Quantum emitters in low dimensional
van der Waals systems

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1 Summary

Recent years have seen the discovery of new types of semi-conductors with the maturation of fabrication techniques and further understanding of traditional ‘three dimensional (3D)’ semi-conductors such as silicon and diamond. The term ‘3D’ is coined due to the dominant covalent/ionic bonds which bind the crystal and prevent isolating a monolayer from the bulk. The discovery of Van der Waals two dimensional (2D) graphene was the dawn of research on 2D materials however it was soon realized that graphene lacks a sizeable band-gap, exhibiting unusual electron transport properties, but made it less suited for optical research. The search was on for new materials that can retain the desired Van der Waals two dimensionality while possessing a band-gap. Research on 3D semi-conductors has already revealed the importance of atomic point like defects which can govern important phenomena from the quality of electrical transport to trapping excited electrons and holes and thus quenching optical fluorescence through different decay mechanisms. In addition, point defects can also be beneficial as they can serve as single photon emitters upon excitations. Experiments on well understood wide band-gap crystals soon lead to the understanding on methods to engineer isolated atomic point defects deep within the band-gap and how to manipulate the electrons trapped at the defect site though optical excitation, magnetic and electrical fields as well as by applying microwaves. A classic example of this is the nitrogen vacancy defect in diamond. Back in the 2D realm different materials with large band gaps range were soon fabricated. The large surface area of a single mono-layer crystal hints to the ease and vulnerability at which a 2D material can acquire various defects either due to mechanical deformation, oxidation, vacancy formation or addition of chemical groups via its proximity to the environment, special handling techniques or deliberate doping. In essence one can think of these materials as an ‘all surface smooth crystal’, typically lacking dangling bonds with the exception to the material’s edges. However, this also allows easier access to a desired atomic lattice site one can think of modifying. If atomic like point defects with similar optical properties to those that are well understood in 3D crystals can be engineered in 2D materials consisting only of a single monolayer, this would open a whole new playing field for optical excitation of deep intra band-gap point defects. For example the proximity of the environment can be advantageous due to the expected increased sensitivity of a para-magnetic point defect to magnetic fields in its proximity. One can envision an engineered point defect as a magnetic sensor using optical detected magnetic resonance (ODMR), similar to that achieved with the nitrogen-vacancy in diamond without the limitation of a minimal distance to the diamond’s surface, thus circumventing the distance “glass ceiling” restriction to the desired probing region arising from three dimensionality. Furthermore, point defects in 2D materials that emit single photos upon excitation should have less light scattering and could be more easily fabricated into tailored nano-structures.
enhancing light collection efficiency. This quantum light can be for example beneficial for entanglement experiments which require a high frequency flux of photons. Thus the merger of intra-band point defect excitation of wide band-gap 2D semiconductors holds many promising functionalities arising from the reduced dimensionality which are not easily accessibly in their 3D counterparts. The aim of this work was to better understand the generation of single photon emitters from semiconducting wide band-gap low dimensional materials, 2D and 1D, through characterizing their optical properties and handling methods with the aim to search for a para-magnetic single photon source. Thus exploiting the possibility to excite states that should be embedded inside the band-gap. This is a new emerging field, and as such, the road for full control and understating of point defects in 2D materials at the time of writing this work is still pre-mature and thus only at its first steps.

In Chapter 2 we introduce information regarding to optical excitation of emitters, point defects in crystals followed by material and optical properties of 2D and 1D crystals. We outline the heterostructure possibilities that arise from combining different 2D materials. Since intra-band gap optical excitation of Van der Waals materials is a relatively new field, the chapter contains a brief literature survey from various sources. The literature information on Van der Waals materials is vast and hard to compress, therefore the focus is on properties important for understanding intra-band excitation.

The achievements of this work encompass numerous aspects, from 2D quantum emitter characterization to discovery of quantum emitters in 1D up to observation of magneto-optic quantum emitters in 2D and observation of ODMR.

In Chapter 3 we demonstrate two methods for generating emitters in h-BN are presented with linkage shown between perimeters in 2D h-BN to the spatial location were emitters are formed. Similar spectral features are present in quantum emitters from bulk down to the mono-layer limit, with comparable optical FWHM. Emission wavelength color diversity and photo stability under ambient conditions and in monolayers is also demonstrated. We conclude that the spectral features are dominated by the interaction of their electronic transition with a single Raman active mode of h-BN.

In Chapter 4 we explore the role curvature can play for the formation of quantum emitters in h-BN. We observe that non-treated ‘out of the box’ 1D boron nitride nanotubes (BNNTs) are an abundant source of stable QEs and analyze their emission features down to single nanotubes, comparing dispersed/suspended material. With the use of high spatial resolution of a scanning electron microscope, we categorize and pin-point emission origin to a scale of less than 20 nm, giving us a one-to-one validation of emission source. We identify two emission origins emerge: hybrid/entwined BNNT. We artificially curve 2D h-BN flakes and observe similar QE spectral features highlighting there
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role in emitter formation. The impact on emission of solvents used in commercial products and curved regions is also demonstrated.

In Chapter 5 we demonstrate for the first time ODMR on a two dimensional van der Waals material. We give a detailed emitter analysis, exploring PL features at 8.5K at various temperature cycling and polarization absorption properties. We gain further insights on the electronic structure and phonon coupling of the emitter which can help to pin point in more precision its exact chemical nature. Comparing observed electron spin resonance hyper-fine coupling frequencies to our observed ODMR line-width allows us to discard some candidates from the defect list narrowing the list to a defect which nature originates from a low atomic number defect.

Finally, Chapter 6 is an appendix with research on other 2D materials and hetero-structures dedicated to initial investigation of 2D SnS$_2$/HfS$_2$/GeS and the combination of some of these 2D materials into hetero-structures is explored.
1. Summary

Zusammenfassung


1. Summary

eine „glas-artige“ Oberfläche des 3D-Kristalls direkt Kontakt zwischen Sonde und Probe verhindert. Darüber hinaus sollten Punktdefekte in 2D-Materialien, die bei Anregung einzelne Fotos emittieren, weniger Lichtstreuung aufweisen und leichter zu maßgeschneiderten Nanostrukturen verarbeitet werden können, was die Lichtsammlungseffizienz verbessern. Dieses Quantenlicht kann beispielsweise für Verschränkungsexperimente nützlich sein, die einen hohen aber sub-Poissonischen Photonenstrom erfordern. Die Verbindung aus Intra-Band-Punktdefektenregung von 2D-Halbleitern mit großer Bandlücke birgt daher viele vielversprechende Funktionalitäten, die sich aus der reduzierten Dimension ergeben. Ziel dieser Arbeit ist die deterministische Erzeugung von Einzelphotonenemitttern in van der Waals Materialien mit breiter Bandlücke und geringen Abmessungen (2D und 1D) und die optischen Charakterisierung von Einzelphotonenquelle in Hinblick auf ihre Anwendung als magnetooptisch aktive Defektzentren.


In Kapitel 4 wird die Rolle der Krümmung einzelner Monolagen für die Bildung von Quantenemitttern in h-BN erörtert. Es wurde festgestellt, dass unbehandelte 1D-Bornitrid-Nanoröhren (BNNTs) eine
1. Summary


Schließlich enthält Kapitel 6 einen Anhang mit Untersuchungen zu anderen 2D-Materialien und Heterostrukturen, die der anfänglichen Untersuchung von 2D-SnS$_2$/HfS$_2$/GeS gewidmet sind, und es wird die Kombination einiger dieser 2D-Materialien zu Heterostrukturen untersucht.
2. Introduction and basic concepts

A quanta of light, single photons, are important building blocks for various optical data based devices. Quantum light can be generated by exciting various systems. A well-studied example of such a system is the quantum dot that involves generating excitons which can emit single photons upon recombination. Nevertheless, quantum dots are problematic due to constraints on temperature operation, broad line-widths and emission intermittency. Of significant importance are solid state systems which have optically addressable electrons at defective sites which are protected states inside the band-gap of a semi-conductor and are highly localized, thus with a wavefunction confined on the atomic scale. Atomic sized point defects in solid crystals such as diamond, silicon carbide and zinc oxide are examples of systems that can host localized electrons near defective points. Quantum dots, which consist of thousands of atoms, have similar optical properties similar to single atoms, but have in comparison a non-localized wavefunction, due to confinement on the nano-scale range, encompassing thousands of atoms. Others systems capable of emitting quantum light are molecular systems embedded inside a host matrix. Quantum light, with the use of entangled photons, has been applied to reduce the resolution of lithography, super-resolution and even to measure the concentration of a blood protein. Thus, quantum light enables reducing the spatial resolution limit from the shot noise to the Heisenberg limit. 3D semiconducting crystals have been in the forefront of research for identifying optically active atomic point defects (color centers) with states within their band-gap for utilizing the system’s transitions for generating single photons. 2D van der Waals crystals, as opposed to traditional 3D crystals, are connected through the layers only by the weakly interacting van der Waals force. This weak force, enables single layer (monolayers) isolation of the semiconducting crystal can be isolated through mechanical and chemical exfoliation. This chapter outlines the techniques used for optically probing single photon defect sources, comparing to those well established in well-known crystals. The differences between intra-band gap quantum emitters to quantum dots is also outlined. An overview on the variety of low dimensional materials is given from 2D van der Waals crystals to 1D nano-tubes. Finally the potential to build custom made devices using 2D hetero-structures is also explained.

2.1 Optical excitation and detection

Optical excitation of deep state point defects in crystals depends on the ability to easily access states protected inside the band-gap with energy equal or above the energy difference between the ground state and excited state while avoiding band to band excitation. In this sense it is advantageous to have the optical excitation pathway configured in such a manner that with relative ease lasers with different energies can be coupled in, especially due to the relatively narrow band-gap of 2D materials of the TMDC family (\(< 2.5 \text{ eV}\)). This can be achieved using a wedge prism which at certain angles will reflect
a broad range of wavelengths. The tradeoff however, is the loss of laser excitation power due to the reduced/enhanced reflection/transmission of the wedge on a broad spectral range, in this case N-BK7 (high purity borosilicate-crown glass). Nevertheless, due to the relatively high brightness of some point defects in 2D crystals (such as in h-BN) and due to the thin (2D) nature of the material which reduces light scattering and total internal reflection, excitation powers in the range of $\sim 100 \mu W$ are sufficient for primary investigation using an air objective with an NA of 0.95. A confocal microscopy setup has the advantage of reduced background. In this configuration, the pinhole rejects light that is not originating from the focal plane. A schematic of the optical setup is depicted in Figure 2.1.

2.2 Single molecule excitation

Single molecule spectroscopy commonly involves exciting an organic (carbon based) molecule embedded in a solid crystal matrix. Carbon can form hybridized orbitals which result in rich chemical diversity. Of these, poly-aromatic molecules represent the most stable molecular configuration due to $\pi$-electrons delocalized over the molecule. These are thought to be the most abundant organic molecules in the universe. The abundance of organic molecules in the day to day laboratory work due to intentional use or contamination is therefore of significant importance, especially when dealing with 2D high surface area materials. The first reported single molecule spectroscopy was done using...
pentacene (Pc) embedded in a p-terphenyl crystal. Single molecule excitation can be achieved with state-of-the-art scanning tunneling microscopy (STM) which relies on electrical excitation, or optical excitation. Electrical excitation in principle can result in ångström resolution, due to the short wavelength of the electron (~ 0.5 nm).

Due to the two dimensional nature and high surface area of Van der Waals material, this model of an organic emitter embedded in a 2D crystal matrix is also a valid picture to interpret single quantum emission in van der Waals materials as will be shown. Figure 2.2 depicts abundant organic molecules such as corenene and pentacene, with photo-luminesce spectra and anti-bunching measurements,
2. Introduction and basic concepts

proving the quantum nature of light that can be emitted from these molecules, as will be explained below. The similar atomic weight of organic molecules, primarily composed of carbon, compared to boron and nitrogen (of which h-BN is composed), can also cause resembling wavenumber optical phonons. Therefore, for work with 2D materials, for correct identification of emitter origin, it is vital to work in an organic free environment.

2.3 Band-gap semiconductors and point defects

2.3.1 Point defect orientation in crystals

Point defects in a crystal, assuming they occupy lattice sites and are not at interstitial sites (sites located between the lattice sites), should have an axis of symmetry. The well-studied principles of studies on polarized light emitted by organic molecules also apply for point defects in crystals and can be utilized to determine the point defect’s axis of symmetry. Pioneering work in this field was first done on centers in CaF$_2$, NaF, LiF and diamond.$^{10}$ An allowed electric dipole transition consists of two types: one corresponds to $\pi$-oscillators and the other to $\sigma$-oscillators. $\pi$-oscillators are an s-p$_z$ transition and have an intensity proportional to $\cos^2(\theta)$, with the angle $\theta$ between the dipole (D) and the E vector of the exciting light, whereas the latter are s-p$_x$,p$_y$ transitions and are proportional to $\sin^2(\theta)$. $^{11}$ $\sigma$-transitions are associated with two dipoles, having an XY dipole. On the other hand, $\pi$-transitions are associated with a single dipole (Z dipole). $^{12}$

![Figure 2.3: Polarization measurements on single defects in a ZnO crystal.](attachment:figure2.3.png)
2. Introduction and basic concepts

2.3.2 Optical excitation of single emitting point defects in semiconducting crystals

The superior high resolution imaging achieved using electronic excitation (STM or cathodoluminescence) can be disadvantageous when studying single point defect emission, due to the high energy involved, which can make it more difficult to isolate confined intra band-gap states and can cause multiple-excitation. This can be counterproductive for the study of point defects' quantum photo-luminescence and level scheme transition rates. For example, cathodoluminescence, despite its superior spatial resolution, gives rise to a range of primary excitations, plasmons and electron-hole pairs with varying energy, where one can detect synchronized emission from multiple defects via one electron excitation, obscuring a single defect emission. Therefore, using a laser excitation source with energy lower than the band-gap, avoiding exciton and plasmon generation, can be used to probe intra band-gap states. A verification of the single quantum emitting nature of a point defect can be achieved using the Hanbury-Brown and Twiss (HBT) configuration. In this configuration photons are registered by two photo detectors which are previously split by a 50:50 beam splitter therefore enabling the arrival of only one photon at a given time slice to the detectors, assuming the emission source is a single quantum emitter. Used in a start-stop mode in this configuration, one can record a histogram of time intervals between two consecutive single photon detections. Assuming the photon detection rate is greater than the decay rate from the excited state, one can record the second-order correlation function \( g^2(t) \). Pioneering work has shown the validity of this method for single atomic ions. In a typical anti-bunching measurement of a point defect, usually at time delay 0 sec, the measurement does not dip exactly to zero due to background light, Raman scattering, excitation light that passes through the optical filter, high transition decay rates beyond the sensitivity of the detectors or the dark counts of the detectors. In addition, typically bunching behavior is seen which is manifested as values of \( g^2(t) > 1 \), resembling long “shoulder” like curves. This behavior has been observed for single organic molecules and the NV center in diamond, indicating an additional metastable state in the photo-excitation cycle. Analysis of this bunching behavior can reveal the lifetime of the metastable and intersystem crossing (ISC) rates. It is worth noting that this analysis is only valid as long as there is no emission intermittency of the emitter - i.e. consistency of emission with no stepwise abrupt switching (blinking) to less/higher emission counts/rates, which can be due to different emitter charge states or local environment fluctuations. The correlation function is power dependent and can be expressed with a rate equation for a three-level model.

\[
\begin{pmatrix}
\dot{\rho}_1 \\
\dot{\rho}_2 \\
\dot{\rho}_3
\end{pmatrix} =
\begin{pmatrix}
-k_{12} & 0 & 0 \\
k_{12} & -k_{21} - k_{23} & 0 \\
k_{23} & k_{32} & -k_{32}
\end{pmatrix}
\begin{pmatrix}
\rho_1 \\
\rho_2 \\
\rho_3
\end{pmatrix}
\]
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With the initial conditions, \( \rho_1 = 1, \rho_2 = \rho_3 = 0 \) for the system prepared in the ground state \( 1 \). \( k_{12} \) is the pump rate coefficient, \( k_{21} \) the fluorescent decay coefficient and \( k_{32} / k_{32} \) shelving state by coefficient. Non-radiative transitions from the shelving state \( 3 \) are neglected. The photon emission probability is proportional to \( \rho_2(t) \) and an expression for \( g^2(t) \) is obtained by normalizing \( \rho_2(t \to \infty) \) resulting in:

\[
g^{(2)}(t) = 1 + c_2 e^{-t/\tau_2} + c_3 e^{-t/\tau_3}
\]

The decay time and coefficients are given by:

\[
\tau_{2,3} = \frac{2}{A \pm \sqrt{A^2 - 4B}}, \quad c_2 = \frac{(1 - \tau_2 k_{32})}{k_{32}(\tau_2 - \tau_3)}, \quad c_3 = -1 - c_2
\]

with:

\[
A = k_{12} + k_{21} + k_{32} + k_{23}, \quad B = k_{12} k_{23} + k_{12} k_{32} + k_{21} k_{32}
\]

When anti-bunching is observed the number of emitters involved in the process at time zero should obey (without background contributions) \( g^{(2)}(0) = 1 - \frac{1}{n} \), with the special case of a single emitter \( g^{(2)}(0) = 0 \) or with background contributions \( g^{(2)}(0) < 0.5 \).
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Figure 2.4 depicts the difference of the $g^{(2)}(t)$ function when causing multiple excitations and a single excitation.

![Figure 2.4: $g^2(t)$ function differences through different excitation energies. (a) Cathodoluminescence $g_2(t)$ function for ~900 NV’s in nano-diamonds and defects in boron nitride, synchronized emission from numerous defects is noted in the pronounced bunching at time zero (b) Intra-band gap laser excitation using a 532 nm laser $g_2(t)$ function for a single defect in boron nitride. The $t \sim 0$ sec dip registers below the 0.5 value, unveiling the single nature of the emitted light.](image)

2.3.3 Point defect charge states

Different charge states of single point defects in a semiconductor can affect defect structure, thermal diffusion rates, trapping rates of electrons and holes and luminescence quenching rates. Native defects can be defined as vacancies, interstitials, an excess of native atoms in the lattice and anti-site defects. These almost always have a neutral charge state due to unsaturated bonding capabilities that facilitate transfer of electronic charge between the host matrix and the defect. Some defects possess significant capacity to store charge within their structure, such as monovacancies in silicon which incorporate four unsaturated dangling bonds, permitting charge states ranging from -2 to +2.

The degree and direction of electron transfer – away or towards the defects (donor / acceptor) depends on the electronic richness of the host semi-conductor. Using electron paramagnetic resonance (EPR) one can deduce the defect’s symmetry, atomic and lattice configuration with the stringent conditions of high concentration of same defect species and long spin-lattice relaxation times.

Surface defects, abundant in 2D materials, can be detected using scanning tunneling microscopy (STM) and transmission electron microscopy (TEM). Point defects induce localized perturbations that give rise to shallow or deep ionization levels in the band gap, voltage dependent depressions surrounding STM imaged surface defects serve as charge state signatures. Surface defect charge states are typically less stable than charge states in the bulk. The geometry and structure of charged defects depend on
crystal lattice structure, for example in crystals with small lattice parameters such as those comprised of atoms with large atomic radii the concentration of interstitial defects should be significantly less.  

A defect’s charge state is of great significance when optically exciting it with sub band-gap excitation, since the state can determine if the defect will behave as a paramagnetic center. A well-known example of this is the NV$^0$ and NV$^1$ charge states, where the -1 charge state is paramagnetic and the 0 charge state is not.

### 2.3.4 Zero phonon line and phonon side band

The electronic band-spectra due to defects in crystals typically display a resonant peak, which is analogous to the Mössbauer effect, associated with zero-phonon (ZPL) transitions.  

These are transitions in which a photon is absorbed without transfer of energy to the lattice phonons and should appear as photo-luminescence lines, which in the ideal crystal at absolute zero temperature should have a width determined only by the lifetime of the excited electronic state. Therefore ZPL peaks have usually three photo-luminescence characteristic properties as a function of temperature: the relative strength, shape, and shift in position and width. The excited state lifetime of the ZPL has a lifetime of $\tau_1$ and the full width at half maximum (FWHM) should be $\gamma_0 = \frac{1}{\tau_1}$. Upon increasing temperature, the thermal motion of the lattice increases and causes a line broadening. Multi-phonon processes give a band typically with a width on the order of the Debye frequency or greater typically designated as the phonon side band (PSB). The Debye-Waller factor gives the relative intensity of the ZPL to the total emission intensity. The probability of an optical transition from the ground state $S_0$ to the excited state $S_1$ is given by Fermi’s golden rule:

$$P_{10} = \frac{2\pi}{\hbar} |\langle \psi_1 | \hat{H}_{rad} | \psi_0 \rangle |^2 g(E - E_1)$$

With $\psi_0$ the electronic wave function of the ground state $S_0$, $\psi_1$ the wave function of the excited state and $g(E - E_1)$ the normalized absorption line shape. $\hat{H}_{rad}$ characterizes the interaction of the emitter with the radiation field of the light source (Stark shift):

$$\hat{H}_{rad} = -\mu \cdot \vec{E}(t)$$

These equations show that the transition probability $P_{10}$ is proportional to the square of the transition dipole moment $\mu_{10} = \langle \psi_1 | \vec{\mu} | \psi_0 \rangle$ where $\vec{\mu}_{10}$ is related to the oscillator strength $f_{10}$. The relative intensity of the electron-vibration bands is given by the Franck-Condon principle which determines
the coupling of vibrations. The probability of transitions that involve energy loss to phonons can be determined by overlapping phonon wave functions in the initial and final energy levels. The Franck-Condon principle states that the electronic excitation is so rapid that the lattice coordinates are not affected. Figure 2.5 depicts the electronic transitions with and without energy loss to phonons as well as a typical photo-luminescence spectra one can expect when a photons from the ZPL are measured.

Figure 2.5: Electronic level diagram and photo-luminesce of various crystals. Two electronic energy levels $E_0$ and $E_1$ leads to a change in equilibrium distance from $q_i = 0$ in the ground state to $q_i = q_{i0}$ in the excited state. In the first harmonic approximation all lattice modes are independent of each other and described by parabolic potentials. At low temperature the lowest electronic state only the ZPL is excited. $A$ is the absorption, $F$ is the Fluorescence. The up arrows are absorption without phonons (Zero phonon line) and with three phonons. (b) Absorption spectrum of the R2 band at liquid helium temperature in several alkali halides. A pronounced ZPL with a Lorentzian shape is seen with the accompanying broad phonon side band.

2.3.5 Cryogenic behavior of ZPL and PSB

Coupling between electronic transitions to phonons gives rise to a phonon sideband. In a crystal this can be due to host phonons or to localizations of modes associated to the structure of the emitting source impurity. Thus temperature reduction (elevation) will have an effect on this coupling which can be seen as a narrowing (broadening) of line-widths and variations in the ZPL shape. In diamond it
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has been established that the mechanism of ZPL broadening for non-degenerate electronic levels has a $T^3$ dependence for the lower temperature regime, and a $T^7$ dependence for the higher one. For degenerate levels an additional dephasing mechanism should be taken into account, yielding a $T^5$ dependence.  

Cooling can cause the host lattice to contract, which can in turn modify the band-gap, leading to a shift of the ZPL center emission energy (wavelength). Experimentally this shift has been shown to follow a $T^2 + T^4$ power law.  

2.3.6 Well-studied 3D Crystals point defects for quantum applications

Known point defects in wide band-gap semiconductors include well-studied materials such as diamond, silicon carbide (SiC) and zinc oxide (ZnO).

Diamond, consisting of carbon atoms and a wide bandgap of ~ 5.5 eV, is an excellent candidate for optical point defect resonance studies not only because of its wide band-gap but also due to its diamagnetic nature, absence of ferromagnetic related phenomena, narrow resonance lines, large refractive index, its tetrahedral symmetry and the simplicity of the lattice sites which makes it easier to study theoretically. An archetypical point defect is the intensively researched nitrogen vacancy center (NV), consisting of a nitrogen atom and an adjacent vacancy defect positioned on the missing carbon atom in the crystal lattice. The NV has been at the forefront of paramagnetic quantum optical point defect research due to its well-understood properties, reproducibility and can be seen as a model point defect. This defect has a trigonal ($C_{3v}$) symmetry around the crystallographic <111> direction connecting the nitrogen and the vacancy. The negatively charged NV$^-$ form has a triplet ($S = 1$) ground state and a zero phonon line (ZPL) at 1.945 eV (637 nm) and at 1.190 eV (1042 nm) and can be operated at room temperature. Optical pumping of the 1.945 eV transition results in a preferential population of the $S_z = 0$ ground state spin level. The NV$^-$ charge state can be described by a six electron model: five unpaired electrons of the nearest-neighbor nitrogen and carbon atoms to the vacancy and an additional electron trapped at the center. Its unique paramagnetic electronic structure is in contrast to that of organic molecules which usually have a singlet ground/excited (bright) state and triplet metastable (dark) state. Thus in the NV$^-$ this enables variation in the emission rates of the bright state once the center is exposed to a magnetic field, which is the basis for optical detected magnetic resonance (ODMR). This observable emission rate contrast is one of the main reasons the NV is superior for ODMR experiments over organic molecules, which require analysis of
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the length of the dark periods (triplet metastable state). A defect in diamond has a spin Hamiltonian of the form:

\[ H = \beta B \cdot g \cdot S + S \cdot D \cdot S + S \cdot A \cdot I + I \cdot Q \cdot I \]

(2.7)

The first term is the electronic Zeeman interaction, the second is the interaction of the electron spin with the crystal field produced by the defect surroundings. The third term is the magnetic hyperfine interaction and the last term the quadrupole interaction. \( S \) is the electronic spin operator and \( I \) the nuclear spin operator. \( g, D \) and \( A \) are tensors. For defects that have a spin \( (S) > \frac{1}{2} \) (such as the NV) a \( D \) term exists in the Hamiltonian, if not the second term can be omitted. The \( D \) term determines the zero field splitting (ZFS), which can cause a spin flip when using the correct frequency when applying ODMR on the resonant ZFS transition. For the NV center \(|D| = 2.87 \text{ GHz}\). For organic molecules the triplet states \( D \) is normally caused by dipole-dipole interactions between two electrons. In transition metal ions the term usually arises from spin-orbit coupling leading to an indirect electron spin-spin coupling.

Figure 2.6 depicts the defect lattice structure, auto-correlation of a single NV, photoluminescence, energy scheme for different charge states and microwave driving schemes between energy levels.
microwave sweep drives the $S = 0$ to $S = \pm 1$ transitions, as depicted on the left. (h) Applying a magnetic field and fixing the microwave frequency drives the $S=0$ to $S = -1$ transition resulting in Rabi oscillations. (d)(g)(h) Were measured in this work.

Silicon carbide, a 2.2 – 2.9 eV semiconductor $^{37}$ (depending on the poly-type), consisting of silicon and carbon atoms, has also seen a surge in research. Due to the dual atomic component of ideal SiC, the variety of lattice site vacancy defects in SiC is greater than that in diamond, which is mono-atomic. Examples of these are the silicon vacancy, carbon vacancy, di-Vacancy and carbon anti-site pair, some of which have shown to exhibit promising optical properties. $^{38}$ The silicon vacancy defects have an $S = 3/2$ ground state (Figure 2.7).

Zinc Oxide (ZnO) is a wurtzite crystal, with a band-gap of 3.455 eV – 3.37 eV. Band-gap engineering can be achieved by adding MgO. Even though several point defects have been recognized in ZnO, a direct assignment of the photo-luminescence properties of the defects to defect type and structure is still under debate. No ODMR has been observed on a single defect level.

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Figure 2.7: Properties of the point defects center in SiC. (a) 6H-SiC polytype lattice showing possible carbon and silicon vacancy point defects. $^{39}$ (b) Room temperature photo-luminesce spectra of a single $T_{2}$ center. $^{40}$ (c) Optical transition between ground state and excited state of the silicon vacancy point defect $^{39}$
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A prerequisite for a suitable host material for point defects, apart from a sizable wide band-gap, is the possibility to grow/engineer a nuclei spin-free species of the host material. Considering the nuclei spin-free atomics species is important for avoiding spin de-coherence originating from the nuclei spin bath of the host material. A sizeable bandgap in the visible range of the spectrum is required due to difficulties arising from the reduced efficiency of standard photo-detectors and different optics components needed for detecting in the far red range of the spectrum. A list of promising host materials from ref. 44 is displayed in Table 2.1.

Figure 2.8: Properties of the point defects center in ZnO. (a) Wurtzite ZnO crystal composed of oxygen (solid circles) and zinc (open circles) atoms. Tetrahedron with four-fold coordination plays a key role inside the structure. 41 (b) Wurtzite crystal with lattice parameters a and c. 42 (c)(d) Room temperature single defect fluorescence from point defect in ZnO. 43 (e) Zinc point defects in a ZnO crystal (left to right): Zinc vacancy -2 charge state, Zinc interstitial +2 charge state, Zinc occupying oxygen site +2 charge state. (f) Oxygen point defects in a ZnO (left to right): Oxygen vacancy +2 charge state, +1 charge state and neutral charge state. 42
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2.3.7 Quantum Yield

Traditionally defined as the ratio between the number of emitted and absorbed photons. Thus using the equation:

\[ Q.\, Y. = \frac{N_{em}}{N_{abs}} = \frac{N_{em}}{N_{Ref} - N_s} \]  

Where \( N_{em}/N_{abs} \) is the total number of emitted/absorbed photons, respectively. The absorption is the total number of photons transmitted by the sample \( (N_s) \) and a (black) absorbing reference \( (N_{Ref}) \). Previous studies on excitons in transition metal (di) chalcogenide (TM(D)C) have shown that the quantum yield is low, in essence a low number of radiating photons as compared to the number of electron-hole pairs generated – indicating a high density of defect states which can mediate non-radiative recombinations.

2.4 Raman spectroscopy of 2D materials

In TMDC material the Raman scattering has been shown to respond differently depending on the number of layers the material has. This is a result of symmetry breaking considerations of the lattice vibrations. For example, MoS\(_2\) is invariant under the 12 symmetry operations in the D\(_{3h}\) point group whereas bilayer MoS\(_2\) is symmetric under inversion. The intensity of the Raman scattering and wavenumber (relative to the excitation laser) is also sensitive to the number of layers the 2D crystal has. This is well known for graphene and boron nitride. For example, a unit cell of graphene is built out of two carbon atoms, A and B, with six phonon dispersions bands, three acoustic and three phonon branches. The phonons are classified as longitudinal (L) or transverse (T) vibrations parallel or perpendicular to the carbon-carbon directions. The most intense features of in a graphene Raman spectra is the G peak at 1580 cm\(^{-1}\) and a band at 2700 cm\(^{-1}\) which is a second order peak of the D peak. Monitoring the intensity and center wavenumber of the 2D peak can shed light on the number of

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Table 2.1: Material list fulfilling the required prerequisites required for a suitable host material for point defects.  

<table>
<thead>
<tr>
<th>Material</th>
<th>Band gap, ( E_g ) (eV)</th>
<th>Spin-orbit splitting, ( \Delta_{SO} ) (meV)</th>
<th>Stable spinless nuclear isotopes?</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C-SiC</td>
<td>2.39 (2 K)</td>
<td>10 (2 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>3.26 (4 K)</td>
<td>6.8 (2 K)*</td>
<td>Yes</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>3.02 (4 K)</td>
<td>7.1 (2 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>AlN</td>
<td>6.13</td>
<td>19 (theory)*</td>
<td>No</td>
</tr>
<tr>
<td>GaN</td>
<td>3.44</td>
<td>17.0 (10 K)</td>
<td>No</td>
</tr>
<tr>
<td>AlP</td>
<td>2.45</td>
<td>50 (theory)*</td>
<td>No</td>
</tr>
<tr>
<td>GaP</td>
<td>2.27</td>
<td>80</td>
<td>No</td>
</tr>
<tr>
<td>AlAs</td>
<td>2.15</td>
<td>275</td>
<td>No</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.64 (6 K)</td>
<td>–3.5 (6 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.72</td>
<td>64</td>
<td>Yes</td>
</tr>
<tr>
<td>ZnSe</td>
<td>3.82 (6 K)</td>
<td>420</td>
<td>Yes</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.25</td>
<td>970 (80 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>CdS</td>
<td>2.48</td>
<td>67 (10 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>Diamond (C)</td>
<td>5.5</td>
<td>6 (1.2 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
<td>44 (1.8 K)</td>
<td>Yes</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>346 (1.7 K)</td>
<td>No</td>
</tr>
</tbody>
</table>
2. Introduction and basic concepts

graphene layers which are probed. This method of establishing the number of layers in 2D materials is very useful for evaluation as it is non-destructive as opposed to electron microscopy which tends to knock out atoms from the 2D lattice.

2.5 Nanomaterial - 2D Crystals

Nanomaterials form a continuous band structure of electronic states when the diameter is comparable to or smaller than that of the bulk exciton. A major difference between 2D and 3D crystals is that because of the 2D nature of van der Waals crystals, a defect/impurity would be closer to the external environment. This results in a heterogeneous environment in which a defect in a 2D crystal resides. As a consequence, photoluminescence (PL) spectrum, lifetimes, and other related phenomena should reflect this heterogeneity. Interestingly, excitation with energies above the band-gap has also shown quantum light phenomena in 2D materials which has attributes of quantum dots. Thus a distinction between intra-band and above band excitation is discussed in this segment.

2.5.1 Van der Waals crystals

The van der Waals forces are governed by the distance between the interacting atoms/molecules. The nature of the attractive force differs from ionic/covalent electronic bonding and are weaker in comparison, showing a \( \sim r^{-6} \) dependence. In two dimensional crystals, this is the governing force \textit{between} single monolayer sheets, along the c-axis, which in a non-defective form, show no interlayer covalent/ionic bonding, allowing the easy ‘scotch tape’ exfoliation of a multilayer crystals down to a monolayer crystal. Thus, non-defective layers are passivated without any dangling bonds.

Graphene, a two dimensional honeycomb hexagonal carbon lattice crystal, can be considered the 2D “founding” material, sparking a wave of research to uncover new Van der Waals materials with different atomic composition and functionalities. A unique property of graphene is its zero band-gap at the K-point in the Brillouin zone, known as Dirac points, which differentiates it from other 2D crystals such as the TM(D)C. Thus, graphene is gap-less and semi-metallic. Atomically, graphene is composed of a single atom component – carbon. The optical properties of graphene arise from additional electrons in the \( p_z \) orbitals of the carbon atoms. These orbitals overlap to form bonding and antibonding states and thus the extended \( \pi \)-bands of graphene. Each interlayer carbon atoms bonds with neighboring carbon atoms by \( sp^2 \) hybridization. The conduction and valance states in graphene are degenerate at the K and K’ points of the Brillouin zone due to the symmetry between the sub-lattice sites (Figure 2.9). Interestingly single layer graphene has properties which are different from those of multilayer graphene.
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Figure 2.9: Structure of graphene. (a) honeycomb lattice of graphene with two in-equivalent carbon atoms sites A and B. (b) energy degeneracy at the K and K' points of the Brillouin Zone which guarantees a linear energy momentum dispersion, i.e. massless spectrum of the Dirac cone, near the two valleys. (c) Full electronic dispersion of the pi-bands in the Brillouin zone.

TM(D)Cs have the chemical formula of MX and MX₂ (for the dichalcogenide species), where the M is a metallic atomic species and the X a chalcogenide atom. For TMDCs, a monolayer is composed of a transition metal atom which is sandwiched between two chalcogen atoms in an X-M-X configuration. Thus a monolayer is in effect an atomic tri-layer. Thus, as opposed to graphene, the composition is bi-atomic. The interaction between each monolayer in a multilayer TMDC is governed by weak van der Waals interactions. Thus different stacking orders lead to a variety of poly-types. The main poly-types are: 2H – two monolayers in a trigonal prismatic coordination and the octahedral and 1T – one monolayer in an octahedral coordination (see Figure 2.10). Each poly-type comprises a bulk primitive unit cell. Examples of TMDC’s which have been recently more researched are MoS₂/MoSe₂/WS₂ and WSe₂. See Figure 2.10 for more examples.
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The poly-type and stacking sequence is of importance as it determines the presence or absence of inversion symmetry. The invariance of the Hamiltonian under symmetry operations usually lead to degeneracies at high symmetry points or directions in the Brillouin zone. \(^{52}\)

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Figure 2.10: 2D material possible atomic components from the periodic table. (a) Periodic table where each element is grouped as either a transition metal, post-transition metal, metalloid, non-metals and chalcogenides. Thus, the variety of possible TMDC types can be envisioned. (b)(c)(d) Crystal structure of graphene, phosphorene and MoS2 bilayers, respectively. (e) TMDC coordination for (left) H, trigonal prismatic (right) T, octahedral poly-types. \(^{53}\)
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The TM(D)Cs family have a relatively narrow band-gap (~ 2 eV) which can be direct/indirect, showing band-gap dependence on layer thickness.

Boron nitride (BN) differs from the graphene and TM(D)C families in its wide indirect band-gap (~ 5.95 eV) \(^5^4\). Nevertheless, despite considerable different electronic and optical properties from graphene, it shares a few commonalities with graphene – Firstly, the atomic mass of the lattice components are comparable to those of graphene, and secondly graphene and BN share similar lattice constants. It is no wonder then that carbon substitution point defect have been visualized in BN monolayers due to these similarities. Furthermore, monolayer h-BN and graphene are the only true 2D crystals where all the atoms which are bounded in a hexagonal lattice occupy the same plane. \(^5^3\) This property of h-BN in addition to its atomically smooth surface without charge traps, its low dielectric constant and high temperature stability and temperature conductivity make h-BN a great gate insulator substrate for graphene. \(^5^0\) The bonds between nearest boron and nitrogen atoms are formed from the combination of B-sp\(^2\) and N-sp\(^2\) orbitals, however due the electronegativity difference between B and N, the bonding has an ionic character, differing from the purely covalent bond in graphene. \(^5^5\) Boron/nitrogen are left/right of carbon in the periodic table, and thus have one electron less/more leading to a lower/higher electronegativity, respectively. Thus for an iso-electronic bond both boron and nitrogen are needed. \(^5^6\) This ionic component of the h-BN bonds is the key to the significant different band structure h-BN has which differs from graphene. The calculated band structure of h-BN is depicted in Figure 2.11

\[ \text{Figure 2.11: Structure of boron nitride. (a) h-BN Honeycomb structure with two triangular sub-lattices A and B occupied by nitrogen (pink) and boron (black), respectively. } \tau_1, \tau_2, \tau_3 \text{ are the vectors joining first neighbors between the sublattices. A unit cell contains one nitrogen and one boron. Right, Brillouin zone of h-BN. (b) Calculated electronic h-BN with total and partial density of states on boron and nitrogen atoms. The orbital character of the state is also indicated.} \]
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Newly emerging 2D materials can also exhibit superconductivity where it has been shows that Cooper pairs can still form in the last two dimensional channel of electron states. For example superconductivity has been measured in few layers van der Waals 2D NbSe$_2$ and MoS$_2$.  

2.5.2 Excitonic effects in 2D materials

Excitons are generated using above band-gap excitation, shooting an electron to the conduction band while generating a hole in its absence in the valance band which are attracted by Coulomb attraction. Recombination of an electron-hole pair can result in the emission of a photon and is the mechanism for generating photons in quantum dots. Dielectric screening in 2D materials differs significantly from those of 3D systems: The former is a macroscopic nonlocal screening and the latter mapped by a dielectric constant. This behavior modifies the optical properties of 2D materials in a fashion that hole doping results in strongly bound localized states with low mobility.

In general one can divide excitons to Frenkel and Wannier type depending on the exciton radius and binding energy. Wannier excitons typically have a large exciton radius and small binding energy. Frenkel excitons are tightly bound excitons with small exciton radii and large binding energies. For two dimensional TM(D)Cs due to reduced dielectric screening and 2D confinement, excitons have both Wannier and Frenkel characteristics. The large binding energies (~ hundreds of meV), enable stability at room temperature. Similarly, excitons can form other bound states such as positively or negatively charged trions (two electrons/holes and one hole/electron - a negative/positive trion, respectively) and with increasing exciton concentration also bi-excitons. For excitons, the population of generated

Figure 2.12: Excitons in 3D and 2D. (a) Real-space illustration of electrons-holes excitons for 3D bulk (a) and a monolayer (b). The dielectric environment is marked by $\varepsilon$. Electron-hole formation in a monolayer is strongly confined to the plane and experiences reduced screening due to the change in the dielectric environment. The electric field lines joining the electron-hole pair being to extend outside the sample, this modifies the form of the interaction potential and changes the energies of the excitonic states.
pairs as a function of excitation power is linear \(^{62}\) whereas for single emitters, even if excitonic by origin, a saturation of the photo-luminescence is expected since the photons emitted are limited by the lifetime of the excited state. \(^{63}\)

\[ \text{Figure 2.13: Power saturation behavior of excitons and of a single emitter. (a) Logarithmic photo-luminescence plot of excitons, trions and biexcitons at 77 K from WS2 displaying a linear dependence.} \] \(^{62}\) \[ \text{(b) Photo-luminescence and saturation plot of an emitter in WSe}_2. \] \(^{63}\)

### 2.5.3 Quantum dots

An exciton generated by above band-gap excitation is an electron-hole pair bounded by Coulomb interaction. Its spatial confinement on the nanoscale depends on the Bohr radius which on the nanoscale ranges from 2 to 50 nm, varying for different materials. For nano-crystals (such as 2D materials) the exciton wave function is affected by spatial confinement. Thus, by changing the size of the nano-crystal, one changes the electronic density of states and the energy separation between them (quantum confinement). Therefore, different materials differ in their quantum confinement size scaling due to material dependent exciton Bohr radius. A quantum dot is defined as a zero dimensional exciton confined in all directions (See Ref. \(^{64}\)). Quantum confinement in the thickness of the material (applicable to 2D materials) can result in a quantum well, and in two planes to a quantum wire. Thus the size and shape of the nano-crystal also has an impact on the exciton fine-structure namely: crystal field asymmetry, shape anisotropy and electron-hole exchange interaction. This is analogous to the singlet-triplet splitting in organic molecules.

Quantum dots have been engineered in semiconducting nano-crystals, typical examples of these are PbS, CdSe and CdTe. These can be seen as 3D potential boxes confining the motion of electrons and holes. \(^{65}\) However, we will focus primarily in this segment on quantum dots in 2D materials. Interestingly the reduced dimensionality of 2D materials together with quantum confinement can result in single emitting bound excitons. One example of this is in atomically thin WSe\(_2\) where quantum
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emission has been related to strain-induced local confinement potentials which trap free excitons.\(^{63}\) Similarly single emitters have been seen in a similar fashion in 2D GaSe.\(^{68}\)

![Figure 2.14: Single emitters in WSe\(_2\) and GaS. (a) Optical microscope image of a thick flake of WSe\(_2\). (b) Optical-microscope scan of the WSe\(_2\) marked with areas exhibiting sharp spectral lines. (c) Narrow line emission spectra at specific edge positions (S4-S6) on the thick WSe\(_2\) flake. (d) Photon coincidence correlation \(g^2(\tau)\) of a one of the localized centers in figure b. (e) Atomic force microscope of a 36 nm thick van der Waals GaSe crystal. (f) Photo-luminescence of the crystal at 10 K. (g) Photo-luminescence spectra of emitters at 295 K and 10 K. (h) correlation \(g^2(\tau)\) function for localized emitter photo-luminescence at 10 K in figure g.\(^{68}\)](image)

2.5.4 Blinking

Under constant excitation, quantum dots, molecular emitters and intra-band defect states can have intermittent emission. This is known as blinking. The emission can be classified as ‘on’ and ‘off’ periods with step like increases and decreases in the photo luminescence count. In quantum dot research it has been shown that coating a semi-conducting nano-crystal with another thin semiconductor can greatly increase the ‘on’ periods, thus hinting to the role the local environment / surface can play. Blinking can also persist at low temperatures which rules out that it is necessarily a thermally activated process. When the rate of Auger-assisted pathways have a higher rate than radiative pathways, the photo-luminescence can be suppressed or quenched.\(^{65}\) Detailed timed resolved photo-luminescence studies of quantum dots using an electro-chemically controlled environment revealed two types of blinking. One due to charging and discharging of the nano-crystal core and the other due to charge fluctuations in the electron accepting surface sites.\(^{69}\) The NV center defect in diamond is extremely photo-stable and thus typically does not blink.\(^{70}\) Nevertheless in nano-diamonds blinking behavior is observed. The similarity of the high surface area of a quantum dot to that of a nano-diamond therefore points out to the role of the surface. An NV in a 5 nm nano diamond crystal can have a large proportion of surface dangling bonds, dislocations and other impurities.\(^{71}\) Thus surface functional groups /
absorbents can create trap states that suppress emission and cause blinking. It comes as no surprise that single emitting centers in 2D materials can also exhibit similar blinking behavior. When focused on a particular spot with the laser, monitoring the time trace signal from the APDs can show the ‘on’/ ‘off’ switching. Blinking can also appear as streaks during a raster scan across a diffraction-limiter laser spot. \(^{72}\)

Figure 2.15: Blinking in quantum dots and h-BN. (a) Blinking states of a NV center in nano-diamonds, a corresponding histogram of the photo-luminescence time trace, showing the ‘on’ and ‘off’ states. (b) An occurrence count of the time trace in (a) fitted with two Gaussians the ‘on’ and ‘off’ distribution of counts is evident. \(^{71}\) (c) Photo-luminescence time trace of a bare CdSe nano-crystal compared to one coated with a shell of 7 monolayers of ZnS, a wider band-gap semi-conductor. The ‘on’ state is more frequent once the nano-crystal is coated. (d) A raster confocal scan pf CdSe nano-crystals using a 532 nm excitation laser. Streaks indicating blinking are seen. \(^{72}\) (e) A confocal raster scan of bulk single crystal h-BN using a 633 nm excitation laser. Similar streaks indicating blinking are also seen (this work).

Recently, in 2D materials, investigating the phenomenon of blinking has taken a new perspective, with the discovery of correlated blinking between hetero-structures of 2D van der Waals materials, shifting the focus from classic quantum dot research while still addressing blinking dynamics of excitons. Combining two different 2D van der Waals materials (WS\(_2\)/MoSe\(_2\), WS\(_2\)/MoS\(_2\), WS\(_2\)/WSe\(_2\), MoS\(_2\)/MoSe\(_2\), WSe\(_2\)/MoSe\(_2\)), correlated blinking can be seen between two monolayers, with bright/dark states in each of the monolayers being negatively correlated (Figure 2.16). Dynamic
variation in exciton emission is due to intermittent and random interlayer carrier transfer, and thus differs from classical blinking interpretations.  

![Figure 2.16: Hetero-structure correlated blinking. (a) Illustration comparing typical blinking behavior in quantum dots (top) to 2D hetero-structures (bottom). Quantum dots exhibit ‘on’ and ‘off’ states whereas hetero-structures exhibit in addition a ‘Neutral’ state. (b) Wide field image of a WS₂/MoS₂ bi-layer hetero-structure. (c-e) Fluorescence images with a color camera taken at different times, the states (c) bright, (d) neutral and (e) dark are seen.](image)

2.5.5 Quantum confinement

In bulk indirect band-gap materials, electron-hole recombination is possible through phonon emission or absorption, due to wave-vector differences which are compensated between the conduction and valence band. One way of converting an indirect optical transition to a direct one, is by forming a super-lattice structure, therefore the Brillouin zone is reduced, folding the conduction band onto the Γ point. Super lattices are artificial periodic structures created at the interface of two layers, by skewing the angle between the two layers of the same material or by due to the different lattice constants of the dissimilar materials. This makes 2D artificially engineered hetero-structures an attractive candidate to achieving this task, possibly enhancing emission rates. Exciton energies are generally shifted to higher/lower energies compared to bulk material with decreasing size. For example, in nano-diamonds, the electronic structure is similar to that of bulk when the size is in the range of μm. However, the exitonic peaks broaden when the sample is in the range of tens of nm, indicating a shift to higher energies with decreasing crystal size. Due to the nm dimensions of 2D materials, quantum confinement effects play a central role, resulting in confined electrons, variability in the photo-luminescence spectrum and can change the nature of the band gap itself. For example, in MoS₂, with decreasing crystal thickness a perpendicular quantum confinement induced shift changes the band-gap from 1.29 eV to 1.90 eV and in the monolayer limit exhibits a crossover from indirect to direct, leading to a 10⁴ fold enhancement of the quantum yield luminescence.

2.5.6 Candidates for intra-bandgap excitation

Using the same criteria as outlined for suitable host materials from 3D crystals, a general outlook can be conceived for which crystals would be the best candidates for exploration of deep band-gap point
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like defects. The different electronic structure of 2D materials spanning from conducting, semiconducting to insulating, also means that they respond to different frequencies (wavelengths) of radiation (Figure 2.17).

![Figure 2.17: Various 2D materials and their possible applications by frequency. (a) Spectral range of 2D materials, including frequency and possible applications. Near infra-red (NIR), Mid infra-red (MIR) and Far infra-red (FIR) are indicated. The atomic structure of h-BN, MoS$_2$, Black phosphorous (BP) and graphene is displayed, for these the electromagnetic spectrum is displayed as a call out from the main arrow. (b)(c)(d)(e) electronic structure of different 2D materials.]

Therefore by looking into available 2D materials which can have been synthesized, evaluating the dominant atomic isotopes and band-gaps, the most promising 2D crystal candidates which would be ideal for hosting paramagnetic point defects can be outlined. These are outlined in green in Figure 2.18, using the criterion that optical excitation of crystals with a band-gap above 2 eV is more facile using conventional visible wave length lastes. Due to the band-gap renormalization of some
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TMDCs at the mono-layer scale, these can also be suitable for a defined layer number. These are outlined in yellow.

![Commercial 2D semi-conducting crystals by nuclei spin composition and band-gap. The majority nuclei atomic spin is designated. Those marked in green and yellow may be suitable for intra-band gap optical excitation research as stated in the text.](image)

**2.6 Nanomaterials – van der Waals 1D Crystals**

Based on their two dimensional relatives, but less explored are one dimensional van der Waals crystals. Due to their van der Waals nature, their 2D relatives are usually studied before their 1D counterparts are.

**2.6.1 Carbon based**

The sp² bonding state of carbon based graphitic structures can lead to a variety of types, such as fullerenes (ball structures) which are composed of C₆₀. This lead to discovery of the first one dimensional crystal, graphitic carbon needles, or carbon nano-tubes (CNNTs). In structural terms, one can envision the nanotubes as rolled sheets of 2D graphene (as seen in Figure 2.19). Interestingly the electronic properties of CNNTs depend on their geometric structure such as chirality and diameter. Thus, the electronic behavior varies from metallic to semi-conducting and can be modified by deformation. CNNTs can be single-walled (SWNTs) or multi-walled (MWNTs). Inspecting the cross-section of SWNTs reveals an armchair or zigzag configuration. These determine if the CNNT is metallic or semi-conductive. 
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These differences in turn modify the optical properties and it has been shown that optically excited states in CNNTs are excitonic by nature. Nevertheless, for exciting states inside the bandgap, the gap that can be opened in CNNTs is only on the order of \(\sim 100 \text{ meV}\), thus making it impractical for intra-band optical excitation.\(^{81}\) Even so, quantum confined excitons\(^{82}\) in CNNTs have been experimentally shown to behave as single quantum emitters.\(^{83}\)

\[\text{Figure 2.19: Structure of carbon nanotubes. (a) Extension of a C}_{60}\text{ molecule leads to a two end capped nanotube. (b) Rolling up a graphene sheet leads to hollow cylindrical carbon nanotubes. (c) 2D graphene sheet with lattice vectors }\ a_1\text{ and } a_2, \text{ the roll-up vector } C_n = n a_1 + m a_2. \text{ Chiral cases of (}n,0\text{) zigzag and (}n,n\text{) armchair are indicated with dashed lines. The shaded region between (}n,n\text{) and (}2n, -n\text{) directions represents the area of unique (}n,m\text{) indices.}^{80}\ (d) \text{Metal to semiconductor transition in CNNT. A metallic zigzag CNNT opens a bandgap } (E_{\text{gap}}) \text{ under tensile strain, rendering the CNNT semiconducting.}^{81} (e) \text{Photoluminescence of single emitters in CNNT for different temperatures.} \quad (f) \text{The corresponding pulsed g}^2(t) \text{for each spectra, proving the quantum nature of emitted light.}^{83}\]

2.6.2 Boron nitride based

BNNTs are analogues to CNNTs structurally where boron and nitrogen atoms substitute the carbon atoms. BNNTs are less explored from their CNNT analogues due to only recently emerging reliable fabrication methods. A distinct difference of BNNTs from CNNTs is the wide bandgap of \(\sim 5 \text{ eV}\), which is independent of non-deformed nanotube geometry\(^{84}\) and helicity.\(^{85,86}\) BNNTs can be single- or multi-
walled. Crystallization of BN layers is governed by strong tendency to have atomically perfect B-N stacked consecutive layers, in contrast to CNNTs where a relative freedom in a rotational disorder between neighboring C shells can lead to various helicities. BNNTs after fabrication come as entwined bundles, appearing as a cotton ball (Figure 2.20).

Figure 2.20: BNNT structure. (a) Structural model of single layered BNNT constructed by wrapping a monolayer of BN. B/N is colored blue/red, respectively. (b) 200 mg BNNT, the cotton ball is evident. (c) A BNNT entwined yarn of ~ 1 mm diameter, 3 cm long, holding a 6 gram coin.

2.6.3 TMDC based

Even less explored than CNNTs and BNNTs are TMDC based nanotubes and nanowires. Examples of those are MoS$_2$, WS$_2$, and GeS. Nevertheless, for the purpose of intra band-gap excitation, these are of less relevance to this work due to their narrow band-gap (< 1.8 eV).

2.7 Hetero-structures

Traditionally, the interfaces of bulk semi-conductors such as AlGaAs/GaAs or InGaN/GaN quantum wells have been studied using state-of-the-art growth methods. An attractive feature of van der Waals materials originates from their 2D nature – the possibility to build, bottom up custom-made, structures composed of different 2D materials, therefore creating new functionalities and artificial interfaces. This also enables the creation of custom Moiré patterns. Two common methods to create
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hetero-structures include in-situ CVD growth and the other is self-assembly using the common exfoliation pickup and transfer of scotch tape material (Figure 2.21).

Figure 2.21: Depiction of hetero-structure assembly. 2D crystals can be analogous to Lego blocks (right panel), the construction of a huge variety of hetero-structures is possible. Conceptually, this atomic-scale Lego resembles molecular beam epitaxy but employs different ‘construction’ rules and a distinct set of materials.  

Scanning tunneling electron microscopy (STEM) research has proven that clean van der Waals interfaces, without external contaminants can be created using this method (Figure 2.22). A property that makes the creation of smooth interfaces between different crystals using exfoliated van der Waals materials feasible is the so-called self-cleaning mechanism. Absorbents such as water, atmospheric gases and hydrocarbons cover surfaces, unless prepared under special conditions, which can hinder contact at the interface. For example, TEM has demonstrated that graphene is covered quickly by dense hydrocarbons soon after isolation in air. However, due to the self-cleaning mechanism these tend to segregate into isolated pockets (bubbles) leaving large micron-sized clean areas of the hetero-structure. When the affinity between two dimensional crystals is larger than that between the crystals and the contaminants, energetically the favorable interface between the hetero-structure is that with the maximum contact of the crystals. Therefore, the contaminants are pushed away.
2.7.1 Assembly

Assembly of a hetero-structure can be done using manual mechanical assembling. Using this scheme various pick up techniques can be utilized for aligning the top layer on the defined bottom layer. The more technical demanding technique is in-situ growth of the second layer of the hetero-structure on top of the first one, thus avoiding breaking vacuum and in a sterile environment void of contaminants.

2.7.2 Band alignment

Once placed in proximity, the electronic band alignment of two different (2D) materials can be classified at the interface. These are classified to type I (symmetric), type II (staggered) or type III alignments, as seen in Figure 2.23. Type I alignments provide spatially confined electrons and holes.
with efficient recombination. Type II are useful for unipolar electronic devices since they allow large offsets on either the conduction or valence band thus allowing strong carrier confinement. Type II has also enabled long lived interlayer excitons. For example, quantum cascade lasers use complex heterostructures stacks to engineer mini-bands and intra-sub-band transitions, allowing efficient light emission from mid-infrared to the terahertz regime. Electrons stream down a potential staircase (type II) sequentially emitting photons at the interfaces. These steps are built of quantum wells where population inversion is achieved between discrete conduction band excited states.

Figure 2.23: Hetero-structure band-alignment. (a) Type I, II and III hetero-structures red (blue) indicate conduction (valence) bands, respectively. (b) Periodic table of hetero-structures, Band alignments Type 1/2/3 are colored green/red/cyan, respectively. Lower left/Upper right of the diagonal line are results computed using the PBE and HSE06, respectively. (c) Conduction band energy diagram of a 25 period section of a quantum cascade laser. Electrons are injected through a 4.5 nm AlInAs barrier. (d) Schematic of the dispersion for $n = 1, 2$ and $3$ states parallel to the layers. $k_{ij}$ is the corresponding wave number.

2.7.3 Moiré engineering in 2D materials
The prospect of a perfect periodic network of defects arising from imperfect layer stacking could lead to a new generation of precision engineering of atomic scale computer chips. The variety of 2D materials with the combination of different stacking angles or lattice mismatches provides a diverse platform, thus accommodating crystallographic mis-registry. Dislocations, for example can give rise to larger core radii. Examples can be seen in Figure 2.24. However, van der Waals dislocations differ from their bulk crystallographic counter parts due to the weakly or non-interacting nature of the 2D materials.
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For TMDCs a super-lattice of MoS$_2$/WSe$_2$ has been realized, yielding a periodic variation of atomic registry with a well-defined periodicity, showing the coupling affects of the electronic structure at different critical points (Figure 2.25).

2.7.4 Interlayer coupling

Interlayer coupling between two hetero-structures can be tuned using annealing, changing the system from the limit of isolated independent monolayer to coupled hetero-bilayers. The change in coupling can be observed using Raman measurements, where the layer on top is sensitive to out-of-plane vibrational changes, whereas the layer touching the substrate does not display a shift. This effect can be seen in a hetero-structure composed of WS$_2$/MoS$_2$ and the inverse MoS$_2$/WS$_2$ (Figure 2.26).
Similarly high resolution transmission electron microscopy (HRTEM) images show a sharpening of the Moiré pattern after annealing.

Figure 2.6: Interlayer coupling of TMDCs. (a) Raman spectrum of WS₂/MoS₂ (top) and the inverse structure MoS₂/WS₂ (bottom). Before and after annealing at 70 °C for 12 hours. Arrows indicate the shifting of the A’ Raman peaks. (b) HRTEM images of MoS₂/WS₂ before (b) and after (c) annealing. Zoom in on before (d) and after (e) annealing. (f) (g) Fourier transform of hetero-structure before and after annealing. ¹⁰¹

The type-II band alignment at the interface of a hetero-structure can cause electrons to accumulate in one layer and the holes in the other layers. This enables the formation of interlayer excitons (IXs) with enhanced lifetime and density. ¹⁰⁰ Thus using optical excitation with various energies, one can excite inside the band-gap of both hetero-structures TMDCs and verify the coupling simply by probing the IXs using a green 532 nm excitation laser.

2.7.5 BN encapsulation and line width narrowing

Exciton photo-luminescence line width has been shown to narrow once the TMDC layers are encapsulated with h-BN. It is assumed that the top/bottom h-BN layers protect the sample from physio-sorption and chemio-sorption and provide atomically flat surfaces that void ripples. ¹⁰² For
MoS$_2$ emission enhancement has also been seen due to encapsulation. Thus for intra-band excitation we can assume a similar effect.
3 Two dimensional hexagonal boron nitride (h-BN)

The following chapter investigates correlations between h-BN structural features and emitter location from bulk down to the monolayer at room temperature, demonstrating that chemical etching and ion irradiation can generate emitters in h-BN. The chapter shows that the emitter’s spectral features are dominated by the interaction of their electronic transition with a single Raman active mode of h-BN with diverse rates between the electronic states of the emitter. Emitters exhibit excellent photo stability even under ambient conditions and in monolayers. Comparing the excitation polarization between different emitters unveils a connection between defect orientation and the h-BN hexagonal structure.

3.1 Structure

Hexagonal boron nitride (h-BN) belongs to the space group $D_{6h}^5$ (P6$_3$/mmc). B–N nearest neighbor atoms have a distance of 1.4 Å, with the 2D layers consist of $sp^2$ covalent bonds with an alternating stacking pattern of boron and nitrogen atoms. As opposed to graphene, all nuclei in h-BN have nonzero spin. The Raman Stokes shift of h-BN is in the range between 1363 and 1370 cm$^{-1}$, depending on the flake thickness. Figure 3.1 depicts the known Raman-Stokes shifts of h-BN, depending on thickness as well as verification of a multi-layer h-BN in this work.
3. Two dimensional hexagonal boron nitride (h-BN)

Figure 3.1: h-BN Raman. (a)(c) Raman-Stokes shift from previous research, anti-Stokes is also shown in (c). (b) Raman peak position’s dependence on layer thickness. (d) Raman spectra confirming h-BN of bulk scale on 180 μm thick SiO₂ for this chapter.

3.2 DFT and defect calculation in h-BN

Nitrogen and boron vacancies and substitution defects include oxygen for nitrogen vacancy sites, dicarbon species have been visualized in TEM/STEM in 2D-hBN. DFT calculations suggest the nitrogen anti-site defect (N₄V₄) and the carbon anti-site defect (V₄C₄). However, these have never been visualized in TEM/STEM technology available today, in particular carbon tends to substitute in pairs in h-BN due to the balancing of the electro-negativity. Nanometer resolution of defect in h-BN has been seen in a combined study of TEM and super-resolution, identifying boron/nitrogen vacancies, three boron vacancies plus one nitrogen vacancy. Nevertheless, optical excitation of these observed defects was done in a liquid environment, rich with oxygen, which has been to shown to exhibit a healing mechanism. Figure 3.2 displays defect types and families which have been visualized in h-BN using TEM imaging. It is important to stress that DFT calculations can deliver results of widely varying accuracy and as such without direct visualization of a point defect and simultaneous confirmation of its optical properties, using DFT to predict optically excited ground/excited states...
can be premature.

Figure 3.2: Defective h-BN. (a) TEM image of defective h-BN. Green/Red/Blue/Yellow represent N/B/O/C, respectively. Carbon tends to substitute only in pairs and not as a single substitution defect, oxygen substitutes nitrogen sites. 111 (b) HRTEM image of the edge of an h-BN layered crystallite, curved edges are seen. 112 (c) TEM image of bilayer h-BN. Magnification shows broken symmetry at defect sites. 113 (d) Boron vacancy model of 3 fold symmetry defect in (c), for two charge states, 0 and -1, left and right, respectively. 114 (e)(f) BN di-vacancy in a BN nano-tube, reconstructing to different bonds. Illustration on left side, TEM image right side. 115 (g) Left, high resolution ADF image of a boron vacancy and three nitrogen vacancies, right, model of the defect. 116

3.2.1 Boron vacancy

The negatively charged V$_B$ has $D_{3h}$ point group symmetry, consisting of hybrid $sp^2$ dangling-bonds and three $2p_z$ orbitals. In this case the atoms are identical and hence so are their dangling-bonds: {$\sigma_1$, $\sigma_2$, $\sigma_3$, $\pi_1$, $\pi_2$, $\pi_3$}
3. Two dimensional hexagonal boron nitride (h-BN)

![Image of electronic level scheme](image1)

Figure 3.3: Boron vacancy electronic level scheme as calculated (a) Ground state of the negatively charged boron vacancy. Spin up level $a'1$ resides in the valence band. Yellow/White arrows represent occupied/unoccupied states, respectively. (b) Defect wave functions corresponding to molecular orbits (c) Excited states for $^{3}E'$ with $D_{3h}$ and $C_{2v}$ symmetries. (d)

3.2.2 Nitrogen anti-site defect ($N_{B}V_{N}$)

The first DFT calculation associating quantum emission in h-BN was done for the proposed nitrogen anti-site defect, where a nitrogen substitutes a boron site and an adjacent nitrogen site is missing a nitrogen (hence a nitrogen vacancy). See Figure 3.4.

Further research has shown that this association is simplistic at best and DFT calculations can be erroneous in estimating the nature of the ground and excited states.
3. Two dimensional hexagonal boron nitride (h-BN)

3.2.3 Boron vacancy with carbon at nitrogen site ($V_{B}C_{N}$)

DFT has predicted that the boron vacancy with a substitution carbon at the nitrogen site should be a plausible defect for the photo luminescence attributed to point defects in h-BN. Nevertheless, it is important to stress that this type of defect has never been visualized before. The electronic structure with the predicted allowed transitions is depicted in Figure 3.5.
3. Two dimensional hexagonal boron nitride (h-BN)

3.3 Band to band excitation

h-BN has been widely studied for its emission in the UV spectral range \textsuperscript{118} and was recently proven to have an indirect bandgap. \textsuperscript{54} Exciton UV emission in the \sim 220 nm spectral range has been attributed to grain boundaries and dislocations \textsuperscript{119} and using cathodoluminescence, for stacking faults localized at fold crossings of the flakes, resulting in local symmetry changes. \textsuperscript{120} For the \sim 300 nm range, nitrogen vacancies and carbon impurities have been ascribed as the source of emission. \textsuperscript{121,122}

3.4 Previous Intra-band excitation studies

Recently, it was demonstrated that h-BN also hosts SQEs in the UV \textsuperscript{123} as well as the visible range \textsuperscript{124,124} (623 nm). \textsuperscript{117} The defect thought responsible for quantum emission at 623 nm was an anti-site complex; i.e., a nitrogen occupies the boron site with a missing atom at the nitrogen site, $N_BV_N$. The high density of emitters found, 21 in account with the fact that due to the 2D nature of h-BN the emitters are exposed to the environment, suggests that sample preparation should have a significant influence on its behavior.

3.5 Common fabrication of BN

Various fabrication techniques of raw multilayer ‘bulk’ BN range from high pressure/ high temperature (HPHT) to chemical vapor deposition (CVD) and chemical synthesis. A standard in high quality single crystal BN flakes (used in this work) are those synthesized by T. Taniguchi and K. Watanabe using the HPHT technique at 1500 °C using barium boron nitride as a solvent starting material. These exhibit a point defect concentration of carbon and oxygen of less than $10^{18}$ atoms/cm\textsuperscript{3}. \textsuperscript{125} Interestingly, for fabrication of high quality BNNT catalyst-free HPHT (although at higher temperatures of 4000 °C) was also employed yielding high quality BNNT and minimizing defects from foreign atomic species (such as carbon). \textsuperscript{87,126} CVD h-BN is typically grown on a Cu foil substrate, where the first monolayer growth is by the Frank van der Merwe model (i.e., layer-by-layer) and afterward changes to Stranski–Krastanov model (i.e., island on layer). \textsuperscript{127} CVD h-BN can also be purchased in dispersed solvents.

3.6 Transfer mechanisms of BN to substrate

BN crystals transfer is rather straightforward and direct. Using Nitto-Denko scotch tape, multilayer flakes of various thicknesses can be transferred to a SiO\textsubscript{2} substrate. CVD grown monolayer h-BN on copper foil requires use of various solvents in-order to isolate the BN sheets. In this work the same transfer method which for CVD BN was used as in ref. \textsuperscript{117} for commercial monolayer BN from Graphene Supermarket. Namely, h-BN on Cu was spin-coated with 100 µl 2% (PMMA) in chlorobenzene for 2 min, dipped in 68% HNO\textsubscript{3} solution for 2 min. in order to remove the Cu substrate. The resultant h-BN were placed on a SiO\textsubscript{2} with fabricated holes and heated to 80 °C under a slow acetone flow for PMMA
removal for 15 min. The sample was then rinsed in acetone and dried under N₂ flow. The sample was then annealed at 850 °C in argon.

3.7 Emitter perimeter location tendency

We confirm the presence of h-BN using Raman spectroscopy (Figure 3.7.a) suspended over a hole in the substrate (Figure 3.7.b). Figure 3.7.c/d shows an unfiltered/filtered (respectively) confocal image of an area of the flake in Figure 3.7.b suspended over a hole (hole marked as a purple circle in Figure 3.7.d). A suspended emitter can be seen in this area (marked in a red circle) in the depth (Z) and lateral (XY) scan. Thus, quantum emitters are not localized on the interfaces between the h-BN flakes and the substrate but are associated with the BN flake. On the exfoliated flakes we see emitter densities of less than 10 emitters per whole flake (∼ 30 μm lateral). We also notice a tendency of bright emitters to appear on the perimeters of the h-BN flakes: either on the boundary of a whole flake (Figure 3.7.e) or at the interface between flakes (Figure 3.7.f/g, filtered/unfiltered, respectively) or clustering along lines inside the flake which show a constant angular multiplicity between them (Figure 3.7.h/g), which, in this case, is α ∼ n × 30° (see Figure 3.6).

However, the confocal resolution is limited at best to 200 nm, and hence we cannot conclusively say that the emitters are precisely positioned on the edges of these perimeters. Subjecting the h-BN flakes to the chemical etching methods increased the emitter density dramatically compared to the exfoliated flakes. The number of emitters found per confocal area increased to 0.09 and 0.54 per μm² for both chemical methods using peroxymonosulfuric acid and the additional phosphoric acid (H₃PO₄) + sulfuric acid (H₂SO₄), respectively (see Table 3.1 for details). In Figure 3.7.j, a confocal scan of chemical etching method using phosphoric acid is shown. The calculated density values are found in Table 3.1.
Table 3.1: Types/Methods for Emitter Generation and the Dependency for Each Method and Relative Density of Emitters per μm². Densities are calculated for areas that showed the maximum number of emitters on a flake, a minimum distance of 0.5 μm between emitters was taken into account.
3. Two dimensional hexagonal boron nitride (h-BN)

Figure 3.7: Spatial occurrences of emitters in h-BN. (a) Raman spectra confirming h-BN of bulk scale on 180 μm thick SiO$_2$. (b) A microscope image of a flake on SiO$_2$ with holes is shown. (c−k) Confocal scans of exfoliated flakes; color coding indicates counts per second. (c) Z-axis, (d) XY-axis of an area of the same flake as in (b) (indicated by the blue dashed arrow), suspended over a hole (marked with a purple circle). Part c is unfiltered and d filtered. For unfiltered scans, the laser power was substantially reduced (nW) to avoid burning the APDs, and the wavelength filters were removed. A suspended emitter is seen (marked in red). (e) QEs appearing at the boundary (f, g) and interface (filtered/unfiltered, respectively) (g) of a flake on top of another, different flake. Thicknesses are indicated (1−3). (h) An angular multiplicity of 30° is found for emitters seemingly aligned along straight lines on an exfoliated flake. (j, k) 532 nm CW confocal scan for a comparison between a chemically etched flake (j) and CVD h-BN (k)
Deducing that an etching (atom removal) mechanism is important for emitter creation, we also attempted ion irradiation on samples with nitrogen (N) and helium (He) (See Figure 3.8). We note that if ion irradiated samples were annealed at 850 °C in vacuum and not in argon, these emitters were less stable than those annealed in argon. Confocal scans of irradiation show higher density than the chemically treated samples. This high density was seen for both irradiations (see Table 3.1), emphasizing the role of inelastic collisions (vacancy creation) for emitter formation in h-BN. Although we are using N ions, N$_2$ ions have been shown to create interstitials in h-BN in addition to vacancies. We discuss below the possible effect of these interstitials. Due to the inert nature of the irradiated ions, it is less likely to implant them in the lattice and therefore we assert that the mechanism of emitter creation is not atom substitution.

Next, we investigated defects in mono-layers. To that end we compared the structural features and density of emitters in purchased mono-layer CVD h-BN to exfoliated flakes and to treated (chemical etched/ion irradiated) flakes. CVD monolayer h-BN reveals non-uniform coverage already on a 20 μm scale, this can be seen in a SEM image in Figure 3.9.

We use the same transfer method procedure described in Ref. also on a 180 μm thick SiO$_2$ with patterned holes for commercially available graphene supermarket h-BN. Probing the sample with a 532 nm CW laser immediately reveals that emitter density (Figure 3.7.k) is larger than for chemically treated flakes, but lower than for high dose ion irradiated samples. Considering the inhomogeneous
h-BN coverage on the Cu foil observed in the SEM image with our observations on the untreated and treated (chemical etched/ion irradiated) flakes, we correlate the high density of emitters with the large number of perimeters appearing in a CVD mono-layers due to the growth mechanism.

3.8 Spectral and autocorrelation properties exfoliated h-BN

We start by analyzing a single quantum emitter (SQE) created using the chemical etching method with the additional $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4$ treatment. Figure 3.10.a/b shows a cross section of an area inside a flake where we compare between a filtered/unfiltered (respectively) image. The SQE is marked in the center of the red circle. We mark areas A and B on the image and measure the Raman signal. For A we get 1365 cm$^{-1}$ and for B we get 1369 cm$^{-1}$ after Lorentzian fitting (Figure 3.10.c), therefore indicating that this area is composed of thicker/thinner (respectively) h-BN.$^{48}$ We measured the emitter PL spectrum (Figure 3.10.d, right) and also show an autocorrelation measurement (inset), proving it is a single quantum emitter ($g^2(0) = 0.26 < 0.5$). At the end of our measurements we significantly increased the excitation power (~mW) to get a Raman signal and took higher resolution PL spectrum. This is shown in Figure 3.10.d – left. A close look reveals that the Raman signal is superimposed on our SQE spectral features. The inset displays the conversion to wavenumbers giving a value of 1367 cm$^{-1}$.

![Figure 3.10: Color diversity and phonon replicas of h-BN emitters.](image)
3. Two dimensional hexagonal boron nitride (h-BN)

Conversion of 23 emitter PL spectra acquired from various sources from treated/untreated flakes to the difference in wavenumber between adjacent peaks as a function of standard deviation

Figure 3.10.d - right shows a typical emission spectrum with an emission origin at 580 nm and two side peaks separated by a wavenumber differences of $1329 \pm 66$ cm$^{-1}$ and $1303 \pm 109$ cm$^{-1}$. These differences between the emission peaks in Figure 3.10.d are very close to the Raman shift of h-BN $^{47,48}$ (Figure 3.10.d upper scale). We therefore conclude that the central peak is the zero phonon line emission (580 nm), whereas the second one is the first Raman Stokes harmonic followed by the second one. Several PL measurements that were done on treated and un-treated h-BN samples have shown that this double peak structure appears on all emitters that exhibit quantum emission traits. However, the third peak is not always prominent enough to be seen. Nevertheless, the possibility of a second ZPL cannot be excluded and further measurements are needed for verification. Figure 3.10.e shows six PL spectra taken from QE on diamond and SiO$_2$ substrates, emphasizing that although emitters occur at different wavelengths, the double peak structure is recurring and is not substrate dependent. All of these six representing spectral features were seen both on diamond and SiO$_2$ and were not confined to the boundary case (Figure 3.7.e). Polarized in-plane modes for h-BN at the $\Gamma$,M and K Brillouin points should have an energy of $\sim$170 meV for both the transverse and longitudinal optical phonons (TO and LO modes), whereas polarization along the c axis is expected for energies below 100 meV. $^{104}$ The spectral difference in the emission origin can arise from strain (shown for SQEs in WSe$_2$ over a range of 170 meV $^{130}$), different dielectric environments and most probably from at least two types of defects or different charge states for the same defect - we discuss later in detail the possible causes. We find a minimum full width half maximum (FWHM, denoted as $\nu$) of 3.96 nm on the PL spectra for non-monolayer flakes.

We perform a similar analysis on 23 adjacent peaks from various sources of h-BN (CVD mono-layer h-BN, treated (chemically/irradiated) and un-treated emitters). We plot the difference between adjacent peaks in wavenumbers as a function of standard deviation (Figure 3.10.f). The majority of wavenumbers are located close to the value of 1363 cm$^{-1}$ with an average value of 1337.6 cm$^{-1}$, very close to that of h-BN (1363 cm$^{-1}$ to 1370 cm$^{-1}$ depending on flake thickness). $^{48}$ We therefore show that the electron interacts with bulk or flake phonon modes rather than with localized vibrational modes as it is the case for defects which do comprise impurity atoms with mass significantly different from atoms of the host lattice. This spectral behavior was seen also for defects in h-BN that emit in the UV range. $^{118}$ The energy difference between the peaks fits the splitting between LO and TO optical phonons. $^{104}$
3.9 Spectral and autocorrelation properties of graphene supermarket CVD h-BN

We next examine the PL spectral features of several emitters in purchased mono-layer CVD h-BN. Figure 3.11.a shows spectral features of three emitters in a monolayer on SiO$_2$. As stated before, a similar Raman harmonic structure appears also in the monolayer. We see that these three emitters have ZPLs of 583 nm, 643 nm and 691 nm with energies in the range of less than 65 meV to those found in thicker flakes in Figure 3.10.e (the pairs of [569 nm, 594 nm], [622 nm, 650 nm], [683 nm, 697 nm]). For comparison, detuning up to 170 meV has been seen for the ZPL of emitters in WSe$_2$.

We find that sharp spectral features are also present in the monolayer regime, with a FWHM $\nu$ minimum of 9.94 nm. This is approximately a factor of 2 larger than the minimum found in thicker h-BN. Figure 3.11.b shows the spectral features of a suspended emitter with a ZPL of 588 nm, similar to that shown in Figure 3.11.d. We find that when probing the CVD monolayer with an orange CW laser (594 nm) defects in monolayers show photoluminescence for several tens of minutes (Figure 3.11.c). In contrast to measurements performed with green laser, where emitters show blinking behavior, with orange excitation this behavior is not seen on stable defects, although sometimes after 7 hours or more of excitation the emitters bleach, perhaps due to an ionization mechanism or oxygen quenching. Near ZPL resonance, excitation stability was also seen for SQEs in WSe$_2$. Figure 3.11.c side demonstrates this stability for photon emission for a 20 $\mu$W 594 nm CW excitation for 45 minutes. In multilayer h-BN emitters could be probed more easily using the 532 nm CW laser and probing with 594 nm was not necessary. Figure 3.11.d side shows PL spectra for four emitters on SiO$_2$ with ZPLs of 629 nm, 640 nm, 643 nm and 657 nm for excitation at 594 nm.

The different layer thicknesses from multilayers to a monolayer implies that the local environment the emitter is exposed to can be significantly different on the c axis (from mostly B-N atoms, to atoms of the substrate, in this case SiO$_2$). We find that for emitters on CVD monolayer the brightness is significantly different for SQEs which have almost identical ZPLs (in the range of 89 meV, Figure 3.12.a). This is surprising due to a more homogenous environment each emitter in the monolayer should have compared to emitters in multilayers.
3. Two dimensional hexagonal boron nitride (h-BN)

Figure 3.11: CVD monolayer h-BN emitters. (a, b) CVD monolayer PL spectra using 532 nm CW excitation: (a) PL spectra for three emitters and (b) PL spectra for a suspended emitter. (c, d) 594 nm CW excitation using a 600LP filter. (c) Emission count from an emitter with a 640 nm ZPL for 45 min. (d) PL spectra for 4 emitters.

3.10 Emitter’s photo-physics

We therefore firstly analyze the photo-dynamics for multilayers to gain insight into the possible mechanisms involved. In Figure 3.12 we analyze the power dependent photo-dynamics for three SQEs with ZPLs: 696 nm (b), 580 nm (c) and 639 nm (e). The insets of Figure 3.12 b, c and e, depict our dynamics’ scheme, for a two level and a three level system, using the rate equation in 2.3.2 where the rate equation is expressed as frequencies. $\lambda_1$ is the excited state transition rate and $\lambda_2$ is the metastable state transition rate, $P_{\text{exc}}$ is the laser excitation power, $\alpha$ is a fitting parameter attributed to the power dependence of the excited state. We denote ‘1’ as the ground state, ‘2’ as the excited state and ‘3’ as the meta-stable state where $R_{ij}^0$ is the transition between the $i \to j$ states for zero excitation power. We assume the inter-system crossing (ISC) $R_{23}^{23}$ is power independent. We note for emitters having $R_{02}^{21} > 500$ MHz the APD jitter can play a role in the measured lifetime. $^{132}$ For these measurements we fitted our data with a convoluted $g^{(2)}(\tau)$ function with a Gaussian function $J(\tau)$ representing our system response time, giving us the de-convoluted values. Power dependent autocorrelation measurements were done on each SQE. For SQEs that showed bunching behavior the decay $\lambda_2$ was extracted by fitting a decaying exponential function. Using the value of $\lambda_2$, the antibunching area was fitted to extract $\lambda_1$. $\lambda_1$ is plotted as a function of excitation power and fitted using...
3. Two dimensional hexagonal boron nitride (h-BN)

the $\lambda_1$ function. We then extrapolate to zero power to extract $R_{01}^{21}$. The same procedure was done for $\lambda_2$ to extrapolate $R_{01}^{31}$ and $R_{23}^{23}$. For emitter (696 nm ZPL) analysis was done as a two level system since no bunching behavior was seen on the autocorrelation curves. We get an excited state relaxation rate of $R_{01}^{21}=1295\pm242$ MHz. For emitter (580 nm ZPL), shown in Figure 3.10.a we get an excited state relaxation rate of $R_{01}^{21}=303.98 \pm 10.30$ MHz, a long-lived meta-stable state with $R_{01}^{31}=162.12\pm92.45$ Hz and an ISC rate of $R_{23}^{23}=3.06 \pm 0.32$ KHz. For emitters in the monolayer (Figure 3.12.a) that showed bunching behavior (ZPLs 660 nm (black), 630 nm (red), 637 nm (blue) and 657 nm (green)) we note that the meta-stable state transition and ISC transition frequencies (Figure 3.12.d) are significantly different for emitters which have almost identical ZPLs. For ZPLs 660 nm, 657 nm, 630 nm, 637 nm we get for $R_{01}^{31} - 2.53\pm0.42$ kHz, 0.59$\pm$0.10 kHz, 2.12$\pm$0.20 kHz, 1.26$\pm$0.34 kHz and for $R_{23}^{23}$ - 2.95$\pm$1.88 kHz, 0.52$\pm$0.39 kHz, 4.49$\pm$1.46 kHz, 2.63$\pm$1.07 kHz, respectively. The emission frequency of emitters is described by the following equations:

$$C_{\text{inf}} = \frac{(R_{01}^{21}+R_{01}^{23})\phi_F}{R_{01}^{23}+R_{01}^{23}} , \quad C(P_{\text{exc}}) = C_{\text{inf}} \left( \frac{P_{\text{exc}}}{P_s} \right)^{\frac{1}{\phi_F}} \frac{P_s}{P_{\text{exc}}}. \quad (3.1)$$

Where $C_{\text{inf}}$ is the saturated emission frequency, $C(P_{\text{exc}})$ is the power dependent emission frequency, $\phi_F$ the quantum yield and $P_s$ is the saturation power. Our meta-stable and ISC rates are all in the kHz scale whereas the excited state rates are in the MHz scale, meaning $R_{01}^{21} \gg R_{01}^{31}, R_{23}^{23}$. Therefore, although the meta-stable and ISC rates are diverse, the dominant factors affecting emission efficiency are the excited state transition rates and the quantum yield. We can ascribe these diversities to different local environments in which the SQEs are embedded, as was observed for e.g. NV defect in nano-diamonds or perhaps due to different charge states of h-BN, which were recently demonstrated for defects in h-BN. The diversity of meta-stable and ISC transition rates, in account with the roughly homogenous environment in the monolayer, are another strong indicator to the possible presence of charge states as will be discussed further. For emitter (639 nm ZPL) the excited state relaxation rate is $R_{01}^{21}=620\pm140$ MHz (Figure 3.12.e – center). Figure 3.12.e (right) shows the different $\lambda_2$ frequency for two CW excitations: 532 nm (green) and 594 nm (orange). The two curves converge upon zero power indicating that the transition frequency is not affected in the meta-stable state. We get $R_{01}^{31}(594 \text{ nm}) = 3.5 \pm 0.3 \text{ MHz}$ and $R_{01}^{31}(532 \text{ nm}) = 3.2 \pm 0.6 \text{ MHz}$ which are well in the range of each other. However, for the ISC we get different rates: $R_{23}^{23}(594 \text{ nm}) = 27.5 \pm 1.9 \text{ MHz}$ and $R_{23}^{23}(532 \text{ nm}) = 13.4 \pm 4 \text{ MHz}$. The ISC transition rate for 594 nm excitation is approximately a factor of 2 larger than for 532 nm. Therefore, 532 nm leads to an efficient de-shelving of the metastable state. This can be seen when comparing the emission counts using the two different
excitations (Figure 3.12.e – left), revealing that emission starts to saturate as we leave the linear regime behavior. Therefore, we extrapolate the saturation curves using \( C_{\text{inf}} \) and \( C \). We see that 532 nm excitation is more efficient, with \( \phi_{\text{F}(532 \text{ nm})} = 0.8 \pm 0.2 \) and \( \phi_{\text{F}(594 \text{ nm})} = 0.61 \pm 0.06 \). To further exclude the source of the defects as external ad-atoms we also attempted to expose exfoliated flakes to different gas environments and different chemical environments. An analysis can be seen in the SI, showing that emitters exhibit the same spectral features after treatment. Previous research using a scanning tunneling microscope has also shown that charged h-BN defects are intrinsic and not caused by ad-atoms.\(^{134,135}\) We therefore sought out to ascertain if the SQEs in h-BN are spatially correlated with the h-BN hexagonal structure. Exfoliated h-BN exhibits more uniform crystallinity. To this end, we analyze an example of two emitters on the same confocal spot and between pairs of emitters on the same flake in close proximity by rotating the polarization of the excitation laser. This analysis is displayed in section 3.13 and shows that emitter orientation is related to the h-BN hexagonal structure. We note that the large number of grain-boundaries in CVD h-BN excluded the option to check the orientation of emitters relative to each other in CVD h-BN in the same fashion. The spectral features we have observed, where the peak energy difference fits the splitting between longitudinal (LO) and transverse optical phonons (TO), is another fingerprint for a defect embedded inside the lattice, as seen also for SQEs in the UV range.\(^{123}\)

Figure 3.12: h-BN emitter’s ZPL variations and emission rates with green and orange excitation. (a) Photon counts for emitters in CVD monolayer h-BN divided into two categories: two-level systems (658 and 646 nm) and three-level systems (660, 630, 637, and 657 nm) for 594 nm excitation. Power-dependent transition rates for 696 nm ZPL (b), 580 nm ZPL (c, d), and 639 nm ZPL (g, h). (f) Photon counts for the 639 nm emitter, for 594 nm excitation, and for 532 nm excitation. Saturation curves were fitted as described in the text. The dashed line indicates crossing of the two curves. (e) Metastable and ISC transition rates for four emitters with ZPLs 660 nm (black), 630 nm (red), 637 nm (blue), and 657 nm (green) in CVD monolayer h-BN for 594 nm excitation.
3. Two dimensional hexagonal boron nitride (h-BN)

3.11 Chemical testing and etching methods

Two chemical etching methods were used to create SQEs. We note for that the majority of the flakes to remain attached to the substrate it is important to anneal the sample first.

For the peroxymonosulfuric resistance test we first placed the sample inside H₂O₂:H₂SO₄ with a ratio of 3:7 at 135°C for 2 hours, which is known not to etch the h-BN.

3.11.1 Etching method I (H₂O₂:H₂SO₄)

For mild etching of the flakes the sample was placed in H₂O₂:H₂SO₄ in a ratio of 3:6 at 135°C for 2 hours. The solution was let to cool down to room temperature and then diluted with distilled water (DI). Finally, the sample was rinsed in DI water, subsequently in isopropanol and dried with N₂ gas.

3.11.2 Etching method II (+H₃PO₄:H₂SO₄)

The sample was first mildly etched using etching method 1 for 20 minutes. After completion of method 1, the sample was placed in a solution of H₃PO₄:H₂SO₄ with a ratio of 1:8 at 75°C for 12 hours. The solution was then diluted with H₂O mixed with DI water. Finally, the sample was rinsed in DI water, subsequently in isopropanol and dried with N₂ gas. This method is similar to the way h-BN functionalization was achieved as in Ref. 136.

3.12 Ion irradiation

Flakes were exfoliated on a patterned SiO₂ substrate in order to identify the flakes that were irradiated.

The sample was then annealed in vacuum to fixate the flakes to the SiO₂ substrate. Afterwards the sample was transferred to an irradiation chamber with a vacuum of 2·10⁻⁷ mbar where homogeneous irradiation of He and N for predefined irradiation doses was done with acceleration energies of 2 keV and 2.5 keV, respectively. After irradiation the sample was annealed again at 850 °C in vacuum. Helium has been shown to convert BN from the hexagonal phase to the cubic phase. However, this was reported for much larger acceleration energies (> 200 keV) far from our working range (<2.5 keV).

Figure 3.8 shows the PL spectra of high dose ion irradiation (10¹⁴ cm⁻²), (left hand) for N (purple curve) and He (black curve). Comparing between both PL spectra we can deduce that the PL spectra is a superposition of many emitters. However, both PL spectra are not dissimilar and can be seen as a shift of one with respect to the other. Right hand of Figure 3.8 shows PL spectra for low dose irradiation. For both atom species a similar PL spectra is seen similar to that obtained from the untreated flakes and chemically treated flakes. Previous research using low energy argon and N₂ ion irradiation (<2 keV) also suggests that the same defects were formed by both irradiation methods 138. Due to the high density (see Table 3.1) isolating SQEs in irradiated sample was more challenging.
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3.13 Emitter pair’s excitation polarization comparison

In Figure 3.13.a1 we plot a QE’s PL spectrum and superimpose autocorrelation measurements on the PL spectra for clarity. PL spectra (Figure 3.13.a1) reveals a sharp peak in the wavelength regime of 550 nm to 575 nm. A closer look shows that it is constructed out of two peaks (Figure 3.13.a1 - inset). We fit this peak with two Lorentzians, which agrees well with the original peak. We associate the first two peaks with two zero phonon lines (ZPL). This is also confirmed by the autocorrelation measurement that goes to a value of $g^2(0) \sim 0.57$ (Figure 3.13.a1- I), indicating it is not a single QE. We notice that the background also emits light in this wavelength (marked as ‘background’ in PL spectra), and therefore would contribute to our measured $g^2(0)$. Changing the spectrum detection range by filtering the PL spectrum on the APDs in the range of 575 nm to 600 nm assists in avoiding background contributions in an attempt to see if the value of $g^2(0)$ goes lower than 0.57. Indeed, $g^2(0)$ decreases to a value of 0.49 (Figure 3.13.a1- II). We therefore conclude that the confocal spot contains two emitters. To better understand the spectral features, we perform cross-correlation measurements when filtering the spectrum on different parts for each APD: one in the range of 552 nm to 576 nm and the other in the range of 640 nm and above (Figure 3.13.a1- III). The value of $g^2(0)$ for this measurement is 0.66. We therefore conclude that the spectral features of both QEs are superimposed on the whole range of our spectral detection range. Asymmetric features appear on the cross correlation curve, which might indicate different excited states’ lifetimes for each emitter.

If the emitters are associated with the h-BN structure, their dipole orientations should reflect the h-BN hexagonal symmetry. Due to the possibility of various crystallinity of h-BN throughout a flake $^{139}$, the case presented above is a perfect test of two emitters in proximity at the same confocal spot.

To that end, we rotate the polarization of the excitation laser and record the PL spectrum. All spectral features of the emitter decrease in amplitude on the PL spectrum but retain their original PL shape as we rotate the linear polarization, and at 90 degrees a flat PL spectral line is recorded (Figure 3.13.a2). It is therefore likely that both emitters are oriented in the same direction or with an angle of 180 degrees between them. This is illustrated in Figure 3.13.a. Because the cross correlation measurement shows that the PL spectral features are overlapping and have a similar structure, it is more likely that a pair of defects of the same type are located on same site location on two different h-BN rings, which are inside our confocal spot.

More comparisons between excitation polarization angles for pairs of SQEs roughly in the range of ~5 µm from each other on the same flakes are seen in Figure 3.13.b. A difference of ~0 or approximately ~30 degrees between SQEs is seen. We note that the polarization curves do not precisely overlap,
perhaps due to curvature of the flake on the substrate which would lead to slightly different angles with the excitation laser between the SQE pairs.

![Figure 3.13: Comparison of correlation, spectral and polarization properties emitter pairs in proximity. (a) PL spectra of emitter pair superimposed by correlation functions for different spectral ranges. For correlation functions I-II the APDs are filtered by the same filter whereas in III the filter range is different. (b) PL spectra for different linear excitation laser polarizations. (c)(d)(e) Emitter pair’s emission while rotating the linear excitation laser.]

### 3.14 Chemical and gas environment treatments

To further exclude the source of the defects as external ad-atoms we also attempted to expose exfoliated flakes to different gas environments and different chemical environments. Firstly we anneal in Ar/H\textsubscript{2} gas environment at 350 °C as described in Ref. 134. Figure 3.14 shows that the associated PL spectra of the emitters with ZPLs in the range of 623 nm to 636 nm are still present after this treatment. h-BN is known for its high chemical inertness, whereas peroxymonosulfuric acid at certain concentrations is known not to harm h-BN during chemical cleaning, depending on acid concentrations 128. To further clarify the origin of the defect we put the sample for 2 hours in an acid solution, after which we scan the flakes. Figure 3.14 shows that QEs of ZPLs ranging from 586 nm to 593 nm are still present after the acid process.
3. Two dimensional hexagonal boron nitride (h-BN)

![Quantum emitters after exposure to different chemical environments. (a) after annealing an Ar/H\textsubscript{2} at 350 °C for 30 min. (b) and after treatment in acid.](image)

**Figure 3.14**

3.15 In-house grown CVD h-BN

We examine in-house grown CVD h-BN on Cu foil and transfer it to SiO\textsubscript{2}, sealing the sample in N\textsubscript{2} environment to avoid oxidation\textsuperscript{121}. We probe the sample with a 532 nm laser with a power of 4.4 mW. We record a confocal image scan, PL spectra from 2 defects and auto-correlation measurement on a flake of micron scale (Figure 3.15). Looking at the location of the defect in Figure 3.15, it seems to be on a line shape on the h-BN flake, possibly indicating a surface perimeter.

PL spectra resemble those recently found in\textsuperscript{124}. We observe anti-bunching behavior. However, the emitter’s \(g^2(0)\) does not go below 0.5 with excited state time (for 4.4 mW) \(\tau_1 = 0.34\) ns and metastable state time \(\tau_2 = 402.35\) ns. The background contribution to the signal is substantial and therefore we calculate the autocorrelation function after background subtraction\textsuperscript{70}. After correction \(\tau_1 = 4.37\) ns.

We note that after correction only one data point on the curve goes below 0.5. Considering our recent findings we note that by filtering one cannot exclude the spectral range of 550 nm to 575 nm as background since QE emission exists in this regime also as was shown in Figure 3.15. We therefore tentatively attribute these features to a superposition of QEs which would result in a very short excited state lifetime.
3. Two dimensional hexagonal boron nitride (h-BN)

Figure 3.15: CVD home grown h-BN emitter properties. (a) PL scan using a 532 nm laser and a 550LP filter. (b) Correlation function for area marked in (a) before and after background correction. (c) PL of 2 emitters from the sample.

3.16 Bulk excitation of an h-BN crystal

Using high power 633 nm excitation (1 mW) and 690 LP filter, we probe a bulk h-BN single crystal. Confirming our previous results, emission originates primarily from the surface interface of the crystal, and not from the deeper internal area of the crystal, as seen in Figure 3.16
Two dimensional hexagonal boron nitride (h-BN)

3.17 Paramagnetic point defects

Interestingly, a small fraction of emitters that on the \( g^2(t) \) correlation function shows traits of single emitters (correlation function dip), responds optically to applied magnetic fields. This magnetic response is first identified as a drop/rise in the fluorescence count from the emitter. Nevertheless, to date, those that respond to magnetic field have PL-emission that starts in the red wavelength of the spectrum (~ > 690 nm). This implies that excitation using less energetic lasers (with wavelengths > 600 nm) is favorable for isolating these emitters and avoiding excitation of emitters of lower wavelengths which do not show this effect. Nevertheless, from our measurements of emitters that do show emission in the above 690 nm, of these only numerous emitters respond to magnetic fields optically. One such emitter can be seen in Figure 3.17 using 730 nm laser excitation. In chapter 5 we study this type of emitter extensively.
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Figure 3.17: Paramagnetic emitters excited with a 730 nm laser with a power of 80 µW. (a) Photoluminescence map using a 750LP filter. Arrows indicate a ‘line’ area on the flake where the emitters are concentrated. (b) Photoluminescence spectra of an emitter displaying an optical response to an applied magnetic field. (c) Photon count distribution for 1000 seconds as a function of counts. When an applied magnetic field of ~1 Tesla is applied there is a reduction of counts distribution (red curve), while without (black curve) the count distribution increases. (d-g) $g^2(t)$ function for this emitter with (red) and without (black) a magnetic field. The amplitude of the correlation function (d) is increased then the magnetic field is present (compared to e), indicating more frequent transitions through the meta-stable (dark) state.

3.18 Conclusions

We now reflect upon the possible effects of sample preparation methods presented. Carbon impurities were shown to account for UV luminescence\textsuperscript{122} and recently for SQEs in the UV range, substituting the N vacancy site.\textsuperscript{123} The chemical treatments and Ar/H\textsubscript{2} environments the flakes were exposed to reduces the probability that organic contaminants are responsible for the emitters seen, unless a carbon impurity was embedded inside and not exposed to the external areas of treatment. Since samples were annealed at 850 °C, oxygen should desorb from the flake (above 300 °C\textsuperscript{140}) as well as gas atoms possibly trapped at interfaces. The suspended h-BN flakes also discard trapped atoms. We thus conclude that it is unlikely that organic additives or trapped gas atoms are responsible for the emitters found. Nevertheless, the chemical treatments done also have a strong oxidizing effect on the flakes\textsuperscript{128} and can incorporate oxygen inside the lattice which cannot be discarded. We find that He irradiation generates the highest density of emitters (Table 3.1). Approximating the He atom inelastic collision to an electron inelastic collision we can compare to TEM research.\textsuperscript{141,142} Temperature variation during irradiation creates different defects shapes\textsuperscript{142} demonstrating that defect formation is dependent on the environment around the defect, emphasizing the importance of using gas during the annealing process compared to vacuum and could explain the difference in emitter stability. The vacancy sizes created cannot only be point-like (atomic) but also nano-sized as seen in the TEM images of Refs.\textsuperscript{141,142} Annealing at 850 °C may cause vacancies to diffuse inside the flake\textsuperscript{143} similar to diffusion...
known for the NV defect annealing in diamond,\cite{144} leaving defects not exposed to the external environment. However, for the mono-layer, the defect is directly exposed to the environment.

Previously, the ZPL of 623 nm was attributed to the anti-site complex ($N_BV_N$).\cite{117} Our data shows the ZPL emission line to be between 1.78 eV to 2.18 eV (569 nm to 697 nm), suggesting that other types of impurities could also be responsible for the observed emission lines. The structural features we have observed indeed suggest a link between structure and defects. We discuss possible links comparing TEM data from previous research and density functional calculations. We note that clear identification of defect structure requires ultra-clean conditions due to the tendency of adsorbents (carbon and oxygen) to substitute defective sites,\cite{111,145} possibly also accountable for emission.\cite{146}

HRTEM has shown interlayer bonding on flake edges (nano-arches),\cite{112} which can also be induced by electron irradiation of h-BN.\cite{147} This can explain our observations of emitters located at perimeters of a flake on top of another flake (Figure 3.7.f/g) or at boundaries (Figure 3.7.e), for untreated flakes and chemically treated flakes, as shown for the SQE in Figure 3.10.a/b. It can also explain our irradiation results.

The B vacancy (visualized in TEM\cite{148,149,113,150}) has a high average density of states in the energy range of 1.78 to 2.18 eV,\cite{151} making it a possible candidate. However, the dynamics behind vacancies in 2D materials can be more complex than in 3D solids: B vacancies exhibit interlayer bonding behavior seen in bi-layer h-BN which do not occur for the N vacancy:\cite{113} N bonds occur in the layer with the defect and one or two B atoms from the intact layer, reducing the symmetry of the vacancy from three- to two-fold,\cite{149} consistent with the symmetry of the $N_BV_N$ complex.\cite{117} This type of reconstruction is not observed for mono-vacancy defects inside multi-layered h-BN which retain their three-fold symmetry.\cite{152} This hints at a connection between the low dimensionality of h-BN to quantum features not seen inside bulk h-BN but occurring at the boundaries of the material, reminiscent of our observations.

Bonds not native to monocrystalline h-BN may play an important role for visible spectrum emission. Due to alternating bonds in h-BN (B-N), a non-native bond would be of the type of B-B or N-N, known as a Homo-elemental bond, which belongs in literature to Stone-Wales defects. These comprise a family of defects which also the $N_BV_N$ complex\cite{117} is included in due to N-N-N bonds. A Stone-Wales defect can create square-octagon/pentagon–heptagon pairs in h-BN, changing bond lengths and having charge state configurations. Monolayer h-BN Stone-Wales defects have been visualized in TEM,\cite{154,155} forming due to grain boundaries between domains, thus decreasing the band-gap and opening new energy states.\cite{154} Calculated energy levels suggest emission in the visible spectral range and with a less dominant phonon DOS of $\sim 41$ THz ($\sim 170$ meV), fitting our TO and LO observations.\cite{157}
We can now link the angular multiplicity we have seen on perimeters where emitters are clustered (Figure 3.7.h/i) as another hint to the presence of Stone-Wales defects or a grain-boundary effect.\textsuperscript{156,157} Grain-boundaries in h-BN have been seen to be up to 90 µm long,\textsuperscript{158} well in range of our perimeter lengths. Although N\textsubscript{2} ion irradiation has been shown to generate primarily N vacancy defects, they can also create interstitials which do not diffuse out of the lattice when annealing at 850 °C. These can create homo-elemental bonds not native to the lattice,\textsuperscript{129} and hence also the similarity to monolayer h-BN. Similarly, local changes in h-BN layer stacking order has been shown via cathodoluminescence to account for a 1 eV range of emission of excitons (originating at ~200 nm wavelength).\textsuperscript{120} This raises questions regarding the value of the band-gap at perimeters in h-BN, which should be smaller.\textsuperscript{154,156}

The quantum nature of emission and the high transition rates ( > 500 MHz) measured for the excited states can arise from the reduced dimensionality of h-BN and the small bond lengths (1.4 Å\textsuperscript{105}) which leads to large overlap between orbitals.\textsuperscript{153} The variety of meta-stable and ISC transition frequencies found in CVD monolayer h-BN can have numerous causes. An intermittent charge state change during the acquisition of photon arrival times in our auto-correlation measurements not distinguishable on the photon trace, similar to the NV\textsuperscript{0} and NV\textsuperscript{−} charge states in diamond\textsuperscript{36} would affect these transitions. Spin-orbit coupling\textsuperscript{29} can also influence these transitions. Oxygen binding to nearby N vacancy sites\textsuperscript{121,111} in proximity to the emitter can affect transition rates\textsuperscript{159} or cause intermittency via charge tunneling.\textsuperscript{160} It is worth noting that two-level and three-level systems have also been seen for the zinc vacancy in ZnO.\textsuperscript{43}

To summarize, we investigated the correlation between different fabrication methods for defects in h-BN and the emitter density, photostability and structural features of h-BN. The creation of defects using chemical exfoliation further demonstrates the role of the exterior surface for QEs in h-BN. Our results demonstrate that the thinner and more edgy the flake is, single emitter density becomes higher. We showed that slow rate chemical etching is a more facile method compared to ion irradiation for single emitter creation in multilayered exfoliated h-BN, since it can be more easily fine-tuned to a slow rate.\textsuperscript{128} Using an insulating mask for ion irradiation might be beneficial to avoid ensemble creation by reducing collision damage of the ions. However, this would necessitate more steps in the process. Previous research has shown that by electron irradiation single emitters can be generated,\textsuperscript{161} the smaller collision profile of an electron can therefore be more beneficial as compared to an ion collision profile for emitter creation. Nevertheless, for inducing vacancy defects in monolayer h-BN, high energy ion irradiation can be a useful method, and using atoms with higher mass than nitrogen might be useful to tailor the type of vacancy created.\textsuperscript{162}
We showed that similar emitter spectral features are present from bulk h-BN down to the mono-layer. We also measured emitters’ ZPL spectral FWHM comparable to that of bulk h-BN and we found emitters which are photo-stable under orange laser excitation.

Our results show color diversity of h-BN consistent with previous reports, with ZPLs in the red visible spectrum, thereby enabling excitation with less energetic lasers, as was done in the h-BN CVD monolayer case. Using pyrolytic h-BN species might increase chemical inertness, reducing free oxygen concentration and impurities in h-BN, thus eventually reducing spectral diffusion and photo-bleaching.

Further understanding of the origin of SQEs in h-BN can lead to more advanced fabrications methods in the CVD growth phase or after the growth phase, using ion irradiation and ion implantation, which has been demonstrated for Si, Be and Ar - embedded in the lattice. Band-gap tuning can be realized using monolayer h-BN as a platform with other monolayer 2D materials, tailoring the emitter’s energy levels inside the band-gap. Clearly, a wide range of parameter adjustment can lead to diverse SQE defects in this wide band-gap material.

The work presented here paves the way for deeper understanding of the origin of QEs in h-BN. It proposes two fabrication methods to create emitters, demonstrating the flexibility of the material and emphasizing the role structure has on defect dynamics in 2D materials. These results highlight the diversity in the new arising field of 2D quantum emitters.
3. Two dimensional hexagonal boron nitride (h-BN)
3. Two dimensional hexagonal boron nitride (h-BN)
In the previous chapter we have linked emitter density in 2D h-BN to perimeters. In this chapter we investigate a curvature-abundant BN system – quasi one-dimensional BN nanotubes (BNNTs) fabricated via a catalyst-free method. Non-treated BNNT is revealed to be an abundant source of stable QEs. We analyze their emission features down to single nanotubes, comparing dispersed/suspended material while combining high spatial resolution of a scanning electron microscope to categorize and pin-point emission origin to a scale of less than 20 nm. This gives us a one-to-one validation of emission source with dimensions smaller than the laser excitation wavelength, elucidating nano-antenna effects. We identify two emission origins: hybrid/entwined BNNT. By artificially curving 2D h-BN flakes, similar emitter spectral features are observed. The impact on emission of solvents used in commercial products and curved regions is also demonstrated and evaluated. The ‘out of the box’ availability of QEs in BNNT, lacking processing contamination, is a milestone for unraveling their atomic features. The data presented open possibilities for precision engineering of QEs, puts h-BN under a similar ‘umbrella’ of TMDC’s QEs, providing a model explaining QEs spatial localization/formation using electron/ion irradiation and chemical etching.
4. One dimensional Boron nitride nanotubes (BNNT)

4.1 Introduction

BNNTs can be seen as the 2D h-BN hexagonal grid rolled into a closed nanotube structure, making them a natural candidate to explore the effect of curvature in BN systems. The 1D nature of BNNTs means that the system should be perimeter (edges, boundaries) as well as curvature-abundant. Both have in-plane sp$^2$ orbitals with similar bond lengths: BNNT - 1.44 Å and h-BN - 1.45 Å. With increasing diameter, the formation energy of BNNTs approaches that of 2D h-BN. BNNTs are also analogues to the more explored system of carbon nanotubes (shown to harbor QEs) with the distinct difference of a wide bandgap of ~ 5 eV, which is independent of non-deformed nanotube geometry and helicity. BNNT's broken sub-lattice symmetry gives rise to a macroscopic electric polarization, whose ground state polarization is an intrinsically nonlocal quantum effect. Small diameter BNNTs buckle - B atoms move inward and N atoms outward - resulting in a dipolar double cylinder shell of a negative/positive outer/inner N/B cylinder, respectively. In an analogous manner, for monolayer h-BN, a dipolar electric distribution has been shown to occur above and below the monolayer, probed by nuclear quadrupole resonance (nuclear spin ≥ 1 in the lattice) using a nitrogen vacancy color center in diamond. BNNTs have shown intriguing physics such as the giant Stark effect and transformation of BNNTs from insulating to semiconducting using physical deformation. Due to their high temperature stability, light weight, high stress endurance, resistance to oxidation at non-defective sites, biocompatibility and potential use as neutron shields/detectors, BNNTs are ideal for emerging space technologies as well as for biological cell research. Photo-luminescence of BN nano-whiskers, using cathodoluminescence, has shown emission in the visible range attributed to point defects, quantum confinement and sp$^3$ bonding. For BNNTs, exciton emission was shown for deep ultraviolet wavelengths. Using near bandgap excitation, defect bound excitons' emission was independent of nanotube diameter and wall thickness (for at least 20 layers) and optically shown to behave as pieces of curved 2D h-BN. Above bandgap excitation energy has shown hints of sp$^3$ bonded defects contributing to emission, whereas X-ray excited optical luminescence was also sensitive to tube curvature. Oxygen defect related radiative transitions have also been proposed. BNNT transmission electron microscopy (TEM) research has visualized induced elastic deformation in tubes for angles larger than 30 degrees, point defects such as boron and nitrogen vacancies, BN di-vacancies (reconstructing to Stone-Wales structures), pentagons and heptagons atomic configurations (Stone-Wales) at tube terminations, and a range of helices (from zig-zag to arm-chair) within a single tube. Less destructive spectroscopy methods combining AFM and near-field infrared scattering have also shown the presence of twists and structural defects. From these atomic resolution and optical observations, it is clear that point-like atomic defect species formation in this flexible nano-material is intimately connected to geometry, curvature, strain...
and proximity to the environment due to its large surface area. Recently, it has also been shown that BNNT can serve as a scaffold for other colloidal wide bandgap semiconductors such as ZnO, thus creating hybrid BNNT. Nevertheless, BNNT research is relatively in its primary stages, due to only recently emerging reliable fabrication methods and difficulties arising in separating the nanotubes after fabrication, which are clustered in a semi ‘cotton’ like fashion in the bulk. Here we make use of commercially available BNNTs fabricated using a catalyst-free high temperature pressure (HTP) laser heating method and use them to further study single QEs in the BN hexagonal systems.

The chapter is divided as follows: BNNT properties are explained followed by a detailed description of the role oxygen has in BN systems. Then, spectral analysis of emission properties of bulk and micro-bundles of BNNT QEs is shown. Afterwards we show that by dispersion methods, quantum emission can be categorized in two PL spectral classes: one with relatively narrow features and the other with broader features. For each class, we conduct a spectral, phonon and lifetime analysis. These are supported by SEM imaging, confirming our classifications. We note that previous reports have shown electron irradiation to induce SQEs in h-BN, therefore all SEM imaging performed here were done after PL measurements. Finally, we demonstrate the role of curvature in low dimensional BN systems by artificially curving 2D h-BN flakes on diamond nanopillars and a ZrO$_2$ hemisphere. All measurements were done at ambient conditions using sub-bandgap excitation energies.

### 4.1.1 Structure and components

HTP-fabricated BNNTs come in a ‘cotton’ like form, consisting of numerous entwined tubes (see Figure 4.1). We define a ‘cotton’ ball of as received material with a radius of ~ > 5 cm as ‘bulk’ BNNT. HTP fabrication is advantageous since it is catalyst-free, produces high quality BNNTs, and minimizes defects from foreign atomic species (such as carbon) to the BN lattice as opposed to other methods (See Ref. for further details). Typical wall thicknesses range between 2 to 5 layers, with diameters of 3 nm to 6 nm and interspacing wall distances of 3.4 Å. Single nanotubes can be up to 200 µm long. Nevertheless, the material also contains 2-dimensional (2D) h-BN, typically in the lateral size range of 50 nm to 200 nm and also boron nanoparticles, visualized by TEM for HTP BNNT, as well as for various fabrication techniques. In addition, for annealed HTP BNNT, 2D BN oxide platelets have been visualized.

For simplicity we denote these nanomaterials, attached to the BNNT tubular structure, as hybrid material and discuss their implication. For the HTP fabrication method the measured bandgap is 5.74 eV, similar to that of 2D h-BN (5.95 eV).
4.1.2 The role of oxygen in BN hexagonal systems

Photoluminescence (PL) comparative studies in vacuum and ambient conditions on TMDCs and h-BN have shown that PL is strongly affected by ambient gas molecules, attributed to exterior surface defects exposed to reactive species which physisorb, such as O$_2$. An oxygen healing mechanism in h-BN for nitrogen vacancies (oxygen substituting nitrogen vacancies) has been observed in PL studies and TEM microscopy, with a time scale of 0.6 µs once exposed to ambient conditions, whereas h-BN was indifferent to N$_2$. In h-BN, stabilizing SQEs has been attributed to high temperature annealing (usually 850 ºC). Intuitively, this annealing should remove oxygen, however this procedure is done in an inert gas environment (typically argon) and not in vacuum. The only report of annealing in vacuum, resulting in less stable SQEs is described in Ref. Studies on annealing of WS$_2$ in an inert argon environment have shown SQE induced on perimeters, attributed to formation of WO$_3$, due to residual water/oxygen in the annealing chamber. It has been suggested there that similar SQEs species could be found in WO$_3$ crystals. Perimeter oxidation has been shown to be preferential in an independent study on WS$_2$ and WSe$_2$.

Core level spectroscopy reveals the effects of oxidizing environments on 2D h-BN in oxygen, demonstrating the creation of BN$_2$O, B-NO$_2$ and B-O$_3$ species as a substituting mechanism for nitrogen sites. A post-anneal in vacuum at 600 ºC demonstrated that B$_2$O$_3$ is formed and oxygen is not removed with a complete destruction of the monolayer. Using x-ray absorption, sputtering h-BN in an inert environment resulted also in B$_2$O$_3$ structures, attributed also to residual water/O$_2$ in the chamber, whereas using a prolonged pre-bake of the preparation chamber reduced the observed oxygen. To the best of our knowledge, in all the annealing procedures to date of h-BN SQEs, no long pre-bake of the annealing chamber was performed prior to annealing in inert gas. Different studies of annealing in air revealed that oxidation can occur for temperatures above 700 ºC for h-BN and BNNT, forming the aforementioned 2D hybrid oxide platelets. Furthermore, a PL study for SQEs in h-BN, post-annealed in vacuum (after annealing at 850 ºC in argon) has shown stable SQEs up to (526 ºC) 800 K, hinting to a connection of the observed temperature stability of oxygen in the other study. It has even been shown that SQE creation is correlated with increasing annealing temperatures in argon with a maximum yield at temperatures of 1000 ºC – well above 700 ºC. We note that in these oxidation studies the threshold temperature for oxidation is given from data acquired from numerous oxygen defects and does not reveal the threshold for creation of point-like minute nano-B$_2$O$_3$. The SQE studies suggest that although oxygen was not directly used in annealing procedures, minute traces of oxygen were present, possibly creating nano-B$_2$O$_3$ structures. In addition, X-ray absorption ion irradiation studies on h-BN and BNNT, have demonstrated oxygen healing once re-exposed to ambient conditions with irradiation favorably
4. One dimensional Boron nitride nanotubes (BNNT)

creating nitrogen vacancies. \(^{209}\) h-BN irradiation was shown to also induce SQEs in other studies. \(^{107,197,199}\) In these SQE studies, irradiating and annealing were independent, \(^{107,197,199}\) therefore exposure to ambient conditions exceeded a time scale of 0.6 µs \(^{121}\) prior to annealing, allowing oxygen healing of freshly induced defective sites.

In our BNNT material, composed of curved h-BN units and also 2D h-BN, \(^{85,176,200,201}\) the surface area is higher than a bulk (or exfoliated) h-BN crystal. The concentration of exterior surface defects is therefore also higher and healed by ambient oxygen. The high temperature method used to create BNNT, annealing done in previous SQE studies of 2D h-BN \(^{117,193,107,163,194,195,197,198,199}\) (as well as in this study, see below and SI) to stabilize emitters, \(^{121}\) chemical oxidation etching shown to induce SQEs, \(^{107}\) oxygen related photochemistry \(^{192}\) of photo-induced modifications of SQEs to blue wavelengths, \(^{194}\) in conjunction with observations written above, warrant an optical investigation of B\(_2\)O\(_3\) to evaluate the role oxygen can play in semiconductors of the boron family. Oxygen can be introduced during fabrication, exposure to air prior to annealing, during annealing in chambers with traces of water/O\(_2\) or during the processing of h-BN in solvents/liquids (processing sensitivity is demonstrated in 4.2.14).

The most common form of B\(_2\)O\(_3\) is vitreous (v-B\(_2\)O\(_3\)), \(^{211,212}\) since spontaneous crystallization of B\(_2\)O\(_3\) is not a simple process. \(^{213}\) v-B\(_2\)O\(_3\) contains BO\(_3\) and planar boroxol rings (an analogous h-BN ring with O substituting N in the center of B\(_3\)O\(_6\), Schematic – Figure 4.2.a), with a bandgap of ~ 6 eV. \(^{213}\) These planar rings can be seen as disordered planar 2D material within the bulk.

### 4.2 Results

![Figure 4.1: An optical picture of ‘Bulk’ BNNT.](image)

**Figure 4.1: An optical picture of ‘Bulk’ BNNT.**

#### 4.2.1 Bulk BNNT

As a first step, bulk BNNT (see section 4.5 for preparation methods) was probed using 735 nm Raman excitation. We confirm the Raman-Stokes shift of BNNT with the main peak at 1379 cm\(^{-1}\) (Figure 4.2.a) corresponding to the \(E_{2g}\) in-plane Raman modes, with a similar PL structure to those seen in previous infrared Raman studies. \(^{200,214,215}\) We surmise that some sp\(^3\) hybridization is present and the peak at ~ 3200 cm\(^{-1}\) can correspond to B-OH/B-O bonds, \(^{200,216}\) or possibly to moisture. \(^{175,200}\) For clarification, on the wavenumber axis in Figure 4.2.a we show the known Raman shifts and optical phonons for four species of the boron family: h-BN, BNNT, cubic BN (c-BN) and Boric acid (c-BN is an sp\(^3\) allotrope of BN...
4. One dimensional Boron nitride nanotubes (BNNT)

which is isoelectric to diamond\textsuperscript{217,218}). See below for a detailed analysis of this PL. An energy-dispersive
X-ray spectroscopy (EDX) measurement on bulk BNNT (Figure 4.2.a – inset) identifies 3 major atomic
components: B/N (0.17/0.39 eV, respectively), as expected, and oxygen (0.53 eV), in agreement with
our Raman measurements. Consistent with previous studies,\textsuperscript{87,126} the carbon signal (0.27 eV) is
extremely weak. Upon 532 nm CW excitation, non-bleaching emitters are immediately evident, with
no slow-rate bleaching. We observe two typical PL spectral features, which as we will show, originate
from hybrid material (narrow PL features) and entwined BNNTs (broader PL features). Previous
research in 2D h-BN\textsuperscript{197} has also suggested that narrow/broad PL features can be an indicator for
different emitter classes. However, in the bulk only entwined BNNTs spectra could be discriminated
(spectral features are discussed below). We estimate an ensemble QE density using 532 nm excitation
of 0.47 µm\textsuperscript{-2} for bulk BNNT. Nevertheless, in the bulk, single QEs could not be isolated.
4. One dimensional Boron nitride nanotubes (BNNT)

Figure 4.2: Quantum emitters in BNNT chemical composition, phonon side band analysis of suspended or ‘on substrate’ emitters. Comparison to quantum emitters in v-B$_2$O$_3$. (a) Raman-Stokes shift measurement using 735 nm excitation for bulk BNNT (red curve). Known Raman shifts are displayed for clarity for h-BN and BNNT (overlapping grey squares and grey lines), c-BN (adjacent blue lines) and B-OH (blue line). Inset – EDX spectra from bulk BNNT. Schematic – unit cell of a typical h-BN unit and unit cells found in v-B$_2$O$_3$. (b) schematic/microscope image of suspended BNNT on Al needles. (c) PL spectra of a QE which is single using 22 µW 594 nm CW excitation but is not single using 22 µW 532 nm CW excitation - indicated by autocorrelation insets ((e) and (d), respectively). (f) PL representative spectral features for dispersed QEs from hybrid BNNT material using a 550LP filter (curve 0), chemically etched h-BN using a 600LP filter (curve 1) and v-B$_2$O$_3$ (curves 3 and 4) (inset - autocorrelation measurement for an v-B$_2$O$_3$ QE, proving it is single (g2(0) < 0.5)) all excited with 100 µW of 532 nm CW.. (g) Graph - PSB detuning from the ZPL, left in wavenumbers, right in energy. The blue dots represent suspended QEs and red dots QEs dispersed on the substrate. Schematic – depiction for different vibronics for an oxygen based defect/interlayer bond defect (left/right, respectively).
4.1 One dimensional Boron nitride nanotubes (BNNT)

4.2.2 Raman analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Hexagonal BN (h-BN)</th>
<th>BN nanotubes (BNNT)</th>
<th>cubic BN (c-BN)</th>
<th>Boric acid (B-OH)</th>
</tr>
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<tbody>
<tr>
<td>(In-plane) Modes</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter [nm]</td>
<td>-</td>
<td>0.7 - 2.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Raman Species</td>
<td>$E_{2g}$</td>
<td>$E_{2g}$</td>
<td>-</td>
<td>$E_{2g}$</td>
</tr>
<tr>
<td>Wavenumber [cm$^{-1}$]</td>
<td>LO: 1453.3 - 1614.8, TO$_{1i}$: 1364.5 - 1453.3</td>
<td>1356 - 1380</td>
<td>TO: 1055, LO: 1304</td>
<td>3251</td>
</tr>
<tr>
<td>Energy [meV]</td>
<td>LO: 180 - 200, TO$_{1i}$: 169 - 180</td>
<td>169.3 - 171.2</td>
<td>TO: 130.6, LO: 161.5</td>
<td>403.3</td>
</tr>
<tr>
<td>(Radial/Out of plane) Modes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.2 to 2</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Raman Species</td>
<td>Radial breathing modes (RBM)</td>
<td>-</td>
<td>-</td>
<td>$E_{2g}$</td>
</tr>
<tr>
<td>Wavenumber [cm$^{-1}$]</td>
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<td>1000 - 200</td>
<td>-</td>
<td>735</td>
</tr>
<tr>
<td>Energy [meV]</td>
<td>TO$_{1i}$: 103 - 90.3</td>
<td>124.1 - 24.8</td>
<td>-</td>
<td>91.2</td>
</tr>
</tbody>
</table>

Table 4.1: Raman modes and optical phonon modes for four boron species: h-BN, BNNT, c-BN and boric acid (for which only the B-OH mode is displayed). Modes are generally characterized as in-plane and out-of-plane. This classification is only valid for h-BN, BNNT and B-OH. For c-BN, whose symmetry is zincblende, the transverse and longitudinal optical phonons (TO/LO, respectively) are classified for convenience as in-plane. Each mode’s Raman species (if named) is specified, as well as the wavenumber and energy. Diameter is valid only for BNNT whose modes depend on them. For h-BN, the flake thickness affects the modes as well, but for convenience it is not specified here.

It is seen in Figure 4.2.a that the Raman peak starts to rise at $\sim 1000$ cm$^{-1}$. Raman-Stokes modes in BNNTs can be more complex than in 2D h-BN: in BNNTs the diameter as well as the number of walls of the nanotube determine the Raman-Stokes shift. The $E_{2g}$ modes of BNNT are analogous to transverse optical parallel phonons (TO$_{1i}$) and longitudinal optical phonons (LO) modes of h-BN. In the limit of increasing tube diameter the Raman shift behavior approached that of 2D h-BN. Nevertheless the broad features of this peak hint to more complex features, other than in-plane modes. For clarification, in Table 4.1 we list the known Raman shifts (in wavenumber and energy) and optical phonons for four species of the boron family: h-BN, BNNT, cubic BN (c-BN) and Boric acid. c-BN nitride is an sp$^3$ allotrope of BN which is isoelectric to diamond. The radial modes of BNNT would fit only the start of the rise of the main peak at $\sim 1000$ cm$^{-1}$. Tube bundling mode-softening is well known from carbon nanotube research. However, ab initio calculations have shown that softening is only on the scale of $\sim 10$ cm$^{-1}$ for all modes in BNNT. Since the BNNT tube diameters we use are in the range of 3 nm to 6 nm and BNNT radial modes are for diameters smaller than 2 nm, we discard them as the cause of the broadening of this peak. Due to contributions in the wavenumber...
range of ~1000 cm\(^{-1}\) to 1379 cm\(^{-1}\) we conclude that some sp\(^3\) bonds (as attributed for higher energy excitations) \(^{181}\) present in our BNNT material could give Raman modes similar to c-BN modes (see Table 4.1). Similar c-BN modes have been attributed to sp\(^3\) hybridization of 2D h-BN at grain boundaries using high-resolution electron energy loss spectroscopy. \(^{219}\) Additionally, a peak at ~3200 cm\(^{-1}\) is visible, which can correspond to B-OH/B-O bonds \(^{216,200}\), or possibly to moisture. \(^{200,175}\) For clarity, the modes of the various BN species are displayed on the wavenumber axis.

### 4.2.3 Power-dependent photo-dynamics for Figure 4.2.c

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**Figure 4.3:** Level scheme, metastable state frequencies and confocal scan of a quantum emitter in BNNT. (a) Metastable state frequencies; Inset: excited state frequencies. Illustration depicts three state energy level scheme. (b) Optical scan using 22 µW 594 nm CW excitation reveals possible isolation of single QEs for BNNT suspended on Al needles

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**Figure 4.4:** \(\text{B}_2\text{O}_3\) PL scan
4. One dimensional Boron nitride nanotubes (BNNT)

4.2.4 Isolating single emitters in BNNT

Due to these observations, we reduce and disperse the nanotube material. Pulling a small string-like amount of BNNTs, we isolate bundles of nanotubes, whose diameters are on the micron scale. Taking advantage of the electrostatic polar nature of BNNTs, we suspend the micro-bundles on two aluminum needles, thus avoiding substrate contributions while preventing contact with the suspended region. A schematic/microscope image seen in Figure 4.2.b, top to bottom, respectively (See Figure 4.3.b for PL confocal scan). Remarkably, with the reduction of the amount of BNNT material and the decrease in excitation energy to the wavelength of 594 nm, single QEs (SQE) were isolated. In Figure 4.2.c-e/f (curve 0)/g we present features of SQEs originating only from BNNT hybrid material. Suspended material data is displayed in Figure 4.2.c-e. An autocorrelation measurement reveals a $g^2(0)$ value of 0.33 ± 0.01 (< 0.5) (Figure 4.2.e – orange curve) indicating the single nature of the emitter. The PL-spectra (Figure 4.2.c – orange curve) reveals a first sharp peak accompanied by a broader peak. We fit both with Lorentzians (blue and red fillings, respectively). Due to the high coefficient of determination ($R^2 = 0.98$) of the fitting and the similarity to PL features established in previous 2D h-BN research, we tentatively denote the lowest energetic emission peak as the zero phonon line (ZPL) and the second peak as the phonon side band (PSB). The ZPL is at the wavelength of 639 nm and the PSB is detuned ~ 120 meV (967 cm$^{-1}$) from the ZPL. We note that for some SQEs the entire PSB was absorbed inside the ZPL and could not be distinguished (see section 4.2.10 for example). We estimate a hybrid material SQE density of 0.17 µm$^{-2}$ using 594 nm excitation in microtubes-bundle.

An analysis of the power-dependent photo-dynamics for the suspended SQE whose PL spectra is displayed in Figure 4.2.c (orange curve) was done in order to gain insight to whether these are comparable to previous reports in 2D h-BN. See SI for details. We denote our level scheme as $1/2/3$ for the ground/excited/metastable states, respectively. $R_{ij}^{0}$ is the transition between $i \rightarrow j$ for zero excitation power. By analyzing the power dependence of the short/long time scale autocorrelation measurements ($|t| < \sim 30$ ns, $> \sim 30$ ns) and converting them to transition rates, the excited ($\lambda_3$)/metastable ($\lambda_2$) state rate can be extracted, respectively (see Ref. 107 for further details). We get an excited state relaxation rate of $R_{21}^{0} = 227 \pm 16$ MHz, a metastable state with $R_{31}^{0} = 594 \pm 221$ Hz, and an inter-system crossing (ISC) rate of $R_{23} = 176 \pm 21$ kHz, resembling those for SQEs in 2D h-BN. Interestingly, for some emitters with similar spectral PL peaks, the excited state lifetime was much longer. Such an emitter can have a ~ 5 times longer excited state lifetime (Figure 4.2.e – black curve). We show below that this can be attributed to material dimensions smaller than our excitation wavelength. Emitters were completely stable under 594 nm excitation for ~ 3 hours of excitation without observable bleaching. Our suspension measurements therefore show that single
QEs in BNNTs fabricated using the HTP method are associated with the material itself, discarding contribution from the substrate. Nevertheless, when switching to 532 nm excitation (focused on the same emitter), additional spectral features appear on the PL-spectra and the isolated emitter spectral features are absorbed in broader features (Figure 4.2.d - green curve). This is confirmed by the higher value of $g^2(0)$ (0.61 ± 0.01 > 0.5), indicating more than one emitter (Figure 4.2.d). A structural defect, extending a line defect, as observed in TEM and cathodoluminescence measurements with different excited state energies (as depicted in Figure 4.2.c – inset), can possibly explain this observation. Alternatively, due to the high density of compressed material in the micro-bundle and BNNT’s large surface area, another emitter can be present inside our confocal volume. Using 532 nm excitation we were not able to isolate single quantum emitters. Furthermore, isolating single nanotubes with precision cannot be achieved using this method.

We therefore apply two methods for dispersion: First, using N,N′-Dimethylacetamide (DMAc), shown not to affect nanotube structure (see Methods for more details). Second, we once again take advantage of the electric polarity of BNNTs – adopting a method of using oxygen plasmas from carbon nanotube research. Namely, oxygen plasma, which slightly charges the surface, is used to treat the surface on which we rub the BNNT material afterwards (See section 4.5 for methods), thus circumventing solvent contaminants and allowing optical isolation of QEs. Using both methods, with 532 nm excitation alone, PL features of a single emitter could be isolated. In Figure 4.2.f – curve 0, a representative PL of emitters which were measured using both these methods is displayed. However, emitter stability was affected using DMAc, limiting excitation time to ~ 1 hour before bleaching, hinting to possible site-specific modification as a result of the use of DMAc. Nevertheless, BNNTs chemisorption of oxygen is not likely to take place using our sample preparation conditions at non-defective sites. However, defective sites such as Stone-Wales defects are more chemically reactive due to local strain and bond frustration. Previous research has also shown that QEs brightness in 2D h-BN is strongly affected by the supporting substrate (or lack of) possibly influencing radiative rates and also stability. This leads us to believe that stability was affected by DMAc or by the substrate. So as to avoid artifacts, we repeated this procedure using only DMAc without BNNTs on SiO$_2$. No QEs could be found using DMAc alone. To further explore the role of oxygen (evident from our Raman/EDX measurements), we also plot the PL spectrum of a SQE (Figure 4.2.f – curve 1), created through oxidizing chemical etching of 2D h-BN (See Ref. 107). In addition, we plot PL measurements from two SQEs in v-B$_2$O$_3$ (Figure 4.2.f – curves 2-3, see Methods for details). The resemblance of the emission wavelength is apparent, with a PSB detuning of 149 meV (1203 cm$^{-1}$) for etched h-BN and 155 meV/113 meV (1258 cm$^{-1}$/914 cm$^{-1}$, curves 2/3, respectively) for v-B$_2$O$_3$, although with a shift in the maximum peak wavelength. The h-BN/v-B$_2$O$_3$
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detuning resemble best the hexagon ring in-plane $E_{2g}$/$E'$ modes, respectively. A third peak is cut off by our 550 LP filter for curve 2. The v-B$_2$O$_3$ SQEs PL spectra (curves 2-3) are also similar to those reported for monolayer h-BN. 

Next, we analyze the PSB detuning from the ZPL for hybrid BNNT, which can be shifted by the supporting substrate (10 meV for 2D h-BN) and by different boron isotopes. Hence, we make a distinction between suspended and dispersed detuning. Comparing the PSB detuning from the ZPL between suspended and dispersed material reveals a different behavior: When dispersed on the substrate, the detuning is shifted up compared to the suspended wavenumber (energy). This is plotted in Figure 4.2.g, where the average wavenumber for suspended material is 821 cm$^{-1}$ (102 meV) and on SiO$_2$ is 1153 cm$^{-1}$ (143 meV). This shift behavior was consistent for all dispersion methods used in this manuscript and was independent of excitation wavelength (see section 4.2.6 for on substrate example using 594 nm excitation). As will be shown, the PL features (Figure 4.2.c, Figure 4.2.f) are related to hybrid material attached to BNNT. This shift hints to a strong impact the local environment has on the emitter. Interestingly, our detuning in the suspended/dispersed (on substrate) case, 821 cm$^{-1}$ /1206 cm$^{-1}$ (102 meV/149 meV), is similar to the detuning seen for v-B$_2$O$_3$ emitters $914$ cm$^{-1}$/1258 cm$^{-1}$ (113 meV/155 meV) curves 3/2, respectively. Coincidently, the vibration of boron oxide anions ($^{10}$BO$_2^-$ and $^{10}$BO$^-$) which due to their bond strength, retain their integrity in complex chemical environments, has an excited state vibrational difference of 340 cm$^{-1}$ (43 meV) similar to the wavenumber difference between our suspended and non-suspended material of 331 cm$^{-1}$ (41 meV).

Alternatively, we can classify the suspended phonon modes to 2D h-BN TO$_\perp$ (ZO, along the c-axis) modes (see Table 4.1), possibly attenuated upon contact with the surface, making the $E_{2g}$ modes more prominent. Therefore, upon dispersion, a chemical change can occur in the emitter or the vibrational freedom is diminished (a schematic is depicted in Figure 4.2.g.), consistent with our observation of hybrid material on the tube exterior exposed to the environment, as will be shown. This behavior has not been observed before for QEs in suspended h-BN, probably because of the relative small area the h-BN flakes were suspended on (on the scale of 10 microns) and the less exposed environment in a 2D h-BN lattice or possibly because of the different origin of emitters in this manuscript. In our experiment, the material is suspended over a scale of millimeters from the supporting aluminum needles. We demonstrate this behavior further below for suspended material with a supporting structure on a smaller scale.
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Figure 4.5: Comparison of Spectral, auto-correlation, spatial confocal and spatial SEM data for broad spectrum quantum emitters in BNNT. (a to c)(1 to 3) compare the PL spectra (a), optical confocal scan (b) and SEM resolution images (c), correlating QE spatial features and emission properties. Substrate types are denoted above each line. Column (a) (1 to 3) displays PL spectra using 532 nm CW excitation. Insets display autocorrelation measurements. (1) and (2) are for BNNT dispersed with DMAc on a TEM grid (2) and (3) BNNT dispersed with DMAc on ITO. (c 1 - inset) graphically enlarged image color coded in cyan for clarity showing a few nanotubes wrapped on a single nanotube, covering the TEM grid. (c2 – inset) a similar singular straight tube (d) \( g^2(t) \) metastable state decay curves for 532 nm CW excitation in logarithmic scale. Blue curve represents low power 40 \( \mu \)W excitation, red curve high power 500 \( \mu \)W excitation. A second decay component is visible on the high power curve. (e) kilo counts per second for two SQEs with the same PL spectra structure, both display different counts as a function of power.

4.2.5 SEM resolution of entwined BNNT SQEs

We now turn to spatial localization and classification of QE’s in the BNNT using SEM resolution. Using 532 nm excitation our spatial resolution is diffraction-limited at best to 200 nm, which makes distinguishing single nanotubes from nanotube bundles impossible. To overcome this, we combine
higher resolution imaging of the SEM and optical laser excitation. To this end, we deposited 200 nm of indium tin oxide (ITO) on SiO$_2$, rendering the substrates transparent and conductive, thus making them compatible with both types of spectroscopy. In addition, quantum dot research has shown ITO to suppress emission blinking due to facile electron transfer (due to ITO’s Fermi level) to possible trap states, thus blocking emitter electron transfer to these states once in the excited state. Due to the proximity of our nano-material to the environment, we expect a similar effect. To probe suspended material, we also used a conductive gold TEM grid. The DMAC drop-casting procedure was applied to two substrate types: SiO$_2$ with ITO and a gold TEM grid.

Figure 4.5 depicts data for QEs originating from entwined BNNT material. Column (a) contains spectral and autocorrelation data, column (b) confocal optical excitation scans and column (c) SEM scans, where each enumerated line connects between the column features. Lines 1 and 2 depict data for suspended BNNT on a TEM grid and line 3 for BNNT on ITO. Surprisingly, on straight single nanotubes (without hybrid material) on the scale size of single nanotubes no QE emission could be exhibited. A comparison between line 1 and line 2 of Figure 4.5 reveals that emission is not originating from single tubes suspended on the grid, but rather from the entwined BNNT. A closer look (Figure 4.5.c1/c2 – insets) shows that these tubes are a combination of a few tubes wrapped on what is most likely one. An autocorrelation measurement (inset Figure 4.5.a1) reveals that this is a single QE ($g^2(0) = 0.4 \pm 0.02 < 0.5$). On numerous instances, when single tubes were isolated, we were not able to see an emission signature associated with QEs. Similar ensemble features can be seen for BNNT on ITO (line 3 of Figure 4.5). However, a cluster of curved nanotubes smaller than 1 micron contributes to emission. Therefore, nanotube termination, known to harbor defects, can perhaps also play a role in emission. For Figure 4.5.a1, using an asymmetric peak fitting function (see 4.2.9) we subtract the broad shoulder of the PL spectra to identify six distinct peaks superimposed on the shoulder. An analysis (see 4.2.7) leads us to conclude that most probably the ZPL is at the range of 589 nm. In Figure 4.5.d we show a representative metastable decay behavior for this class of emitters for a similar SQE dispersed on ITO using the plasma dispersion method. Photo-dynamics reveal at least two components affecting the metastable decay ($|t| > ~ 40$ ns), one only prominent at high excitation powers ($> 500 \mu$W). This is plotted in Figure 4.5.d on a time logarithmic scale. We attribute the short component to a possible dark state, indicating an intermittent blink to trap states or a different emitter charge state, as seen for the silicon vacancy defect in diamond. We get an excited state relaxation rate of $R_{21}^0 = 570 \pm 76$ MHz, a metastable state with $R_{31}^0 = 0.24 \pm 0.03$ kHz, and an ISC rate of $R_{23} = 140 \pm 8$ kHz. Photobleaching was not observed for this SQE, attributed to the stabilizing effect of the ITO substrate. Interestingly, two separate SQEs of this type show different photon emission counts power saturation behaviors (Figure 4.5.e). This can be attributed to different dielectric environments.
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around the SQEs or to variations in excitation/collection efficiency due to the circular quasi 1D nature of BNNT on which the emitter can be spatially located.

Figure 4.6: Comparison of Spectral, auto-correlation, spatial confocal and spatial SEM data for quantum emitters originating from hybrid material in BNNT. (a to e)(1 to 5) compare the PL spectra (a), optical confocal scans (b) and SEM resolution images (c)(d)(e), correlating QE spatial features and emission properties for BNNT dispersed using DMAc on SiO$_2$ with 200 nm ITO (1-4) and on a TEM grid (5). (a,b) (1 to 2) displays PL spectra using 594 nm CW excitation, (a)(1) Inset displays an autocorrelation measurement. (a,b)(3 to 4) PL spectra using 532 nm CW excitation (c) secondary electron SEM image of a nano-tube cluster, some containing segments of singular nanotubes. (d) Higher resolution SEM image of segments, revealing single nanotubes branching from the nanotube cluster (upper inset) and twisted tubes when tilting the detection by 30 degrees (bottom inset). Note – d4 was graphically enlarged. "A" and "B" (in blue) are markers for the eye. (e) SEM backscattering images revealing hybrid material attached to nanotube clusters. ITO grains are visible on the substrate. (b,c)(1 to 4) have the scale of 2 µm, (b,c)(5) have the scale of 1 µm.
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4.2.6 BNNT Exfoliation

We also attempted to exfoliate BNNT material, similar to the methods used for 2D h-BN. However, emitters bleached after ~1 hours of stable excitation. These samples were prepared using the same methods as h-BN exfoliated in chapter 3, with the difference that at the end of the exfoliation procedure they were submerged for 10 minutes in ethyl alcohol and afterwards dried in N2 gas.

Figure 4.7: Exfoliated BNNT with 594 nm excitation (a) photo-luminescence of 3 emitters (b) confocal scan reveling highly localized emitters.

4.2.7 SQE spectrum and ZPL analysis

Figure 4.8: Detuning of the five spectral peaks to the last spectral peaks in energy for broad spectrum BNNT QE.

For the PL spectra in Figure 4.5.a1, peaks were fitted individually with Lorentzian/Gaussian functions. These were then renormalized to portray the peak they represent on the original PL spectra. We denote the first peak as a potential ZPL, whereas the remaining five as potential PSBs. Using this classification we subtract the energy between adjacent peaks. This is seen in Figure 4.8. Using Table 4.1, the energy detuning is closest to the range of the Radial Breathing Modes (RBM) of BNNT. In some instances, we observed that when switching to 594 nm excitation on the same emitter, the
emission spectrum is not seen. This leads us to believe the first peak, at ~ 589 nm, is the ZPL, which can be shifted by the local electric environment.

4.2.8 SQE photo-dynamics analysis

In Figure 4.5 for low excitation power (40 µW) only one time decay exponent can be fitted, whereas for high power (500 µW) a shorter decaying exponent is seen. To gain insight, in Figure 4.9.a we plot the normalized emission photon trace by setting the average emission as zero for two powers (low/high) for 60 seconds (Figure 4.5.a bottom/top, respectively). The average emission traces are the blue/red curves, respectively. For the low power trace the emission is dispersed evenly ~ 50% below and above the average emission. However, for the high power trace we see bursts of down-shifted emission well below the distribution of emission around the average. We note that these down shifts do not have the same percentage and we can roughly classify ~ 20%, 45% and 84% shifts. This indicates a switch of the emitter to a dark state which can occur on a time scale faster than our photon detection whose duration can vary, thus the different down shift percentage. Therefore, the emitter can be trapped in a dark state due to an intermittent blink to trap states or a different emitter charge state. Using this interpretation, we can now attribute the short decaying component to the switch of the
emitter to the dark state, whose duration can vary and does not always register fully on our time photon trace. Therefore, our photodynamic analysis is for a three state system. The second order correlation function describing the photo-physics of our emitter can be well described using the $g^2(t)$ function derived in 2.3.2. The parameters can be derived from a three-level model, which better explains the observed experimental data. The three-level system consists of a ground, excited, metastable state and an additional high-lying state to which the metastable is coupled to optically. To find the transition rates of the model $k_{ij}$, we follow the approach applied to describe the photophysics of the silicon-vacancy color center in diamond. These frequency rates are shown in Figure 4.9.c, on a logarithmic scale for $\lambda_2$ for both components. Figure 4.9.b displays the $\lambda_1$ frequency. When the power exceeds 120 $\mu$W a high frequency (MHz) component is seen (red dot – red curve added for emphasis) larger by a few orders of magnitude than the original decay frequency (black dots). The limiting values (i.e., $P \rightarrow 0, P \rightarrow \infty$ (2000$\mu$W)) of various parameters that go into the analysis are:

$$
\tau^0_1 = 1.75 \text{ ns}, \tau^0_2 = 4.175 \text{ ms}, \tau^\infty_2 = 1 \mu\text{s}, a^\infty = 0.16
$$

### 4.2.9 PL spectra asymmetric fitting functions

The following function was used, where $f(x)$ denotes the normalized PL intensity and $x$ denotes the wavelength:

$$
 f(x) = y_0 + A \left( \frac{1}{1 + e^{-\frac{(x-x_c+w_1)}{w_2}}} \right) \left( 1 - \frac{1}{1 + e^{-\frac{(x-x_c-w_3)}{w_3}}} \right)
$$

### 4.2.10 Example of absorbed PSB for suspended material

The long pass filter is designated by the dashed line (Figure 4.10).
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4.2.11 SEM resolution of hybrid material SQEs

In Figure 4.6 we analyze the spatial localization of emission from hybrid material dispersed using DMAc (see section 4.5.3 for details). For lines (1) to (4), isolated nano-tubes clusters from a diluted BNNT DMAc solution, containing isolated segments of single nanotubes were probed. Line 5 is for a suspended cluster on a TEM grid. Columns (a) and (b) are similar to those in Figure 4.5, whereas columns (c), (d) display SEM imaging with different resolutions, tilting angles and column (e) with backscattering imagery. Purple lines/circles connect between the column features, whereas cyan lines/rectangles mark entwined tube areas. From columns (b) and (c) we deduce that emission originates from the tube structure and not from the ITO substrate. We see a clear tendency of entwined twisted tubes (cyan rectangles) to exhibit concentrated emission areas, whereas isolated single nanotubes do not emit, consistent with our previous observations. All cyan rectangle areas resulted in a broad PL spectrum and not with the sharp narrow PL features displayed in column (a). The single QE in line 1 of Figure 4.6 (g^2(0) < 0.5), reveals that emission originated from hybrid material and not from the continuous nanotubes. The brighter color of the hybrid material compared to the darker color of the tubes in the SEM backscatter images (Figure 4.6.e1, Figure 4.6.e2) can indicate a different crystallographic orientation, possibly due to a differing orientation of 2D h-BN, causing the SEM electrons to scatter differently, or different conductivity due to a changed ratio of less boron atoms in this area or a higher atomic number, like oxygen, as indicated from our bulk Raman/EDX measurements (Figure 4.2.a). Hybrid nanomaterial comprising of 1D BNNT and 2D BN oxide platelets have also been reported for high temperature annealed BNNT. The minute size of the hybrid material is insufficient for EDX spectroscopy. The good dispersion, tube structure isolation and the long magnetic stirring process involved in dispersion (see section 4.5) evident from Figure 4.6 leads us to believe that the hybrid material is part of the tube structure and not attached
via weak non-covalent bonds, normally holding non-defective BNNT walls together. These are also similar in appearance to hybrid material identified from the same vendor using TEM, confirming attachment between the BNNT and the hybrid material. A similar analysis is valid for the purple lines 2-4 of Figure 4.6. The point-like emission originates from hybrid material smaller than our excitation wavelength (Figure 4.6.e2). Therefore, the dielectric nano-antenna effect can also govern the emission mechanism for this QE class, affecting emission rates and saturation behavior, thus explaining our diverse lifetimes in Figure 4.2.e. The PL spectrum in Figure 4.6.a(1,4,5) are consistent with that of Figure 4.2.f (curves 0/1) and structurally with that in Figure 4.2.e (orange curve) and for Figure 4.6.a(2,3) to those seen in suspended material where the PSB was absorbed in the ZPL (not shown). Tilting the SEM image by 30 degrees (Figure 4.6.d1 – bottom inset), reveals the entwined tube areas in more detail and the hybrid material. Interestingly, line 5 in Figure 4.6 shows that suspended entwined BNNT tubes can seemingly also give sharp spectra. Nevertheless, this is the only instance where we have seen this behavior, leading us to believe that hybrid material is present in the suspended micro-tube. The PSB detuning from the ZPL is 1322 cm\(^{-1}\) (164 meV), which we categorized in the ranges of ‘On substrate’ in Figure 4.5.h. However, in line 5 of Figure 4.6 the BNNT material is located at a distance of ~ 1 \(\mu\)m from the supporting frame of the gold TEM grid and from densely entwined tubes (not shown). Therefore, the PSB detuning behaves like the ‘On Substrate’ case.
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Figure 4.11: Artificial structures on diamond used to curve 2D h-BN flakes for generating QEs. (a) 532 nm CW reflection measurement of a h-BN flake placed on top of diamond pillars. Pillars where QE were observed are marked with purple circles from ‘1’ to ‘6’. Pierced pillar areas are clearly seen. (b) SEM image of a typical pillar (c) 550LP filtered area of (a). (a),(b) and (c) have the same scale of 5 µm. (d) 30 degree tilted SEM image of the h-BN flake, scale bar marked with a white line is 200 nm long. The inset of pillar ‘1’ was graphically filtered highlighting the ‘tenting’ topography of the flake. Piercing is seen on other pillars. For pillar ‘6’ (inset), ‘tenting’ is seen at the edge of the flake (a dim gray half circle is seen). (e) Autocorrelation measurements from pillars ‘1’, ‘6’, and a folded area of the flake. (f) Top SEM view of the h-BN flake, pillar ‘1’ – inset, graphically filtered image highlighting ‘tenting’ effect. Fold inset, magnification of folded region. (g) PL spectra for QE, ‘0’ is the diamond pillar background where h-BN does not cover the pillar (normalized relative to QE PL spectra), ‘1’ to ‘6’ are the PL spectra of QEs, ‘7’ is a QE PL spectra from a different BNNT sample for which background was subtracted. Arrows indicate resembling peaks (h) Detuning of the PSB from the main peak for QEs ‘1’ to ‘5’. Left scale is in wavenumbers, whereas the right scale is in energy.
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4.2.12 Artificial curving of 2D h-BN

It has been demonstrated that SQEs in h-BN can be spatially correlated with wrinkles on an h-BN flake. Therefore, to show that BN nano-material artificial curvature can be spatially correlated with QE location, we fabricated sharp diamond pillars ~554 nm high with the top/bottom base diameters of 93 nm/200 nm, respectively. Figure 4.11.b displays a SEM scan of a typical pillar. Single crystal 2D h-BN flakes with different thicknesses were transferred on top of the diamond substrate so that they would artificially curve on the pillars and then annealed (see section 4.2.13 for details). Some pillars also pierced the h-BN membrane. Figure 4.11.a/c shows a reflection (no wavelength filters) / 550 LP filtered 532 CW excitation confocal scan, respectively. To gain higher structural resolution insight, in Figure 4.11.d/f, a SEM scan of this flake, 30 degree tilt/top view, respectively, is presented. Pillars in which QEs were observed are marked with numbers between ‘1’ to ‘6’. In addition, QEs could be found in perimeters of flakes. Comparing between Figure 4.11.a/c/d/f, QE ‘1’ is spatially localized with the curving of the h-BN membrane on the pillar and, as opposed to Ref. 107, no perimeters can be seen. Both QE ‘1’ and ‘6’ are in a non-pierced area and exhibit a ‘tenting’ effect, however, QE ‘6’ is also on the h-BN edge (insets of Figure 4.11.d, Figure 4.11.f). An AFM scan (see section 4.2.13) reveals the peak of QE ‘1’ to be ~1 µm above the h-BN flake flat plane fitting exactly the convergence height from our pillar bases (1 µm), therefore the top is not in contact with the pillar (of 554 nm height), with an opening angle of 16.7 degrees, wider than the pillar bases convergence point angle of 11 degrees. Presumably, curving commenced when the flake started to touch the pillar bases on one side, which could have been modified afterwards by annealing. An autocorrelation measurement of QE ‘1’ is displayed in Figure 4.11.d, proving its single nature ($g^2(0) = 0.37 ± 0.02 < 0.5$). We note that due to the small diameter of the pillars, pillars without h-BN flakes emit background upon laser excitation. Autocorrelation measurements using the same power (50 µW) were also conducted on these pillars revealing no quantum signature - validating quantum emission association to the h-BN flakes. Pillars with h-BN on top near flake boundaries (~1 µm away) also showed QEs clustering which resulted in more than one emitter. This is seen for QE ‘6’ (Figure 4.11.e), yielding $g^2(0) = 0.82 ± 0.01 > 0.5$. QEs ‘2’, ‘3’, ‘4’ and ‘5’ are clearly pierced, (Figure 4.11.a,d,f). Nevertheless, these areas also displayed a quantum signature, consistent with previous work, where SQEs were measured in an area of a chemically etched hole or boundaries in the h-BN flake (See chapter 2). 107 We discuss below in detail the difference between curving (tenting) and piercing. For pillars marked in black lines in Figure 4.11.d, no QEs were found. A rough comparison to the other pierced pillars (Figure 4.11.d) shows that they have not penetrated as deeply into the flake as the other pillars, inducing less curvature in the surrounding area, possibly hinting further to the role of curvature or other mechanisms in QE formation. To further demonstrate the role of perimeters and curvature abundant in the h-BN (or
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created ‘naturally’ by exfoliation), an area marked with ‘Fold’ in Figure 4.11.f is shown and its quantum nature (Figure 4.11.e – autocorrelation measurement). An AFM scan shows the fold height to be ~ 250 nm with a slope angle of ~ 2 degrees. Figure 4.11.g shows the PL spectrum for QEs from pillars ‘1’ to ‘6’ (curves 1 to 6), and for the QE marked with ‘Fold’ (QE ‘8’) and another QE from a different BNNT sample (QE ‘7’). Figure 4h displays the PSB detuning from the ZPL for all QEs ‘1’ to ‘5’ (omitting QE ‘6’ from the analysis due to its ensemble nature). We identify the same two-peak structure as identified for hybrid material in BNNT when dispersed on the substrate (Figure 4.6.a1,a4 / Figure 4.2.1g). In addition, a similar average wavenumber (energy) detuning is seen 154 / 149 meV (Figure 4.11.h / Figure 4.2.1g – red line, respectively). Intuitively, a pillar which would cause the 2D h-BN flake to curve near its edge would have quasi-1D features, similar to the structure one finds in nanotubes. Comparing between the PL spectra of QEs from pillar ‘6’ and QEs from a BNNT sample (Figure 4.11.g curves 6 and 7, respectively) we see similar spectral features, although the peak maxima are shifted with respect to one another. Similar local maxima are marked by arrows (up/down, BNNT/h-BN pillar, respectively). Therefore, curved areas can result in resembling PL spectra in h-BN and BNNT consistent with studies showing that optically BNNT can behave as curved 2D h-BN. Furthermore, the PL spectral features are different from the QE in the area marked as ‘Fold’ (curve 8), emphasizing the difference between edge artificial curving and ‘natural’ curving in h-BN. We also attempted to see QEs on thick h-BN flakes (> hundreds of nm). On pillars on which thick h-BN was placed, QEs could not be seen (not shown). Due to the higher thickness we think that the flake is mechanically more resistant to deformation and piercing, and as such QEs could not form. Finally, h-BN flakes were exfoliated on a hemisphere of ZrO₂ to insure the flake contains long segments of curved areas. The effect of as-exfoliated compared to flakes exposed to a liquid environment was tested, confirming the sensitivity of BN processing chemicals (see section 4.2.14).

4.2.13 Preparation of pillar sample and AFM topography

h-BN was exfoliated on a Si/SiO₂ substrate for maximum optical contrast. Using a PDMS stamp transfer method the flakes were then transferred to the diamond pillars. The samples were annealed at 500 °C in an Ar/H environment for 1 hour, which should not damage the h-BN layers. An AFM scan is displayed below in Figure 4.12.c, with the corresponding heights for each line (1) and (2) (Figure 4.12.a and Figure 4.12.b, respectively).
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The annealing procedure used removes organic contaminants and does not introduce pinholes for temperatures below 600 °C. 

4.2.14 Curved 2D h-BN on ZrO₂ hemisphere

A hemisphere of cubic ZrO₂ with a diameter of 3 mm (A.W.I. Industries Inc.) was cleaned in the same method as described as cleaning SiO₂ for the BNNT oxygen plasma method (piranha + plasma). The half sphere was then fixated to a clean SiO₂ substrate using glue. Single crystal h-BN was then exfoliated on the sphere (as depicted in Figure 4.13.a). Thus ensuring that adhesion to surface would be imperfect – creating curvature in the flake for the areas not in contact with the hemisphere. A large flake containing curved regions was located using a wide field microscope (Figure 4.13.b and Figure 4.13.c – with different focus regions due to the substrate curvature, Inset Figure 4.13.b – curved region, where red arrow is for emphasis of the curved flake area). PL measurements of this flake were conducted in two modes using 12 μw, 594 nm excitation: The first mode is directly after exfoliation. The second mode is after cleaning the sphere in acetone at 80° C for 15 minutes, 15 minutes of room temperature ethyl alcohol and 15 minutes of minutes of room temperature isopropyl alcohol followed by drying the half sphere using pure N₂ gas, similar methods used for preparing the h-BN material in
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Ref. 117. As we will show, this resulted in different results.

**Figure 4.13:** Curved 2D h-BN on a ZrO$_2$ hemi-sphere wide field images. (a) Illustration of sample preparation scheme. (b),(c) microscope wide field images of large exfoliated flake on the half sphere. Inset displays curved areas in detail.

**PL mode 1 – directly after exfoliation**

We probe a large area of the flake which in the reflection scan (nw power with no filters) shows multiple curved areas (Figure 4.14.a – indicated by the red curved arrow). A 600LP filtered scan reveals (Figure 4.14.b, X/Y axis and X/Z axis) *almost no photoluminescence* except for one region (Figure 4.14.c). This tendency of few (perhaps one or two) emitting areas in a ~ 40 x 40 µm$^2$ scan was consistent throughout this flake. The PL spectra for two segments denoted D1 and D2 is displayed in Figure 4.14.d-D1 has broad spectral features whereas D2 has sharp features. We tentatively assign the features in D2 to sharp emitters of Type ‘2’ as described in Ref. 196, or possibly to defect energy states of the ZrO$_2$ hemisphere, due to the consistency of these sharp peaks to appear always at ~ 692 nm with no detuning, whereas detuning is typical for emitters in h-BN. However, these were the only areas showing emission in this segment of the flake. Emission from these were completely stable with no sign of bleaching or blinking. If we assume these originate from the h-BN, we can possibly attribute the stability to a the ZrO$_2$ hemisphere substrate, presumably similar to the stabilizing effect assigned in Ref. 196 to Al$_2$O$_3$. 


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**Figure 4.14:** Curved 2D h-BN on a ZrO$_2$ hemi-sphere confocal and spectral data. Reflection / PL confocal scan of a ~ 40 x 40 micron scan range (a,b, respectively). (c) enlarged PL segment for only area where emission is seen. d. PL spectra for both area named D1 and D2 in c.

**PL mode 2 — after exposure to solvents**

The picture of isolated (if any) emitting segments in Figure 4.14 changed drastically after the exposure to solvents. Figure 4.15.a/b displays the reflection / PL (respectively) of a cross section area inside a flake after solvent exposure. We note that due to the non-straight topography of the flake our z focus point along the x axis for the PL emission is limited. This limited focus area is depicted in Figure 4.15.b. The reflection image does not suffer from this limitation due to the high brightness. The reflection image reveals in detail wrinkled lines are on the flake. Red arrows mark the pronounced curved regions of the flakes. Clustering of isolated emission point along these lines are visible (Figure 4.15.b). These emission points exhibited blinking behavior, a time trace of 200 seconds of such behavior is depicted in Figure 4.15.c. We mark three of these as D3, D4 and D5. Figure 4.15.d displays the PL spectra. The PL spectra resembles that seen in Figure 4.2.f, in the section 4.2.1. We note that these spectral features were not seen prior to solvent exposure. Due to the blinking nature of the emitters, a clear anti-bunching signal is difficult to observe, nevertheless for emitter D4 an indication of anti-bunching could be seen (Figure 4.15.e). The other emission points which were not along the wrinkled lines were unstable and immediately bleached. The correlation of the emission areas with the h-BN flake structure and lack of almost any emission of the material prior to solution exposure is a strong indicator of a reaction of the flake with the seemingly benign solvents. Due to the non-invasive nature
of the solvents, we can assume that the interaction is on the surface area of the flake, possibly oxide groups attach to the flake exterior favorable at defective sites. These results can indicate that emitters seen in commercial h-BN dispersed in ethanol/water can originate from the reaction of h-BN with liquids. Thus defective sites more prevalent in monolayer 2D h-BN would be reactive in such a solution.

Figure 4.15: Curved 2D h-BN on a ZrO$_2$ hemi-sphere after exposure to solvents. (a) Reflection PL inside a flake region, pronounced wrinkled lines are marked with red arrows. (b) Filtered PL of the same region. Isolated emission points are marked with D3, D4 and D5. The z axis focus area visible on the x axis is marked with a half orange circle. (c) Emission time trace for
4.3 Discussion

The classification of emission from hybrid material (Figure 4.6) can have two interpretations: A simplistic one where the defect responsible is presumably contained only in the hybrid material. However, the formation of hybrid material attached to the nanotube structure is an indicator of nanotube reconstruction, which would disrupt the nanotube structure due to defects, as previously observed. Thus, possibly a vacancy defect, shown to cause sp³ bonding between BNNT walls during the growth phase of the tube, might be located on the exterior BNNT wall and thus sp³ bond the whole complex. Electron energy-loss spectroscopy (EELS) spectroscopy has also shown that curvature in BNNTs can induce sp³ hybridization. The hybrid material could be 2D h-BN or possibly boron oxide, due to its different color in the SEM backscatter detector. The narrow PL features in the nano-tubes clusters in Figure 4.6 seen where hybrid material is present, demonstrates it plays a vital role for this type of emitter formation. SQEs seen in v-B₂O₃ strengthens the role oxygen defects can play in boron systems, proving that similar PSB detuning can be obtained also in v-B₂O₃ to that of hybrid BNNT SQEs. Moreover, the planar structure of B₃O₆ and the similar PL to that of monolayer h-BN SQEs hints to an analogy between them. The oxygen atomic mass would not compromise significantly the 2D h-BN host lattice mass, yielding similar Raman signatures. The abundance of SQEs and the larger surface area exposure to the environment of BNNT material compared to a bulk h-BN crystal also strengthen these observations. Possibly, nano-B₂O₃ areas present in the BN lattice can be partially responsible for emission in previous 2D research attributed to h-BN, Interestingly, BN₃O and B-NO₂ point defects retain the h-BN’s planar structure while B-O₂ has a random orientation, possibly resolving recent optical polarization measurements. Another possibility would be BN di-vacancies, reconstructing to Stone-Wales defects (seen in TEM, BNNT / h-BN), point defects or combinations with oxygen.

For emission from BNNT entwined material (Figure 4.5), oxygen structures calculations (B₃O₆ structures present in v-B₂O₃) yielded energy states in the visible range (~ 2 eV). We can also interpret interlayer bonding, due to the inability to see SQEs on single straight tubes lacking interlayer bonding or curvature, as a source of emission. At a first glance the structural effect of piercing and curving of h-BN on pillars (Figure 4.11) are different, however they can have similar effects. Namely, the former creates a micro-defect/rupture in the membrane visible using SEM microscopy and the latter lowers the formation energy of defects, thereby making a point atomic defect formation more likely, visible using TEM microscopy. Full
piercing would create curvature in the membrane, surrounding the pillar (as shown in Figure 4.11.c), thereby making it also a combination of both effects. Nevertheless, the natural abundance of point defects in h-BN or absorbed atoms (As demonstrated in 4.2.14), with the combination of curvature may give rise to QEs. Possibly, oxygen healing, stabilized by annealing, occurs on the curvature induced or pierced (perimeter) defective sites which are very reactive, causing oxidation to be energetically favorable, even more so favorable with the abundance of surface boron vacancies causing atomic curvature. Alternatively, similar to the entwined BNNT case, interlayer bonding between h-BN layers and strain modified energy states can also play a role.

4.4 Conclusions

We uncover a new material of the BN family for SQE use. Our results strengthen previous observations in 2D h-BN, correlating perimeters and the role of thinner material with the increase of QEs, due to the lower energy formation of defects on the exterior. Isolating SQEs was possible upon the reduction of excitation energy and of BNNT material or their dispersion, demonstrated by three methods: BNNT ‘string’ pulling using 594 nm excitation or DMAc/oxygen plasma dispersion using 532 nm excitation. The high quality of fabricated BNNT / hybrid material, combined with dispersion using the oxygen plasma method, allows literally ‘out-of-the-box’ emitters avoiding the use of solvents and any further fabrication processing (such as annealing) to work with SQEs. In addition, the combination of 1D material with hybrid material allows easy suspension, avoiding solvent and substrate contaminants, which could advance BN QE research further. The lack of processing contaminants is a key milestone for unraveling the atomic structure giving rise to QEs, with precision atomic spectroscopy technologies available. The minute nature of the material as seen in SEM, offers potential background-free QEs upon suspension. We find that conducting surfaces, such as ITO, are advantageous in avoiding QE excited electrons falling into possible trap states. For the first time, we show a one-to-one optical correlation of visible wavelength SQEs in BN with SEM spatial resolution, for suspended and on-substrate material, possibly confirming previous observations in h-BN. Material with features smaller than our excitation wavelength elucidates dielectric nano-antenna effect, varying excitation lifetimes. The 1D nature of BNNT can allow bio-adsorption of nanotubes with QEs for intra-cell imaging, making a single BNNT tube a natural QE carrier, using less energetic laser excitation. The spatial localizing of curved areas and QEs puts h-BN under a similar umbrella with QE observations seen in other semi-conducting TMDC QEs (with the distinction of the large bandgap and 2D h-BN annealing procedures). This also allows us to interpret previous observations of creation of QEs in 2D h-BN: induction by electron/ion irradiation, chemical etching and spatial localization on edges and between different emitter layers. Namely, all of these methods induce curvature/strain and the spatial localizations are correlated with areas (such as edges) that are
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more likely to be curved than perfectly flat, and thus would be more reactive. We can also think of annealing, typically used to stabilize QEs, as a mechanism to ‘fixate’ the curvature of bubbles or to concentrate large bubbles near perimeters in a 2D flake, thus localizing smaller bubbles inside the flake and thus resulting in more localized QEs. We prove that h-BN PL features are sensitive to the external environment, such as solvents/liquids (see SI), and therefore some of the SQEs in commercial BN dispersed in liquids could originate from interaction with the liquids. Bulk BNNT can be viewed as a ‘cheese’ with holes, namely, the environment surrounds the whole bulk. Further research on techniques to manipulate SQEs energy levels in BNNT could lead to sensing routes of these emitters, exposed to the environment. Isotopic engineering of the boron species can be done to dramatically reduce SQE phonon-electron broadening. Our results indicate that artificially bending BNNTs might be beneficial for engineering QE formation in BNNTs, but this is beyond the scope of this work. These results further highlight the high quality of material which can be obtained with high temperature fabrication for QEs in BN systems. Implementation of the techniques in this work with TEM and STEM technology is straightforward, highlighting the potential of low-dimensional wide bandgap semiconductors as emerging platforms for deep bandgap point-defect engineering.

4.5 Methods for BNNT measurements

4.5.1 Bulk BNNT sample preparation and measurement

Cover slides of SiO$_2$ were thoroughly cleaned in a peroxymonosulfuric acid (H$_2$O$_2$:H$_2$SO$_4$) solution for 2 hours and afterwards rinsed in DI water, isopropyl alcohol and dried in pure N$_2$ gas. Glue was placed on the cover slides and a substantial amount of BNNT was extracted from the bulk “cotton”-ball, and placed on the glue. The sample was mounted to a room temperature setup at ambient conditions. We avoided excitation of the area the BNNT was glued to the cover slide and concentrated on areas tens of microns away from the surface. Photo emission was detected using two avalanche photo diodes (APDs) in a Hanbury Brown and Twiss configuration.

4.5.2 BNNT suspension using needles

A smooth steel board with an elongated line drilled in the center with two separate square SiO$_2$ slides with dimensions of 0.5 × 0.5 × 0.5 cm glued on top was prepared. The two square slides had a ~1 mm spacing between them and were placed parallel to each other on the opposite edges of the x axis of the board substrate so that on the y axis there is a non-intersecting area above the drilled lined. Afterwards two conductive needles were glued with their bases glued to the x axis of each of the SiO$_2$ slides. From bulk BNNT a small string-like amount was isolated with diameters on the micron scale using tweezers. Each end of the BNNT string was placed on the conductive needles. After contact with the conducting needles no further fixation of the BNNT string was needed.
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4.5.3 BNNT QE dispersion using DMAc

For dispersed material in Figure 4.2 and Figure 4.5, the exact same method of BNNT dispersion was used as in Ref. [200]. Magnetic stirring was applied via a Teflon-coated magnet for 4 days. For Figure 4.6 we used a substantially reduced amount of BNNT, namely the smallest micro-bundle one can extract simply using a tweezer. The same DMAc stirring procedure was afterwards applied. For dispersion on SiO₂ and SiO₂ + ITO, SiO₂ was first cleaned in a peroxymonosulfuric acid (H₂O₂:H₂SO₄) solution for 2 hours similar to the procedure described previously. In order not to damage the ITO, SiO₂ + ITO were cleaned in hot acetone at 80 °C for 1 hour, and hot isopropyl alcohol at 65 °C for 1 hour, finally rinsed in cold isopropyl alcohol and dried in pure N₂ gas. The TEM grids were placed in a holder where the TEM grid is suspended on the grid areas. All substrates were placed on a hot plate and preheated to temperatures between 185 °C to 200 °C. The DMAc + BNNT solution was always pre-sonicated for 30 min. (in accordance with Ref. [200]) before drop casting the solution. Drop casting was done in a fume hood and the hot plate was left on for 5 minutes. Afterwards, the hot plate was turned off and let to cool to room temperature. We could re-use dispersed DMAc + BNNT solutions weeks after dispersion, since BNNT did not create sediments at the bottom of the solution, in accordance with Ref. [200].

4.5.4 BNNT QE dispersion using oxygen plasma

SiO₂ and SiO₂ + ITO slides were pre-cleaned using the procedures described above. The samples were then exposed to O₂ plasma for 5 minutes in vacuum. This further cleans the surface from undesired organic contaminants (which can obstruct optical excitation) and slightly charges the substrate surface, increasing BNNT affinity to the substrate. Therefore, by simply rubbing a small portion of material, BNNT is dispersed on the surface to allow optical isolation of QEs. Immediately after exposure, a sample amount of BNNT was extracted from the bulk using a clean tweezer, and the side opposing the tweezer contact point was rubbed on the substrate while viewed under the microscope to see the BNNT placement on the substrate. The sample was then placed on an unheated hot plate (to promote adhesion of material to the substrate) which was then heated to 70 °C. Once 70 °C was reached, after 5 minutes we turned off the hot plate and let it cool to room temperature.

4.5.5 BNNT EDX

EDX was performed using an SDD detector with a NSS system from Thermo Fisher.

4.5.6 v-B₂O₃ preparation and measurements

The material was acquired from the vendor ‘Suprapur’. SiO₂ cleaned in peroxymonosulfuric acid as described previously was used as a substrate. Glue was placed on the substrate and immediately afterwards bulk v-B₂O₃ (~cm sized) was placed on top. After waiting for the material to fixate we probed v-B₂O₃ using the 532 nm laser and a 550 LP filter far away from the substrate contact point.
Point like emitters could be immediately seen once probed. To verify that we were looking inside the bulk material once focused on an emitter and not on the surface we reduced the excitation power to ~nw and removed the filter, therefore probing the reflection. This confirmed we were focused in the bulk of the material. Afterwards PL spectra was collected and anti-bunching measurements were performed.
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5. Paramagnetic emitters in 2D h-BN

A glove fit lattice host for point like defects that are magneto-optic emitters for nanoscale probing are semi-conducting two dimensional Van der Waals crystals. In this chapter we explore a quantum emitting magneto-optic source embedded within hexagonal boron nitride (h-BN). We show that for the first time that under cryogenic conditions optical magnetic resonance (ODMR) can be observed, extracting the relevant gyromagnetic ratio and a possible zero field splitting (ZFS). Photoluminescence behavior under temperature cycling and different excitations are presented, assigning probable zero phonon lines (ZPLs) and phonon side band (PSBs) to emission peaks while estimating the emitter’s Huang-Rhys factors. Response to rotating linear excitation is also shown. Combining in-depth analysis from these observations we prove through the narrow ODMR line width that a foreign atom to the host must take part in atomic defect formation, responsible for magneto-optic emission. Our results constitute in-depth insight on a photon source which can be utilized for nano-magnetic sensing.

5.1 Introduction

Nano-magnetic sensing is significant for understanding a range of phenomena. These range from deciphering the structure of bio-molecules to nano-scale ferromagnetism, utilizing numerous techniques: Nuclear magnetic resonance (NMR),

\footnote{238} electron paramagnetic resonance (EPR),

\footnote{239} superconducting quantum interference device (SQUIDs)

\footnote{240} and optical detected magnetic resonance (ODMR) using single photon sources (SPS) such as molecules and intra band-gap paramagnetic atomic point defects in bulk solid semi-conducting crystals. Miniaturizing nano-magnetic sensors as much as possible without impeding their sensitivity would be highly advantageous. Van der Waals two dimensional (2D) materials allow the isolation of one monolayer to few layers of a crystal as thin as \( \sim 0.5 \) nm and could possibly circumvent the size limitations by providing a host for a SPS magnetic
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Sensor. In WSe$_2$, a narrow band-gap 2D material (1.35 eV\cite{241}), SPS originating from quantum dots (QDs) whose emission wavelength is sensitive to large magnetic fields have been reported.\cite{57,66} A natural question arises - **which SPS in a 2D crystal would be suitable for ODMR?** QD’s confined electronic structure typically lack a meta-stable state, a prerequisite for spin polarization and ODMR contrast, rendering them less suitable. Point defects with electronic states inside the band-gap can be highly localized with wavefunctions confined to the atomic scale\cite{1} whereas QDs with bound excitons can have relatively large spread wavefunctions due to confinement on a nano-scale range, encompassing thousands of atoms.\cite{2} Furthermore, for quantum technologies based on manipulating electronic spins coherence times in point defects are far longer than those achievable in QDs. A well understood SPS in diamond is the negatively charged nitrogen vacancy (NV-) with a triplet (S = 1) ground/excited state and a singlet metastable (dark) state with spin polarized electronic transitions due to preferential population of the ground state spin level upon optical pumping.\cite{30,32} NV- emission rate (bright state) variations when exposed to magnetic fields occur due to changes in the decay rates of spins relaxing through the meta-stable (dark) state, which is the basis for observing ODMR. Organic molecules, disadvantageously, usually have a singlet ground/excited (bright) state and triplet metastable (dark) state and for ODMR require tedious analysis of the time scale length of the dark periods.\cite{34} A graphene analog van der Waals material with a band-gap of 5.95 eV,\cite{54} similar in size to diamond,\cite{27} is hexagonal boron nitride (h-BN). Various SPS spanning a large emission wavelength range have been attributed to h-BN in the 2D\cite{117,107,194,161} and 1D form\cite{109} with their chemical structure not conclusively identified but rather computationally conjectured using DFT.\cite{117,108,110}

Thin 2D crystals have a large ratio of surface area/volume and it is becoming clear that both sample preparation methods and source material have a huge impact on the defect density in host crystal.\cite{109} For example, chemically functionalized 2D graphene, lacking a band-gap, is also a room temperature SPS originating from bound excitons excited with energies larger than graphene’s (zero) band-gap, placing them under the category of quantum dots (QDs)\cite{242} and not under intra band-gap point defects.

In the following we demonstrate for the first time that a paramagnetic emitter in h-BN\cite{243} exhibits ODMR upon intra-band excitation once applying a microwave at cryogenic conditions. We study the emitter’s gyromagnetic factor, PL behavior under cryogenic conditions and absorption polarization. From the data we debate the possible spin configurations and structure. We use single crystal h-BN as our source material from Ref.\cite{125}, which has become a hallmark for high quality h-BN in research.
5.2 Spatial properties, room temperature photoluminescence and cryogenic polarization

In Figure 5.1 we first analyze a paramagnetic emitter in terms of spatial location, PL, anti-bunching and magneto-optic response at room temperature followed by PL and absorption polarization at cryogenic conditions. SPS in h-BN suspended from a substrate emit with a reduced count rate, \(^{197}\) therefore for increased collection efficiency our h-BN is placed on SiO\(_2\) substrates, allowing us to collect photons at a maximum rate of 250 KHz using 633 nm excitation. (See Figure 5.1.f). Probing a h-BN multilayer with dimensions of \((\sim 1 \times 2 \ \mu m)\) using 3 linearly polarized excitation lasers \((594nm/633nm/730nm)\) reveals a bright emitter which is similarly spatially localized for all excitations roughly at the center of the flake (Figure 5.1.a). Reflection measurements and wide bright/dark field images reveal the flake structure, hinting that the spatial location of our emitter is not in a flat region, but rather a bended one or broken edge, similar to previous reports. \(^{112}\)

Reconstructing the room temperature PL spectra using Lorentzian and Voigt functions (Figure 5.1.b) yields a good agreement to the measured PL for all three excitations. We enumerate these peaks as \(P_i(T)\). We enumerate some peaks together using the \(P_{i+j}\) label as they overlap or, as will be shown in cryogenic conditions, are composed of two main peaks. According to Ref. \(^{243}\) the room temperature ZPL of emitters that respond to magnetic fields is located at 727 nm which correspond to our peaks \(P_{4+5} (T)\) \((594nm/633nm) (298K) = 727 \pm 18 / 729 \pm 29 \ \text{nm}\) in Figure 5.1.b. A close observation in Ref. \(^{243}\) also reveals a small peak at 812 nm, hardly visible using our 594 nm excitation but easily identified using longer wavelengths excitations, \(P_7 (633nm/730nm) (298K) = 812 \pm 2 / 813 \pm 4 \ \text{nm}\). In brief, we surmise, that peaks in the range of \(i > 3\) have spectral components of our paramagnetic emitter, whereas Peaks 0-2 most probably arise from a nearby defect(s). These components are analyzed in detail below. For more details, see Figure 5.1 caption. Next, we test the emitter’s magneto-optic response to a magnetic field generated from a permanent magnet. A Gaussian fitted count distribution using 633 nm excitation (Figure 5.1.d), shows a non-over lapping center peak, indicating a similar magneto-optic response, previously reported for 594 nm excitation. \(^{243}\) This response was also seen for 730 nm (not shown). Hanbury Brown and Twiss autocorrelation measurements \((g^2(t))\) can reveal the number of emitters involved in the emission process, yielding insights on the electronic structure. In Figure 5.1.e the red dashed lines of values ‘1’ / ‘0.5’ represent the threshold for bunching/single emission of the system for \(|t| > \sim 10 \ \text{s} / |t| < \sim 10 \ \text{s}\), respectively. Our \(g^2(t)\) function (for \(|t| > \sim 10 \ \text{s}\) is above 1, indicating the presence of a meta-stable state (bunching), which is of significance to observe ODMR. However, for \(|t| < \sim 10 \ \text{ns} of g^2(t)\) function doesn’t go below 0.5 and thus more than one SPS dominate the emission process. Using the formula from 2.3.2 we calculate 3.5 emitters round to 3 emitters.
Looking into the spatial spread of our emitter (Figure 5.1.c) compared to a different non-paramagnetic emitter of singular nature ($g^2(0) < 0.5$), reveals that the emitter has a larger spatial spread for all 3 excitations and has an additional ‘bump’ on the right side. This bump disappears only for 730 nm excitation suggesting it can belong to another center. This spatial information further confirms the non-single nature of our emitter. Similarly, in Ref. 243, the $g^2(t)$ function was not conclusively below 0.5. Thus one can speculate that this type of emitter tends to form in proximity to others of the same type, undistinguishable using our spatial resolution ($\sim 594 \text{ nm x 0.5}$). Applying / removing the magnetic field (Figure 5.1.e. On/Off) modulates the bunching/anti-bunching behavior as the frequency of decay rates from the excited to ground and metastable states are changed, most prominently seen on the $\tau_2$ component, consistent with reduction of emission count (Figure 5.1.d). For reported paramagnetic SPS in h-BN 243 the magneto-optic response was seen both as a emission reduction but also as an increase in emission. We show below under different measurements conditions that the same emitter also exhibits this behavior and we offer a possible explanation. These observations indicate that the emitter behaves equivalently to that of Ref. 243. For further analysis of transition rates see Ref. 243, which are of similar order.
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Figure 5.1: Spatial, photoluminescence properties at room temperature and cryogenic absorption polarization. (a) Bright field and dark field images of the h-BN flake on a SiO2 substrate. 4 panels display the emitter under 594nm/633nm and 730 nm and a reflection image using low power 532 nm excitation. The emitter is localized in the same spatial coordinates under all excitations. The reflection measurement reveals the emitter is in a spatial area containing perimeters. (b) Room temperature PL spectra using 3 linearly polarized excitations of 594nm / 633 nm / 730 nm (top to bottom). Peak numbers are enumerated as Pi(0≤ i ≤ 8) for each Lorentzian fit. Note that a Voigt fit yielded the best fit for 730 nm excitation. Excitation wavelength and optical filters used are marked in the graphs. Peak 7 is enlarged for clarity for 633 nm excitation. (c) High resolution confocal scan of the emitter for 594nm / 633nm / 730 nm excitation (orange,red,purple curves, respectively). The emitter is less localized in comparison to the confocal spread of another non-paramagnetic emitter of singular nature, (black bar comparison in x and y profiles). (d) Gaussian count distribution modulation with/without a magnetic field (black/blue, respectively). The peaks contributing to the emission are marked. (e) Auto-correlation measurements with/without a magnetic field (black/blue, respectively). A modulation is more prominently seen in the t2
Rotating the linear excitation polarization can reveal information regarding emitter absorption polarization and orientation. In Figure 5.1.g-i we study this dependence by monitoring emission count rate and PL spectral features at cryogenic conditions of 8.5 K. The emission intensity variation as a function of excitation angle (grey points) of the 633 nm laser is fitted using a \( \sin^2(\theta - \theta_0) \) (Figure 5.1.g, red curve). As revealed in the auto-correlation measurements in Figure 5.1.e, the emitter is non-singular. Thus at first sight the fit indicates that the emitter consists of linearly polarized dipoles, in agreement with other SPS measurement in h-BN. To see if this argument holds for the emission peaks we also record the PL for a subset of excitation angles from maximum to minimum emission counts (Figure 5.1.h). The cryogenic PL in Figure 5.1.h PL reveals two peaks which were unresolved (\( P_{4+5} \)) at room temperature, \( P_{4(633 \text{ nm})(8.5K)} = 719 \) and \( P_{5(633 \text{ nm})(8.5K)} = 725 \) nm. The filled dark red curves reveal that the emission wavelength components are all unilaterally reduced until extinction when upon rotation to the minima angle. However, using a natural logarithmic function to increase the intensity of the low signal values reveals that Peaks 3/4/5 are not completely extinguished (non-filled red curve, 240°). The intensity image per peak of these is plotted for all excitation angles in Figure 5.1.i (right), with the intensity sum profile per angle (left). Peak 4 and 5 show similar periodicity (\( \sim \sin^2(\theta - \theta_0) \)) whereas Peak 3 exhibits two different periodicities fitted best with a quadrupole function (\( \sim \cos^2(\sigma - \sigma_0)\sin^2(\theta - \theta_0) \)). Therefore Peak 3 exhibits one component aligned with Peaks 4-7 and a different component which deviates at \( \phi \approx 86 \pm 7^\circ \) from the other peaks. The linear polarization angle of excitation used in the following ODMR measurements is indicated by the blue arrows. Each peak polarization’s are superimposed on the total emission count in Figure 5.1.g (rescaled for clarity). We can account for the incomplete reduction of Peaks 4,5 at the minima angle due to their high sensitivity to deviations in the polarization angle due to surface or flake curvature, which is known in h-BN SPS.
5.3 Cryogenic variations in green/red excitation photoluminescence and phonon mapping

While PL measurements of various SPS sources in h-BN at cryogenic conditions have been reported \(^{245,244,196,163}\), none address the cryogenic PL of a paramagnetic emitter in h-BN. In Figure 5.2 we display the emitter’s main PL features, line-widths, and luminescent phonon behavior. It has been proposed on two different SPS in h-BN that if the energy difference between the excitation laser and the ZPL is above h-BN’s maximum phonon energy, a Huang-Rhys (HR) two level electronic model is inadequate to explain the emission mechanisms in h-BN.\(^{195}\) In addition, for lower energy ZPLs it has been proposed that excitation is mediated by cross relaxation and not through direct laser excitation.\(^{163}\) Exciting with different energies can also shed light on possible charge states.\(^{246,36}\) Thus in the following we excited the emitter with 633 nm/ 532 nm excitation separately (All features in the figure are color coded in red/green, respectively). In Figure 5.2.a we display the PL intensity in a natural logarithmic scale at 8.5K, and color bars of the PL intensity in natural logarithmic scale for decreasing temperatures (bottom to top). In Figure 5.2.b, for each peak, we display the decomposed components (denoted \(\alpha, \beta, \epsilon, \eta\)) using Lorentzians. Immediately noticeable are the variations in the PL features for different excitations (marked by the black arrows). Peak 3/4 and components \(\epsilon/\eta\) of Peak 7 are absent using 532 nm excitation throughout the whole temperature range in Figure 5.2.a, Nevertheless Peak 5 retains the largest intensity for both. To gain insight we measure the count rate distribution and high resolution PL of the emitter without/with a field of 130 G (Figure 5.2.c black/blue curve, respectively). The 130 G magnetic field measured by the NV (not shown) corresponds to a +25% emission contrast of the h-BN emitter, in agreement with contrast vs. magnetic field values in Ref.\(^{243}\). Comparing the 130 G PL (blue curve) with the 0 G PL (red curve) reveals which peaks are affected by the magnetic field. The integrated \(\Delta\) function (bottom charts Figure 5.2.c, grey curve) yields the percentage (blue bars) and weight (blue lines) of increased photons due to the magnetic field for each peak, revealing the dominant role of Peak 5 (Total 27%/45.6%, percentage/weight, respectively). See figure caption for all values. Thus Peaks 3/4/5/7 are the main peaks involved in the magnetic response. In Figure 5.2.b the FWHM widths in meV (\(\gamma\)) (black lines) for each component are displayed. As most components have a width of \(<\sim\) 3 meV, smaller than that of the bulk h-BN phonon DOS (\(\sim\) 5 meV),\(^{163,247}\) we cannot rule out multiple ZPLs. Therefore the temperature dependence behavior is analyzed for all peaks as if each were a ZPL in the following (Figure 5.3). Resonant excitation is required for further verification. With that said, in the following we discuss a probable scenario with more than one ZPL, assigning each peak component a role in emission. The narrowest component for 633 nm excitation is Peak 5,\(\beta\) \(~\sim\) 0.25 meV (Figure 5.2.b) with the highest intensity for both excitations and a dominant role in the magnetic response. Therefore we tentatively assign Peak 5,\(\beta\) as a ZPL. To see how the other peaks
with respect to Peak 5, we plot in Figure 5.2.a $\delta_5$ as a detuning scale in dark blue. Typically SPS in h-BN display a PL with a well separated PSB shifted from the ZPL, corresponding to $\sim 169$-$200$ meV. Additionally, ungapped low energy acoustic phonons can cause multi-phonon sidebands obscuring the ZPL. Taking all of these into account fits well with our observations in Figure 5.2. The adjacent peaks of $5/\alpha/\epsilon$ are acoustic phonons detuned by $\sim < 5$ meV, obscuring the ZPL ($5\beta$), peak $7\alpha$ and $7/\beta/\epsilon/\eta$ fall in the range of the stokes LO and TO$_{||}$ optical phonons, respectively (marked as superimposed blue double arrows in Figure 5.2.a). For both excitations, the LO/TO$_{||}$ optical phonons energy range engulf Peak 7 for the full temperature range (color bars, Figure 5.2.a). Peak 3 at first glance seems more challenging to assign, as it is anti-Stokes detuned and not in the energy range of the typical optical phonons ($\sim 25$ to $50$ meV, Figure 5.2.d). Nevertheless, the intensity behavior of Peak 3 is correlated with Peak 5 and Peak 7 for red excitation (evident from Figure 5.2.a, red color bar and discussed below). Furthermore both Peaks 3 and 7 have the same number of components (Figure 5.2.b) under red excitation with similar internal peak energy spacing of $\delta_3(\alpha,\epsilon) =$ $\sim \delta_5(\alpha,\epsilon) =$ $\sim \delta_3(\beta,\eta) =$ $\sim 12$ meV and similar energy spacing between each component $\delta_c(3,7) =$ $\sim \delta_p(3,7) =$ $\sim \delta_c(3,7) =$ $\sim \delta_3(3,7) =$ $\sim 225$ meV. Calculating the energy difference between the excitation lasers to peak $3\alpha$ yields $\sim 570$ / $199$ meV for $532$ nm / $633$nm, respectively. Thus for $532$ nm excitation the energy difference is more than two times the energy of the optical phonons ($169$-$200$ meV) whereas for $633$ nm it falls at the end of the optical phonon energy range. This picture fits well with the following: using $532$ nm excitation Peak 5 is a ZPL which is directly excited by the laser whereas using $633$nm excitation Peak 3 and Peak 5 are both ZPLs which are mediated through cross relaxation and Peak 7 is the PSB of Peak 5 (or possibly both). This analysis is counter-intuitive to the model proposed in Ref. However, our excitation energies are both above/equal to the maximum optical phonon energies and the model in ref. addresses two different SPS with different wavelengths. Peak 4 with a narrow FWHM of $\sim 0.56$ meV suggests that it can also be a possible ZPL. However, it’s intensity was too weak to assign it to a possible role. However, the same analysis can done with Peak 4 as the ZPL or part of Peak 5, as it is detuned from Peak 5 by $15.7$ meV. We note that no magneto-optic response was seen using $532$ nm excitation. A detailed phonon map under red and green excitation is displayed in Figure 5.2.d as function of energy detuning from Peak 5, highlighting the dominant LO(T) optical phonon mode, which is a fingerprint and evidence of the emitter’s coupling to the h-BN lattice. Extracting from each peak the PL intensity function (See below) and their relative spectral weight we can estimate the HR factors. We get HR values of $S_{532nm}^{532nm} = 1.4 \pm 1$, $S_{633nm}^{532nm} = 5.0 \pm 0.4$ indicating different electron phonon couplings for different excitations. See Figure 5.2.e for further details. The different electron-phonon couplings for each excitation can be responsible for the variations in the feature of Peak 3 and 7,
However the doubling of the spectral features (with 633 nm excitation) seem to indicate an intermittent Stark shift effect which would shift the ZPL, obscured by acoustic phonons, which would translate to a shift in the optical phonons possibly due to a charge state switching.

Figure 5.2: Cryogenic PL under red/green excitation analyzed with a detailed phonon map. (a) Temperature dependent intensity PL in natural logarithmic scale of the emitter using 633nm/532nm excitation, red / green curves, respectively. The color baths underneath each represent the natural logarithmic scale of the PL intensity as a function of temperature. Note that the temperature scale is not linear but consists of the temperature points depicted in Figure 5.3. The temperature outer boundaries are noted (8.5K and 295K, 8.5 and 249K, 633nm/532nm excitation, respectively). Peak numbers are displayed in the upper frame. The dark blue scale represents the energy detuning of the spectra from peak 5 (δ5). The optical phonon energy range is displayed on the scale. Black arrow display features which are absent between both excitations possibly due to charge state switching (b) Normalized PL intensity for each peak at 8.5K in (a), decomposed with Lorentzians, upper graphs represent excitation with 633nm and bottom with 532 nm. Guides to the eye lines connecting components are displayed on top as they have similar energy spacing as described in the text FWHM of each components in (b) in (γ) meV are super imposed (c) Gaussian count distribution modulation (inset) with/without a magnetic field (black/blue, respectively). Due to the magnetic field increases the emission count be 25%. Top charts - PL spectra of the emitter with/without a magnetic field of 130 G (black/red curve, respectively). The difference in the PL spectra is the blue colored area. Bottom – The integrated Δ function (grey curve). Categorizing the different spectral ranges we calculate the percentage of increase and weight for each range. P3, P4+5, P4+5 till P6, P7, P8, Percentage: 18.7%, 33.2%, 39.3%, 1.9%, 6.9%, Weight: 13.2%, 67.8%, 7.3%, 8.9%, 2.8%, respectively. (d) Detailed phonon composition of the intensity PL in natural logarithmic scale for red (upper) and green (bottom) excitation. An exponent line was subtracted from the signal to display the dominant contributions (dim red/green lines). The phonon DOS is superimposed in blue adapted from Ref. 248. The dominant
5. Paramagnetic emitters in 2D h-BN

LO mode is visible in both red/green excitation, interestingly for red excitation the LO mode is replicated twice, possibly due to charge state switching. (e) Electron phonon coupling (HR factors) for each peak for green/red excitations.

5.4 Peak shift under temperature cycling and intensity behavior

In Figure 5.3.a, we analyze peak position/FWHM change, (Eδ/Width, upper/bottom, respectively). At elevated temperatures, not all features could be distinguished and thus the analysis is valid for the first peak component displayed in Figure 5.2.b. In semi-conductors such as diamond / GaN / AlN the band-gap is blue shifted upon cooling due to lattice contractions and temperature dependent electron lattice interactions. For the NV in diamond it has been suggested that the ZPL shift is related to this band-gap shift. However, in h-BN the band-gap dependence is different: above/below 100 K the band-gap is red/blue shifted, respectively, due to h-BN’s negative in-plane thermal expansion coefficient for T > 70K. Thus we tend to discard band-gap variations as the sole cause of the ZPL shift. We adopt the ZPL shift behavior known for defects in diamond which obey a power law of \( \sim a_T T^2 + b_T T^4 \) with an added \( f(T) \) of higher T powers to best describe our data. Other major mechanisms defining the ZPL structure profile are inhomogeneous and homogeneous broadening. Previous studies yielded a T\(^3\) line width behavior on the h-BN defects and for the NV in diamond a power law \( \sim a_T T^3 + b_T T^7 \) with a possible \( c_T T^5 \) contribution. We fit our data with all these powers that describe best the width behavior. Peaks 5/7 display similar energy variations. To gain more insight we plot the intensity of peaks 5/7 (Figure 5.3.b). The higher energy excitation (532nm) resulted in the brightest intensity and thus the data is normalized by Peak 5, 532 nm excitation. We identify two temperature regimes for 532/633 nm excitation where the intensity fits well with an exponent function (T > 100K/ 70K, respectively, dashed blue line). Below this regime the emission mechanism appears more complex, evermore so with 633 nm. Possibly this is linked to h-BN’s band-gap shift behavior. The intensity of both Peaks 5/7 display a similar behavior, as expected, indicating their correlated behavior. The ratio between the intensity of Peaks 5/7 for both excitations (Figure 5.3.c top panel) and the ratio between the same peak for each excitation (bottom panel, P5 / P7, black/grey curves, respectively) have similar scale, with 532 nm resulting in the higher intensity in all cases. Subtracting the fitted Eδ shift functions (Figure 5.3.d.) of peaks 5/7 and 5/3 reveals that for the simulated temperature range the energy difference of peak 7 fits the LO/TO\(_{11}\) optical phonons (δ\(_{5,7}\)) (as shown also in Figure 5.2.a), and that the energy spacing between Peak 5 and Peak 3 (δ\(_{5,3}\)) changes in a similar fashion to that of δ\(_{5,7}\), another indication to correlation between peaks 3/5/7.
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Figure 5.3: Photoluminescence and intensity as a function of temperature. (a) Peak energy detune / width as a function of temperature, upper/bottom, respectively. The detune is from the energy listed on the top left for both green and red excitation. (b) PL intensity for peaks 5/7/3 (noted in the upper right corner) using 532 nm and 633 nm excitation. The scale is multiplication, noted on the right side. The temperature scale is split from 0 K to 60 K and from 60 K to 250 K. The blue dotted lines represent the regime where the intensity behavior is modified (c) Upper chart - Intensity ratios between peaks 5 and 7 for the 532 nm and 633 nm excitation (green/red, respectively). Bottom chart – Intensity ratio for 532 nm and 633 nm excitation for Peak 5 (in black) and Peak 7 (in grey). (d) Energy detuning as a function of temperature from of Peak 7 from 5 (upper) and Peak 3 from 5 (bottom).

5.5 EPR experiments on h-BN

Previous research using electron paramagnetic resonance has been done on bulk h-BN material irradiated by electron or gamma radiation to induce defects. These have uncovered two major paramagnetic centers: a nitrogen vacancy interacting with a single boron (one-boron center) and a nitrogen vacancy interacting with three nearest neighbor borons. For example the one-boron center due to the higher abundance of $^{11}$B (80.42%) would be seen in EPR as four lines ($2I + 1, I = 3/2$). The EPR measured spin-lattice relaxation time ($T_1$) for the nitrogen vacancy in h-BN improved two order of magnitudes upon cooling down to cryogenic temperatures, highlighting the importance of working in cryogenic condition in order to see ODMR.

5.6 Optically detected magnetic resonance (ODMR)

In Figure 5.4 we display ODMR of the emitter at 8.5K. To get a close estimation of the magnitude of the applied magnetic field, a diamond with a NV SPS was placed in proximity to our sample. Interestingly, ODMR from our h-BN emitter (Figure 5.4.a) exhibits increased...
photon emission when sweeping the MW frequency for an applied fixed magnetic field. Increased ODMR emission is also reported for defects in silicon carbide. This hints to an initial preferential spin polarization of the dark state in the h-BN emitter, modified to the bright state by the MW, as opposed to the NV which is preferentially spin polarized in the bright state. We note that when no magnetic field was applied we could not observe an ODMR peak, using our MW frequency sweep range. We discuss below the implications of this. ODMR measurements can contain elements arising from inhomogeneous broadening (a Gaussian signature) and homogenous broadening (sharp Lorentzian transitions). Sharp Lorentzian transitions occur due to hyperfine coupling arising from atomic nuclei with non-zero atomic spin (which consist the entire pristine h-BN lattice). The Gaussian contribution can be due to dipolar interactions, spin lattice relaxation or unresolved hyper fine structure creating a Gaussian envelope.
Figure 5.4: ODMR of the emitter under cryogenic conditions. (a) Normalized ODMR contrast of MW sweeps for the h-BN emitter at different fixed magnetic field values. Parallel magnetic field values are indicated in blue. The ODMR MW frequency increases as the magnetic field is increased. Each peak is fitted using one or more Voigt functions. (b) For each ODMR peak measured in (a) a center peak frequency is extracted and is plotted in 3D as a function of absolute magnetic field value and magnetic field angle. The center peak frequency is displayed as a function of angle/parallel magnetic field value (left/right, respectively). A schematic of the emitter and the magnetic field is also displayed. (c) A schematic of the configuration used to apply ODMR. A 20 μm conducting copper wire is spanned in proximity to our emitter in order to emit microwave photons. The emitter is simultaneously excited with a continuous wave (CW) 633 nm laser.

Thus, as customary in EPR measurements, we firstly fit the entire ODMR signal with a Voigt envelope which is a convolution of a Gaussian and a Lorentzian and can give insights on to which elements the ODMR packet contains. We note that some of the ODMR peaks contained asymmetric features and required more than one Voigt envelope to achieve a good total envelope fit. This is seen as blue lines in Figure 5.4.a. Taking advantage of ODMR of a NV\textsuperscript{-} defect whose electronic structure and zero field splitting (ZFS) of D = 2870 MHz is well known, using the equations for the magnetic field and magnetic field angle, respectively (adopted from Ref. \textsuperscript{255}):
$B(v_1, v_2) = \sqrt{\frac{v_1^2 + v_2^2 - v_1 v_2 - D^2}{3 \left(\frac{\gamma_{NV}}{2\pi}\right)^2}}$  

(5.1)

$\Delta = \frac{7D^3 + 2(v_1 + v_2)(2(v_1^2 + v_2^2) - 5v_1 v_2 - 9E^2) - 3D(v_1^2 + v_2^2 - v_1 v_2 + 9E^2)}{9(v_1^2 + v_2^2 - v_1 v_2 - D^2 - 3E^2)}$  

(5.2)

$\Delta \approx D \cos(2\theta)$  

(5.3)

Where $E = 0$ and $\Theta$ is the magnetic field angle. We calculate the magnetic field and angle relative to a NV using NV ODMR peaks where $v_1$ and $v_2$ denote the ODMR peak frequencies and $\gamma_{NV}/2\pi$ the NV gyromagnetic ratio in units of MHz/Gauss. The magnetic field angle is translated to the plane of the emitter as seen in Figure 5.4.b where we denote $\theta$ the angle between the magnetic field and the emitter in the plane of the emitter. Using these recalibrated values we test our fitting and quantify the Zeeman interaction, we plot the ODMR center peaks extracted from the weight of the Voigt function(s) envelope of the h-BN emitter as a function of magnetic field angle and size in Figure 5.4.b. The angular dependency reveals that the peak position is mostly independent of the angle but is determined by the size of the magnetic field, thus indicating an isotropic gyromagnetic ratio. Extrapolating the slope/intercept point with the frequency axis we extract a $g$ factor (gyromagnetic ratio - slope) of 2.06, as described for the Hamiltonian in 2.3.6. Our gyromagnetic ratio is of similar magnitude to that of the NV$^-$ point defect in diamond and paramagnetic defects in h-BN measured via EPR. The intercept value, close to 0 [MHz], could indicate at foresight that the ZFS $\leq$ 0 [MHz]. However, taking into account possible magnetic field measurement errors (crosses Figure 5.4.b) and our limited MW frequency range ($\leq$ 10 MHz), we can shift the linear fit up and down (purple dotted curves) while maintaining a similar gyromagnetic factor of between 1.97 to 2.14, shifting the intercept point between 10 to -10 [MHz] (Purple line). Thus increasing the range of a possible ZFS. We discuss this further in detail below. To get insight on the possible atomic composition of the emitter we simulate DFT calculated hyperfine values for a C$_N$ point defect and EPR literature hyperfine coupling values for the well-
studied three boron center (TBC) in Figure 5.5.a superimposed on the ODMR peak 32 gauss in Figure 5.4.a. The large discrepancy between the wider TBC ODMR FWHM compared to that of the BN emitter immediately discards the known TBC center as a possible source for our para-magnetic center whereas the C\textsubscript{N} point defect yields a possible match. To gain insight on the possible number of hyperfine components, in Figure 5.5.b we de-convolute 3 different ODMR measurements with 3, 4 and 7 Voigt functions which correspond to hyperfine coupling to 1N, 1B and 2B atoms, respectively. To estimate the best fit we plot also the ratio of the Lorentzian to Gaussian FWHM (\(\sigma^L/\sigma^G\)) in logarithmic scale as a function of components frequency detuning from one Voigt envelope. Immediately evident is the asymmetric shift of the peaks from the center envelope to the right. The best \(\sigma^L/\sigma^G\) ratio is seen for coupling to 1 boron center which yields 4 components. Using this de-convolution as a guideline, we do a series of different MW power measurements to evaluate the systems T1 and T2\textsuperscript{*} using a hyperfine coupling of 13.5 MHz to 1B atom (4 hyperfine peaks). The superposition of all power measurements is depicted in Figure 5.5.c as a superposition of all power measurements.

Using the following relations:

\[
\text{Contrast } (P) = \frac{CaT_1T_2^*P}{1 + \alpha T_1^*T_2^*P} \quad \text{(5.4)}
\]

\[
\sigma^L(P) = \frac{\sqrt{1 + \alpha T_1T_2^*P}}{T_2^*} \quad \text{(5.5)}
\]

\[
[(\sigma^L)^2 \times \text{Contrast}] (P) = \frac{CaT_1P}{T_2^*}
\]

Where \(\sigma^L\) is the Lorentzian FWHW, \(\alpha\) is a constant that determines the microwave photon efficiency of absorption and \(C\) is a constant evaluated from the multiplied function of \((\sigma^L)^2\) by the contrast. We extract a primary parameter \(\alpha\) from other ODMR measurements with the same wire geometry, \(^40\) which we afterwards improve via fitting to the one valid for our experiment. We extract from the power dependent contrast fittings and the Lorentzian FWHW component of the Voigt fittings \(T_1 = 17 \pm 4\) µs and \(T_2^* = 57 \pm 10\). The FWHW and contrast power dependence are in agreement with reports for NV ODMR. \(^35\) ODMR at room temperature was not seen possibly due to rapid spin-lattice relaxation time \((T_1)\) which improves upon cooling down to cryogenic temperatures. \(^254\)
Figure 5.5: ODMR de-convolution. (a) Schematics of two point defects in h-BN, a carbon substituting a nitrogen atom and a nitrogen vacancy, all hyperfine coupled to three near boron atoms. The expected ODMR spectra for the configuration of each of these is displayed below. The relatively larger FWHM of the TBC point defect rules it out as possible candidate for the observed para-magnetic emitter. A carbon substitute atom fits under the experimental envelope of the ODMR signal. (b) Using multiple Voigt functions we estimate the contribution for a different set of hyperfine components of the homogenous (Lorentzian) to non-homogeneous (Gaussian) FWHWM ratio ($\sigma_L/\sigma_G$) in Log scale. A representative ODMR spectra is displayed on the left. The number of components are 3, 4 and 8. For three different ODMR measurements this ratio is displayed on the right. Coupling to one boron atom (4 components) yields a relatively large ($\sigma_L/\sigma_G$) ratio whereas coupling to one $^{14}$N yields a poor ratio. (c) Superposition of all ODMR power dependent measurements with a
decomposition assuming a hyperfine coupling of 13.5 MHz to 1 boron atom (\textsuperscript{11}B). (d) Power dependent measurements for a fixed magnetic field, for which we extract $T_1$ and $T_2^*$ assuming a coupling to one boron center. Note that the outer components signal are too weak to estimate and thus $T_2^*$ is calculated using only Peaks 2 and 3.

5.7 Conclusions

We now reflect upon the data to deduce the possible electronic configuration. Calculations on the possible spin configurations in Ref. 243 have suggested that a spin system (S) of $S > \frac{1}{2}$ should be capable to exhibiting ODMR. Such a system should have a ZFS which we have not observed in our measurements. However, taking into account our MW sweep range and the possible calculation error, it is possible that our ZFS was below our sweep range. Typically, for higher order systems ($S \geq 1$) more than one satellite ODMR peaks should appear, which we have not observed. Thus we conclude that a probable candidate for this system is $S = 1$. More detailed measurements should be conducted in the future for verifications. ODMR can be seen as the counterpart of EPR, where in the former the MW frequency is swept and in the latter the magnetic field is swept. EPR can give valuable information regarding defect structure, spin configuration, transition frequencies and line widths when the density of the same defect is extremely high in the sample. A literature survey reveals that our narrowest ODMR line width of 31 MHz (Figure 5.2.d) is in the same order ($< \sim$100 MHz) to some of to those seen in other EPR studies.\textsuperscript{257,258} Nevertheless, the hyperfine interaction, typically seen in h-BN for the nitrogen vacancies electron interacting with one/three boron(s) center(s) (OBC/TBC, respectively),\textsuperscript{254,257,259} which should split the ODMR satellite in our measurements is unresolved. Interestingly for carbon and hydrogen/oxygen defects in h-BN a similar EPR line width has been observed also lacking a hyperfine interaction.\textsuperscript{254} For carbon, hyperfine splitting can be eliminated due to rapid electron exchange of nitrogen vacancies and nearby carbon(s). This can be caused by disorder, resulting from a high lattice defect concentration,\textsuperscript{260} or reduction in the electronic delocalization on neighboring boron atoms.\textsuperscript{254} A degree of delocalization can be a cause for the additional PL spectral features seen in Figure 5.3.a. This agreement between our ODMR observations and the EPR suggests that the defect structure consists not only of vacancy defects but also additive impurity atoms which could be introduced during exfoliation or thermal annealing.\textsuperscript{109,260} similar to DFT predictions of point defects such as the $V_N C_B$ defect,\textsuperscript{108,110} and in agreement with our autocorrelation measurements ($g^2(0) > 0.5$, Figure 5.1.d). Another possibility which requires further study is a hyperfine splitting anisotropy which at a specific magnetic field orientation would render the hyperfine satellites unresolvable as seen in EPR.\textsuperscript{260} Assuming a low frequency ZFS we can also explain the decrease and increase of our emission rate when a magnetic field is applied. It is shown that ferromagnetism can be intrinsic in h-BN due to edge N-terminated h-BN with a Curie temperature above room temperature.\textsuperscript{261} Furthermore calculations predict the nitrogen vacancy in h-BN to induce a long-range magnetic interaction.\textsuperscript{262}
Even though our spatial resolution cannot conclusively pin-point the emission source as coming from the edge, there is mounting evidence that point defect tend to form more easily in vicinity of these. Thus in order for the count rate to be truly un-effected from a magnetic field, the applied magnetic field must first overcome an intrinsic magnetic field.

In summary we demonstrate for the first time ODMR on a two dimensional van der Waals material. We displayed the detailed non-resonant PL features of the emitter at 8.5K at various temperature cycling and polarization absorption properties. Our results give further insights on the electronic structure and phonon coupling of the emitter which can help to pin point in more precision its exact chemical nature. Our observation of a low energy peak at > 800 nm (peak 7) can assist in future research to identify to isolate more emitters with these properties as the emission in this wavelength is known to be scarce for SPS in h-BN.

5.8 Additional Data

5.8.1 T2* and T1 spectra and magnetic field tilt simulation

In Figure 5.6.a the ODMR spectra for different MW power which was used to construct Figure 5.5.d. The contrast using 4 voigt fits shows a clear power dependence (in Blue). Nevertheless the FWHM of each fit does not conclusively vary as the MW power is changed. This can be due to unresolved structure in the measurements. Therefore the Lorentzian component of the two inner Voigt fits are displayed to show and these show a clear FWHM change as a function of power.

![Figure 5.6: ODMR power dependence data and hyperfine magnetic field angle simulation dependence. (a) (In blue) For four different MW powers the ODMR spectra is de-convoluted using Voigt functions showing a clear contrast vs. MW power dependence but no clear FWHM dependence. (In magenta) The Lorentzian components, representing the resolvable hyperfine components, of the fitted Voigt functions in (a) are displayed exhibiting the that the FWHM is dependent on the](image-url)
5. Paramagnetic emitters in 2D h-BN

MW power. (b) Simulating the tilting of the magnetic out-of-plane angle results in variations of the ODMR envelope, with a good fit to the data envelope, confirming our interpretation of unresolved hyperfine components in our ODMR signal.

To justify our interpretation of unresolved hyperfine coupling we simulate the behavior of the ODMR envelope when the magnetic field has an out of plane angle tilt. This is seen in Figure 5.6.b. This tilting show a clear variation in the FWHM of the ODMR envelope, thus approving our unresolved hyperfine interpretation.
5. Paramagnetic emitters in 2D h-BN
6.1 2D Hexagonal Tin Di-sulfide (SnS$_2$)

6.1.1 Structure

A semiconducting indirect wide band gap van der Waals material with an optical band gap $\sim$ 2.2 eV$^{263}$ composed of earth abundant atom species, Tin (Sn) and sulfide (S). SnS$_2$ consists of two poly-types: 2H/4H, for growth conditions below/above 800 °C, respectively.$^{265}$

![Figure 6.1: SEM imagery of SnS$_2$ (a) Bulk SnS$_2$, (b) exfoliated SnS$_2$ on SiO$_2$ coated with ITO for conductivity.](image1)

![Figure 6.2: Growth tube of SnS$_2$ with SEM imagery. (a)(b) CVT Grown SnS$_2$ crystals, the orange color indicates the 2.2 eV band gap. (c)(d) Higher resolution SEM images of SnS$_2$ – revealing the van der Waals layered structure.](image2)

![Figure 6.3: TEM imagery of SnS$_2$.](image3)

6.1.2 Fabrication

Commonly done using the CVT (Chemical vapor transport) growth method. Typically this is done in a horizontal tubular furnace as seen in Figure 6.2, using Iodine as the optimum carrier agent. Growth is done using pellets of elemental tin and stoichiometric amounts of sulfur with Iodine as the carrier.
6.1.3  **Band to band excitation**

Bulk SnS$_2$ was glued to a SiO$_2$ substrate so half of the flake is suspended, the suspended area was probed with a 532 nm excitation laser. This is seen in Figure 6.4.

![Figure 6.4: Bulk SnS$_2$ excitation with a 532 nm laser. (a) photo-luminescence, (b) confocal scan with a 550LP filter.](image)

6.1.4  **Intra-band excitation**

Probing the suspended bulk with intra-band (594 nm) excitation reveals distinct PL spectrum peaks and anti-bunching features, although at a certain point of time bleaching occurs. This is seen in Figure 6.5 and Figure 6.6.

![Figure 6.5: Room temperature Bulk SnS$_2$ intra-band point defect excitation with a 594 nm laser. (a) Photo-luminescence spectrum, (b) auto-correlation, (c) photon emission time trace.](image)
6. Appendix: TM(D)C and Hetero-structures

6.2 2D Hexagonal Hafnium Di-sulfide (HfS$_2$)

6.2.1 Structure

The Hf atom is sandwiched between two S atoms attached covalently. Photoemission studies of HfS$_2$ have obtained an indirect band gap of 2.85 eV between the $\Gamma$ and M/L points, however optical results yield a 2 eV gap.\footnote{266} See Figure 6.7.

6.2.2 Fabrication

Methods for fabrication of 2D HfS$_2$ include CVD growth using HfCl$_4$ as the Hf source and sulfur pieces as the S source, with the use of the following reaction:

$$\text{HfCl}_4(\text{g}) + 2\text{S}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{HfS}_2(\text{g}) + 4\text{HCl}(\text{g})$$

See Figure 6.7.c

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.6.png}
\caption{Room temperature photo-luminescence of Bulk SnS$_2$ intra-band excitaiton with a 594 nm laser. (a)(b)(c) for three point defects.}
\end{figure}
6.2.3 Band to band excitation

Bulk HfS2 was glued to a SiO2 substrate so half of the flake is suspended, the suspended area was probed with a 532 nm excitation laser. The photo-lumencence spectra and confocal scan are displayed in Figure 6.8.
6. Appendix: TM(D)C and Hetero-structures

Figure 6.8: Band to band excitation of bulk HfS$_2$ with a 532 nm laser.

6.3 2D Germanium sulfide (GeS)

6.3.1 Structure
Germanium sulfide has a direct and indirect band gap in the range of 1.55 to 1.65 eV. With an orthorhombic crystal structure. A closely related van der Waals crystal, namely GaSe has shown to exhibit single quantum emitters near areas where strain is present due to residual Se spheres resulting in curvature of the 2D crystal.

Figure 6.9: GeS Structure. (a)(c) Crystallographic structure of GeS. (b) SEM image showing the van der Waals nature of the 2D GeS crystal.
6.3.2 Band to band excitation

Figure 6.10 contains confocal imagery and PL measurements for band to band excitation at room temperature for GeS. Interestingly we see a correlation between structural crystalline like formation visible with the SEM and to position where to emission is localized. This is similar to reports seen for quantum emitters in GaSe. 68

![Confocal Imagery and PL Measurements](image)

Figure 6.10: Excitation of Bulk GeS, spatial and spectral properties. 532 nm PL confocal scan of bulk GeS, (a) reflection, (b) 550 LP filtered image. (c) SEM images of bulk GeS, crystalline structures are seen on the exterior. (d) Literature image for localized single emitters in the related GaSe van der Waals crystals. Selenide pockets were identified as the source of emission causing curvature in the GaSe layers. 68 (e) Band to band excitation of bulk GeS with a peak at ~ 1.65 eV using a 633 nm excitation laser. (f) Comparison to literature Band to band PL of GeS 271 in agreement with (e).

6.4 Hetero-Structures

6.4.1 Introduction

Assembly of hetero-structures can have numerous advantages functionalities as outlined in the introduction. The variety of materials that can be assembled, the different thicknesses of the layers involved, the different alignment angles at the hetero-structures and different lattice constants
leading to different stacking configurations all contribute to the numerous functionalities which can be achieved by their construction. In optical research this has lead to the discovery of inter-layer excitons at the interface of semi-conducting interfaces, which have the electron and hole separated in the different crystals at the interface. 272, 273, 274

In this section we have explored using intra-bandgap excitation h-BN encapsulation of two unexplored wide-band gap TMDCs, SnS$_2$ and HfS$_2$, in a hetero-structure design, before and after annealing. See Figure 6.11.a for the detailed structure.

### 6.4.2 Room temperature excitation

The band gap of SnS$_2$ and HfS$_2$ is 2.2 eV 263, 264 and 2 eV gap 266, respectively. Using a 730nm excitation laser (1.69 eV) localized intra-band emission could be seen on the edges of the hetero-structure in the h-BN encapsulated area, nevertheless, these were not stable and either bleached or ionized quickly (Figure 6.11.b).

![Figure 6.11: Confocal images of a h-BN/SnS$_2$/HfS$_2$/h-BN hetero-structure. (a) Wide field image of a custom-made heterostructure (b) 730nm laser excitation with a 750LP filter pinpointing localized emission (c) dark field image of same heterostructure.](image)

### 6.4.3 Annealing Procedures

A hetero-structure is composed of materials that have different temperature oxidation thresholds, thus the most suitable annealing temperature and environment can vary. Here we test different annealing procedures to determine which one would be most suitable for an h-BN encapsulated hetero-structure with SnS$_2$ and HfS$_2$. In Figure 6.12.a/b wide bright/dark field optical images are seen prior to annealing, respectively. From previous research, we can already conclude that the layers are not necessarily in the closest proximity. After annealing in an Argon/Hydrogen environment at 300 °C, bubbles are formed indicating a clustering of possible residue in-between the different 2D materials.
interfaces. A large clear area is also formed, indicating the proximity of the other areas after the annealing.

Figure 6.12: Wide field images of a hetero-structure after before and after argon/hydrogen annealing. An encapsulated hetero-structure of (top to bottom) h-BN/SnS2/HfS2/h-BN on SiO2. (a)/(b) Bright/Dark field images of the hetero-structure, respectively, before annealing. (c)/(d) Bright/Dark field images of the hetero-structure, respectively, after annealing in an argon/hydrogen environment at 300 °C for 12 hours. The formation of bubbles (red arrows) and of the clean interface (green arrows) after annealing are an indication to the reduced proximity of after the annealing.

In comparison to annealing in argon/hydrogen at low temperature (Figure 6.12) low temperature annealing in vacuum of a SnS2 to high temperature annealing the SnS2 encapsulated with h-BN shows the formation of more bubbles and therefore we concluded that low temperature annealing in argon/hydrogen is favorable. Perhaps the gas pressure insures the formation of smaller bubbles in addition to the forming gas effect. To compare the tolerance of SnS2 to high temperature annealing the SnS2 encapsulated with h-BN was annealed to 700 °C in argon/hydrogen for 2 hours. Bright field images clearly show structural damage (Figure 6.13.b). Thus we conclude that it is more favorable to anneal at 300 °C in an argon/hydrogen environment to get a good interface proximity.
Figure 6.13: Wide field images of a hetero-structure after low and high temperature annealing. An encapsulated hetero-structure of (top to bottom) h-BN/SnS$_2$/h-BN on SiO$_2$. (a) Low temperature annealing in high vacuum at 150 °C for 12 hours. (b) High temperature annealing in an Argon/Hydrogen environment for 2 hours. Structural damage is evident after the annealing perhaps due to the reduced temperature tolerance of SnS$_2$ material as compared to h-BN.
7 Conclusions

This work presents the first steps in understanding and controlling the properties of quantum emitters in the new material realm of semiconducting van der Walls crystals. In depth understanding of these properties with the possibility of fine tailoring them, can unleash a new realm of magnetic field sensing and tailored positioning of quantum emitters with the ease of integrated on chip devices. This is true for 2D materials and with the advancement of fabrication techniques of 1D materials the same methodologies could be applied. The focus of this work was hexagonal boron nitride which is the easiest to explore due to its wide bandgap. The large energy range spanning the emission of quantum emitters in h-BN indicates a large number of defect structures which are optically active. The observation of magneto-optic sensitive emission paves and of optical magnetic resonance for the first time in a 2D crystal paves way for a new platform of magneto-optic sensing. Our discovery of quantum emitters hosted in SnS$_2$ and the first photo-luminescence spectra of HfS$_2$ and GeS can be a paradigm shift for paramagnetic defects hosted in a nuclei spin free lattice. The full understanding of interface engineering of hetero-structures could lead to 2D bi-layer chips whose periodicity or stacking faults are utilized to engineer their electronic structure and thus their optical emission properties.
7. Conclusions
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