previous work of our group, might originate from C_B/V_B -related DAP transitions [329]. Finally, we have demonstrated the neutron-induced formation of blue emitters, whose ZPL closely matches that of B-centers in rBN. Their generation is accompanied by a decrease in the intensity of UV defect emission. This observation strongly supports the hypothesis of B-center generation; however, further studies are required to verify the nature of the newly formed defect. Should this hypothesis be confirmed, it would

challenge the current model of the B-center formation mechanism, which assumes a crucial role of the electric field that drives the transport of charged species. It could also enable the design of BN-based devices hosting both quantum sensors (V_B^- centers) and B-centers formed in a single process.

Chapter 7

Summary and Prospects

In this work, we explored quantum emitters in large-area MOVPE-grown BN, which, in contrast to small exfoliated flakes, reveal the potential for future applications. The scope of the research discussed covers fundamental studies of the nature and properties of the emitters, as well as their engineering during growth, post-growth modifications, and the development of a new strategy for emission enhancement.

First, we demonstrated that high-quality epitaxial BN provides an ideal platform for SPEs emitting at room temperature in the green spectral range and subsequently investigated their optical properties, including spectral distribution, emission purity, and phonon-mediated broadening. Through detailed statistical analysis of emitter spectral properties, we demonstrated the existence of at least three distinct types of green-emitting centers, which may differ in their atomic structure or the symmetry of their local environment.

Potential applications utilizing BN-based green SPEs require control over their formation. To address this issue, we analyzed the influence of various technological growth parameters - temperature, TEB flow rate, and BN thickness - on the formation and properties of the emitters. Our findings demonstrate that a growth temperature as high as 1400 °C is necessary to form well-isolated, bright color centers. As the material becomes thicker, the SPEs exhibit higher stability because the topmost BN layers shield point defects embedded in the inner planes from the influence of the environment. We further demonstrate that the last analyzed technological parameter, the TEB flow rate, affects emission purity. Namely, after reaching a threshold value, we observe a crossover from the growth regime favoring formation of high-quality SPEs to a regime in which most formed emitters do not satisfy the $g^{(2)}(0) < 0.5$ condition. These results impose quantitative limits on technological parameters, making a valuable contribution to the engineering of further BN-based quantum devices.

While the excellent properties of quantum emitters are required for applications, another key aspect is their concentration. Its engineering is not straightforward

because BN thickness and TEB flow both affect the density of green SPEs. The observed correlation between the concentration of green-emitting centers and the TEB flow rate suggests that carbon-related impurities play a key role in their formation. To simplify the optimization of emitter density, based on experimental observations, we introduced a simple model of defect formation. Within the developed framework, the emitter density is described by a single effective parameter that incorporates both the BN thickness and the TEB flow rate. Since the emitter concentration reaches its maximum at a specific value of this parameter, the BN thickness corresponding to the maximum emitter concentration can be readily calculated for any given TEB flow rate. Therefore, the introduced model significantly facilitates the engineering of quantum devices based on green SPEs in BN. While quantitative results are specific to our BN growth procedure, the demonstrated strategy for controlling emitter concentration can also be applied by other groups. Notably, the observed correlation between the concentration of green-emitting centers and the TEB flow rate suggests that carbon-related impurities play a key role in their formation.

In the next part, we investigated bubbles induced in MOVPE-grown BN via electron exposure. This formation method is limited to epitaxial BN, as it requires the presence of wrinkles that provide channels for water intercalation. Due to a specific formation mechanism, based on detaching consecutive mesh units of the wrinkle pattern, the explored bubbles exhibit extraordinary mechanical properties that cannot be described by common theories. We demonstrated that bubble formation results in a significant enhancement of BN-based color center emission. We proved that this phenomenon is caused neither by the electron irradiation itself nor by the strain within bubbles. Instead, we showed that the enhancement is governed by interference-like effects occurring between bubbled material and a substrate. Notably, this strategy for increasing SPE intensity does not require material transfer, thereby avoiding the risk of material damage or contamination. In fact, it can be applied directly to large-area material. Obviously, to utilize this effect in applications, precise control of bubble position and size is required. To address this issue, we developed the mask-assisted strategy of bubble generation. By applying lithographically fabricated masks to BN prior to e-beam exposure, we achieved regular bubble arrays. Although future optimization of electron-exposure parameters and mask fabrication is still necessary, the presented results constitute a first step toward the scalable, transfer-free fabrication of regular bubble arrays for SPE enhancement.

Finally, we investigated the formation of defects in MOVPE-grown rBN under thermal neutron treatment. This procedure is commonly used to fabricate V_B^- centers in exfoliated BN flakes. We demonstrated that in the case of carbon-doped

epitaxial material, neutron irradiation introduces additional defects, suggesting the crucial role of boron vacancies in their formation. In particular, for the first time, we observed neutron-induced generation of blue emitters. Notably, up to now, the only known mechanism leading to their formation was e-beam exposure. If further studies demonstrated that both neutron- and electron-induced blue emitters arise from the same defect, the current model of their formation, which suggests the crucial role of the e-beam electric, would need to be reconsidered.

We believe that our results on growth parameter manipulation and on bubble-mediated emission enhancement will contribute to the development of quantum devices utilizing SPEs in large-area epitaxial BN. Parallely, we hope that our findings on the presence of various types of green emitters and on new neutron-irradiation-based mechanisms of color center formation will stimulate further fundamental studies concerning the nature of point defects in BN.

Academic Achievements

Author Metrics

The author has contributed to 10 published scientific articles and 1 preprint. Additionally, 3 articles related to the thesis are in preparation. According to Scopus, the author was cited 77 times, and his h-index is 6.

Publications Related to the Thesis

P. Tatarczak, T. Fąs, J. Pawłowski, A. K. Dąbrowska, J. Suffczyński, M. Tokarczyk, P. Wróbel, A. Wysmolek and J. Binder, “*Deterministic hBN Bubbles as a Versatile Platform for Studies on Single-Photon Emitters*”, Adv. Funct. Mater. 36, no. 24 (2026): e26312

B. Kaczmarek, **P. Tatarczak**, A. K. Dąbrowska, J. Binder, A. Wysmolek, “*Strong coupling of visible color centers in epitaxial hBN with out-of-plane phonons revealed by temperature-dependent photoluminescence*” - in preparation

P. Tatarczak, T. Fąs, A. K. Dąbrowska, B. Kaczmarek, G. Szwed, J. Iwański, M. Tokarczyk, J. Suffczyński, A. Wysmolek and J. Binder, “*Green single-photon emitters in MOVPE-grown BN: properties and engineering*” - in preparation

P. Tatarczak, T. Fąs, A. K. Dąbrowska, M. Tokarczyk, Ł. Kipczak J. Suffczyński, M. Molas, J. Binder and A. Wysmolek, “*Defect formation in carbon-doped MOVPE-grown BN irradiated with thermal neutrons*” - in preparation

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M. Grochowska-Tatańczak, **P. Tatańczak**, A. K. Dąbrowska, M. Tokarczyk, M. K. Dudek, J. Binder, A. Wyszmołek, and K. Kazimierzczuk, “*Experimental and computational ^{11}B NMR comparative study of MOVPE-grown rhombohedral and bulk hexagonal boron nitride*”, ChemRxiv. 15001103 (2026).

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Projects

Principal Investigator, NCN PRELUDIUM 21: *“Deterministic activation of single-photon emitters in hexagonal boron nitride”* (2022/45/N/ST7/03355), 2023 - 2027.

PhD Student Scholarship-Holder, NCN SONATA 16: *“Single photon emitters and innovative optical cavities based on epitaxial hexagonal boron nitride”* (2020/39/D/ST7/02811), 2021 - 2024.

Student Scholarship-Holder, NCN OPUS 17: *“Epitaxial boron nitride - universal platform for novel van der Waals structures”* (2019/33/B/ST5/02766), 2020 - 2021.

Oral Presentations

“Bubbles in MOVPE BN for quantum emitters”, Nanophotonics of 2D Materials, Toruń, Poland, 2025.

“The impact of carbon impurity concentration on the properties of single photon emitting defects in epitaxial hBN”, International School & Conference on the Physics of Semiconductors Jaszowiec, Szczyrk, Poland, 2024.

“Single-photon emission from hBN activated by deterministic bubble formation”, Defects in Solids for Quantum Technologies, Budapest, Hungary, 2024.

“hBN bubbles as a tool for deterministic activation of single-photon emission”, 14th International Conference on Nitride Semiconductors, Fukuoka, Japan, 2023.

“hBN bubbles – a way of deterministic activation of single-photon emission from defects in hBN?”, 36th European Conference on Surface Science, Łódź, Poland, 2023.

“hBN bubbles – a step towards deterministic activation of single photon emission”, International School & Conference on the Physics of Semiconductors Jaszowiec, Poland, 2023.

Poster Presentations

“Single-photon emitters in BN - formation, tuning and signal enhancement”, International Nano-Optoelectronics Workshop, Wrocław, Poland, 2025.

“Tuning MOVPE BN properties for quantum light applications by changing precursor flow”, Boron Nitride Workshop, Nashville, USA, 2025.

“How does the carbon impurity concentration affect single-photon emitters in epitaxial hBN?”, Graphene Week, Prague Czech Republic, 2024.

“Impact of bubble creation on optical properties of h-BN”, Boron Nitride Workshop, Montpellier, France, 2023.

“Photoluminescence correlation studies of defect-related transitions in MOVPE h-BN”, International School & Conference on the Physics of Semiconductors Jaszowiec, Szczyrk, Poland, 2022.

“Dramatic reduction of the interaction between MOVPE h-BN and sapphire induced by wrinkle formation – Raman spectroscopy studies”, International Workshop on Nitride Semiconductors, Berlin, Germany, 2022.

Patents

Pat.246379: “Sposób wytwarzania zwierciadeł Bragga w pojedynczym procesie oraz zwierciadło Bragga wytworzone sposobem”.

Awards

Best Student Award at the 14th International Conference on Nitride Semiconductors ICNS-14 (Fukuoka, Japan, 2023), for the presentation “hBN bubbles as a tool for deterministic activation of single-photon emission”.

Best poster award at International Workshop on Nitride Semiconductors (Berlin, Germany, 2022), for the poster “Dramatic reduction of the interaction between MOVPE h-BN and sapphire induced by wrinkle formation – Raman spectroscopy studies”.

Commendation for Exemplary Teaching, Faculty of Physics, University of Warsaw — Winter Semester 2021/2022.

Research Internships

Three-month scientific visit in the group of Prof. G. Cassabois and Prof. B. Gil (Charles Coulomb Laboratory, University of Montpellier) funded by The Excellence Initiative - Research University (IDUB), (03.2023 - 05.2023).

One-month internship in the group of Prof. Cz. Skierbiszewski (Institute of High Pressure Physics of the Polish Academy of Sciences), (09.2020 - 10.2020).

Other

Co-supervisor of the Bachelor in Science thesis at the Faculty of Physics, University of Warsaw: *“Influence of TEB flow on the properties of carbon-related colour centres in MOVPE grown hBN”*, (2025).

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