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Single photon emitters in boron nitride: More than a supplementary material

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ABSTRACT

We present comprehensive optical studies of recently discovered single photon sources in boron nitride, which appear in form of narrow lines emitting centres. Here, we aim to compactly characterise their basic optical properties, including the demonstration of several novel findings, in order to inspire discussion about their origin and utility. Initial inspection reveals the presence of narrow emission lines in boron nitride powder and exfoliated flakes of hexagonal boron nitride deposited on Si/SiO_2 substrates. Generally rather stable, the boron nitride emitters constitute a good quality visible light source. However, as briefly discussed, certain specimens reveal a peculiar type of blinking effects, which are likely related to existence of meta-stable electronic states. More advanced characterisation of representative stable emitting centres uncovers a strong dependence of the emission intensity on the energy and polarisation of excitation. On this basis, we speculate that rather strict excitation selectivity is an important factor determining the character of the emission spectra, which allows the observation of single and well-isolated emitters. Finally, we investigate the properties of the emitting centres in varying external conditions. Quite surprisingly, it is found that the application of a magnetic field introduces no change in the emission spectra of boron nitride emitters. Further analysis of the impact of temperature on the emission spectra and the features seen in second-order correlation functions is used to provide an assessment of the potential functionality of boron nitride emitters as single photon sources capable of room temperature operation.

1. Introduction: boron nitride emitters among other single photon sources

Hexagonal boron nitride (hBN), a layered material known also as white graphite, is customarily used in cosmetic and metallurgic industry whereas its high purity single crystals promise the optical devices operating in the UV spectral range [1–11] and are extensively used in the research on atomically thin crystals [12–14], serving as nearly lattice matched and/or protecting layers for graphene and other two-dimensional systems [15–19]. The recent addition to explorations of hBN is the discovery of specific centres in this material, which rise a quantum light, the single photon emission (SPE) [20–27]. Known sources of quantum light are individual objects such as single atoms, molecules [28], defects in bulk crystals [29–31], nanocrystals, quantum dots [32,33] and other localised/confined systems, such as, for example those lately reported to appear in thin layers of semiconducting transition metal dichalcogenides (s-TMDs) [34–38]. hBN is characterised by a large optical bandgap (E_g = 5.5 eV) but most of SPE centres in this material can be effectively excited and emit light in the mid gap spectral range. The nature of SPE centres in hBN is unclear, though they are likely associated with the mid gap defects, similar to those found in other large band gap materials such as diamond [29,30] or SiC [31]. The identification of SPE centres in hBN remains a challenge and has motivated the herein presented, extended characterisation of those centres. Our studies are focused on SPE centres which are found in easily fabricated samples made of commercially available hBN powder (Sigma Aldrich supplier). Specific locations which give rise to sharp emission lines (SEL) and indeed display the SPE character can be relatively easily found in our structures with mapping of the micro-photoluminescence signal. These lines cover rather broad spectral range, located in visible region roughly between 500 and 700 nm. Single isolated lines, when investigated at multiple locations, reveal a pattern of occurrences, which can be described statistically in terms of a number of lines per energy

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unit. Such distribution overlaps well with spectra showing broad band-type emission in hBN powder samples, which may therefore arise from ensembles of individual emitters. Such interpretation of the origin of two different types of optical response seems to be further supported by the following inspection of the polarisation properties combined with measurements of excitation spectra. For the completeness of characterisation, we discuss later on the impact of magnetic field and temperature on SEL. The latter analysis is particularly useful for judging the quality of SPE, which is crucial for consideration of their potential functionalities.

2. Appearance of single emitting centres in hBN powder and exfoliated hBN flakes

The study presented here concern mostly the samples with hBN powder in form of grains of average diameter smaller than 150 nm deposited on Si/SiO_2 substrate. In this case, the process of sample preparation deserves some special attention, because, taking into account its simplicity, the resulting quality of the observed optical response is astonishing. After several try-outs (involving dissolving the powder in ethanol, annealing the samples in ambient conditions, etc.), a simple approach to distribute the hBN powder on a piece of a polydimethylsiloxane (PDMS) film, which acts as a transparent and flexible support typically used in the exfoliation technique of various layered materials (graphite, TMDs and also boron nitride), and to press it afterwards against the substrate for an extended period of time (about 30 min) turned out to be sufficient to observe bright SEL.

The samples have been characterised in a micro-optical setup, firstly by the photoluminescence (PL) mapping of their surface at helium temperature, about 4.2 K, with a laser beam focused to an area of about 1 μm diameter. Indeed, individual spots could be found, of the size below the spatial resolution of the set-up, which give rise to an optical signal in form of SEL. A unique pattern of lines represents each spot. Sometimes PL signal from such centres takes form of simple spectra with only a single line, but in most cases complex ensembles of lines are observed. They cover a relatively large spectral range in the visible region, reaching up to about 700 nm on the low energy side. As narrow lines can be found at the very edge of the transmission band of the filter used to suppress the laser light, clearly the observation of the high energy lines is limited by the energy of the laser excitation — usually Ar^+ 488 nm line. Particular SEL can be robust in intensity, but they require a rather high laser excitation power, probably due to sub-bandgap excitation leading to low absorption of the laser light. Typically, 1 – 2 mW of the laser power was delivered to the surface of sample in the mapping experiments, which is comparable to the excitation power typically used for quasi-resonant (below the band gap) excitation of, e.g., semiconductor quantum dots.

Representative results obtained from the μPL mapping of the hBN powder sample are presented in the left panel of Fig. 1. The colour map illustrates the spatial distribution of the intensity monitored at a particular energy, 2.374 eV. Therefore, bright spots reveal places, where a spectral line appears at that chosen energy value. Three selected spectra originating from this map come from places marked as M1–M3. They represent a distinct character of each emitting centre, including the case with only a single spectral line (M2). The distribution of the emitters on the surface of the sample is rather scarce — they tend to appear as single and isolated spots, as demonstrated by the colour map.

Even though the presence of the isolated emitting centres in the hBN powder samples is beyond doubts, one could still argue that their origin may not be related to hBN at all. A scenario that the chemical substances used at any step in the production of the hBN powder play a substantial role is sound and cannot be *a priori* excluded. A possible route to shed some light on this issue could be the examination of hexagonal hBN flakes obtained from bulk crystals - a material of well-established crystal structure and composition. Therefore, the hBN flakes exfoliated with a standard method developed mostly during studies of TMDs and graphene structures, have been deposited on Si/SiO_2 substrates to undergo similar mapping experiments as the hBN powder samples. In the right panel of Fig. 1, the results of investigation of a selected bulk flake are summarised. The image from an optical microscope shows, based on the colour contrast with respect to the substrate, that the flake is thick and composed of multiple segments. Most of the characteristics of the flake's shape and structure can be reproduced in the mapping experiment by monitoring, for instance, the intensity of the scattered laser light at the consecutive spatial positions. Such faithful reproduction of the flake's geometry allows us to quite accurately establish a relation between spots in the map and particular places visible in the optical image with precision determined by the size of the laser spot. The centres emitting narrow spectral lines appear also in exfoliated flakes, as seen in the spectra originating from spots P1–P3 indicated in the image and in the map. Generally, the spectra are overall similar to the ones obtained for hBN powder sample with the exception that the narrow lines overlap with a broad background of significant intensity, which constitutes a disadvantage for further optical studies. The origin of the background signal is most likely related to the bulk luminescence. Even though the bulk emission is expected to reside predominantly in the UV region, its tails may reach into visible spectral range. The observation of SEL in exfoliated hBN flakes provides a solid argument in favour of the hypothesis, that their origin is related to defects in hBN material. Yet, due to superior quality of the spectra obtained for hBN powder samples, they were used in all the proceeding investigations.

As a first step towards the characterisation of the optical properties of the emitting centres in hBN, we examine the dependence of their emission spectra on the energy of the laser excitation. In Fig. 2 three spectra for the same location are presented, obtained under the excitation of 488 nm and 514 nm Ar^+ laser lines and 566 nm rhodamine dye laser line with a comparable excitation power of about 0.5 mW. An evident influence of the excitation energy on the intensity of individual lines can be observed. Multiple lines are seen in all three spectra at exactly the same energy, which provides a direct evidence that they appear indeed due to photoluminescence and not a Raman scattering process. Some of the lines clearly exhibit markings of a resonant character, for instance the most robust line in the spectrum for 566 nm excitation is barely visible in the spectrum for 488 nm excitation. Besides that, particular lines can demonstrate various dependence on the excitation energy. The intensity of the line **N° 1** is roughly constant for all three excitations. The line **N° 2** has an apparent maximum of intensity for the intermediate excitation. At the same time, the intensity of line **N° 3** progressively decreases when the excitation energy approaches the emission energy. Such diversified behaviour of the SEL must signify a complex energetic structure of the associated defects, which should be studied systematically and in details. Some preliminary attempts to unveil the energetic landscape and the nature of the light–matter coupling for the emitting centres in hBN are discussed here through the analysis of the excitation spectra combined with the inspection of polarisation properties.

From the point of view of more advanced spectroscopic experiments, as well as potential utility of the emitting centres in hBN, the matter of their stability plays a fundamentally important role. Also in this aspect, the hBN emitters provide a ground for further exploration. A vast majority of them give rise to narrow lines, which exhibit a perfect stability in temporal domain. That statement is valid for short sub-second timescale, in which no trace of telegraphic noise of the emission lines is observed, as well as longer periods of several hours, when no deterioration of the optical signal occurs during long-time experiments. A temporal evolution of a spectrum recorded for such a stable emitter is shown in left panel of Fig. 3. A small number of emitting centres exhibit peculiar blinking effects, occurring in the timescale of seconds or even tens of seconds. In such a case, one can distinguish two states of the emitter, which clearly cannot coexist at the same time. An example of an emitter exhibiting this kind of blinking is presented in the right panel of Fig. 3. Similar effects in other systems, such as semiconductor quantum dots,