

Nanoindentation for Tailored Single-Photon Emitters in hBN: Influence of Annealing on Defect Stability

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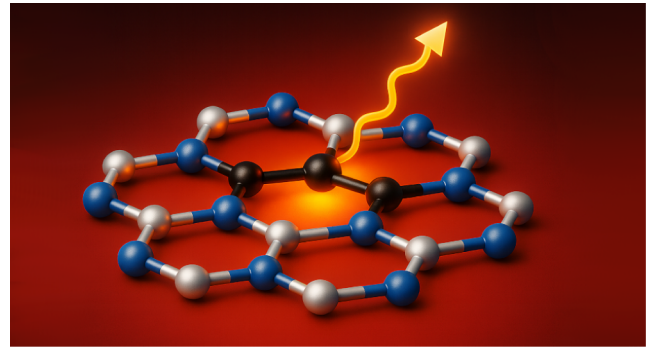
ABSTRACT: Quantum emitters in multilayer hexagonal boron nitride (hBN) are created by nanoindentation by using atomic force microscopy (AFM). Carbon-coated AFM tips are pushed into hBN flakes, creating localized carbon-based defects with spectrally tailored optical emission. We identify four predominant classes of single-photon emitters (SPEs) and show that our fabrication technique provides a high yield of bright emitters with narrow line widths and common dipole orientation, most of which exhibit a weak electron–phonon interaction because the SPEs are decoupled from the local atomic environment. We demonstrate that high-temperature annealing causes etching of hBN even in an inert environment. This defect engineering offers a controlled pathway for the creation of SPEs in hBN as a prerequisite for scalable quantum photonic applications.

KEYWORDS: 2D materials, hexagonal boron nitride, nanoindentation, thermal annealing, carbon defects, quantum emitters, polarization

INTRODUCTION

Quantum emitters in multilayer hBN have attracted significant interest across multiple disciplines due to their broad potential in quantum technologies.¹ As a two-dimensional (2D) material, hBN is inherently compatible with on-chip device integration. It has long been used as an insulating layer in heterostructure devices and has gained attention for hosting SPEs even in an hBN monolayer as shown in the pioneering work by Tran et al.² hBN is commercially accessible and cost-effective compared to other solid-state quantum emitter platforms, such as diamond, quantum dots, and SiC. Its versatility allows its use in a wide range of applications. Notably, its physical properties vary with thickness and structure, e.g., whether it is grown on a chip or used as a crystalline solid or a powder. In all cases, the surface topography of this 2D material plays a crucial role: surface defects and contaminants significantly influence electronic properties during device integration and can strongly affect the emitter's performance, which is highly sensitive to the local atomic environment.

hBN is a wide-band gap semiconductor in which the electronic states of light-emitting defects lie deep within the



band gap, ensuring high defect stability. Nevertheless, surface contaminants and charge buildup can introduce midgap states in the electronic structure of these defects, potentially causing optical instabilities such as blinking, bleaching, or spectral diffusion.^{3–5} However, with appropriate fabrication techniques, it is possible to create emitters with prolonged photostability.⁶ If they are electron-spin active, such emitters are excellent candidates for quantum coherent manipulation and sensing.^{7–10} Furthermore, emitters in hBN are known to be bright and are often generated near the surface, which enhances photon extraction and sensitivity. They are characterized by a high zero-phonon line (ZPL) to phonon sideband (PSB) ratio, making them highly suitable for quantum optical applications.^{11–13} Exceptionally bright emitters have shown great promise for quantum information processing.¹⁴ Therefore,

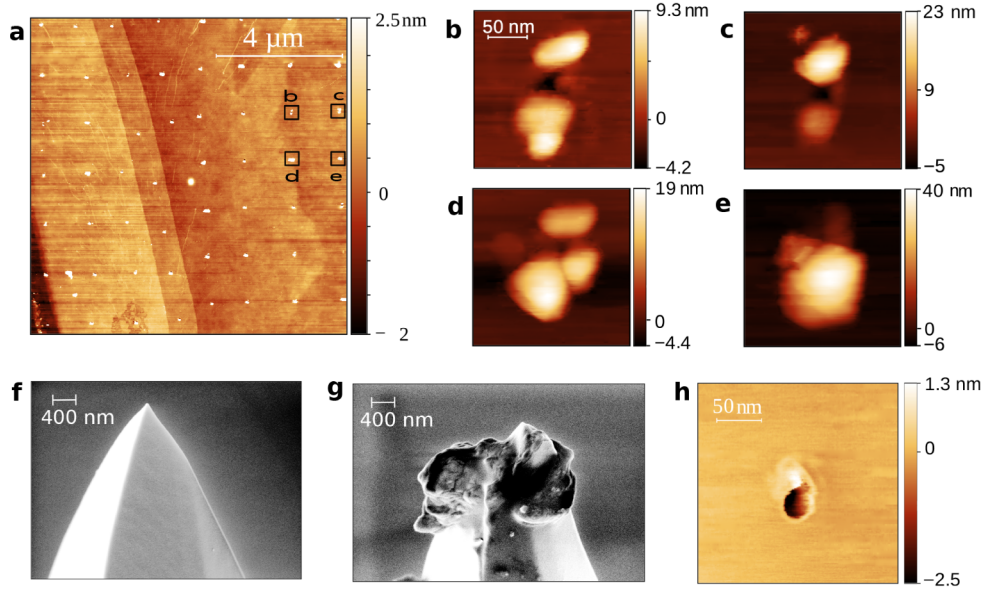


Figure 1. AFM nanoindentation on hBN. (a) AFM tapping-mode scan after indentation. (b), (c), (d), and (e) High-resolution images of the individual indentations. (f,g) SEM images comparing a diamond-like carbon (DLC)-coated tip before (f) and after (g) indentation on hBN flakes. (h) High-resolution scan in the tapping mode of an indentation after AFM contact-mode cleaning. Color bars indicate an increasing height from dark to bright.

numerous research efforts have been made over the past decade to understand and control the light-emitting defects of hBN. Advanced fabrication techniques such as femtosecond laser fabrication, focused ion beam (FIB) milling, gas annealing, e-beam irradiation, mechanical indentation, confined hBN growth, or layer engineering have successfully demonstrated the creation of emitters in hBN^{15–20} although their electronic structure remains to be explored in detail. Current research is driven by the goal of reproducibly creating identical defects in different samples, particularly for emitters in the visible-light spectrum of 532 to 650 nm wavelength. However, achieving nanoscale-positioned and identical emitters in this range with a high quantum yield remains a challenge.

In this work, we employ AFM nanoindentation to generate quantum emitters in multilayer hBN. This method was first employed by Xu et al.,¹⁶ demonstrating a radiation- and lithography-free route for the deterministic creation of SPEs in hBN. In contrast to methods such as reactive ion etching (RIE) and FIB milling, this mechanical approach avoids the accumulation of surface charge on the flakes. In the work of Xu et al., the indentations were made through the entire flake down to the Si substrate, and the relation between the indentation width and the creation of emitters was studied. In the present work, the indentations are carefully created in the near-surface area of the hBN flake to prevent the formation of large and closely spaced indentations that could lead to an ensemble of emitters. Subsequent thermal annealing is applied to activate SPEs in hBN.¹³

While most studies concentrate on fluorescence yield, only a limited number have addressed the accompanying topographical changes during SPE formation in hBN flakes under annealing.¹⁷ Hence, in this study, we investigate the structural properties of indented hBN regions by AFM and transmission electron microscopy (TEM) before and after thermal annealing. We find that even within a chemically inert environment, annealed hBN flakes experience surface etching.

This results in clean indentations with no protruding hBN around them and in hBN lattice planes that seem to be continuous up to the rim of the indentation. However, enhanced etching in an increased Ar flow results in a reduction of the flake thickness.

By using a refined fabrication procedure in which each nanoindentation incorporates carbon residues from the AFM tip indenting into the hBN flake, we achieve highly photostable and spectrally deterministic SPEs at room temperature. The most stable emitters showed no blinking and bleaching effects for an entire measurement period of several weeks and could also be measured again two years from the fabrication date without additional reactivation. These isolated SPEs are characterized by high Debye–Waller factors, minimal phonon sidebands, and decreased blinking and bleaching. Such properties make these SPEs particularly useful in techniques like optically detected magnetic resonance (ODMR) and for defect-state manipulation.^{14,21} In addition, polarization analysis shows that the majority of SPEs on one flake exhibit a common direction of dipole orientation, which is important for their potential integration into optical cavities or waveguides.

RESULTS AND DISCUSSION

Nanoindentation. AFM nanoindentation was carried out on hBN flakes using diamond-like carbon (DLC)-coated AFM tips. This method produces some protruding debris that surrounds the indentation. Figure 1a shows a regular array of such features made on a multilayer hBN flake with a 40 nm thickness. In this case, during indentation, the lowering of the AFM tip resulted in a slight movement along the axis perpendicular to the scan direction. After the indentations were performed, the sample was rotated 90° clockwise for imaging. This rotation was done to study the effect of indentation orientation on the shape of the produced feature. The protruding features of the array have an average height of approximately 7.7 nm. However, the height of individual features can range up to 40 nm. We observe that indentation is

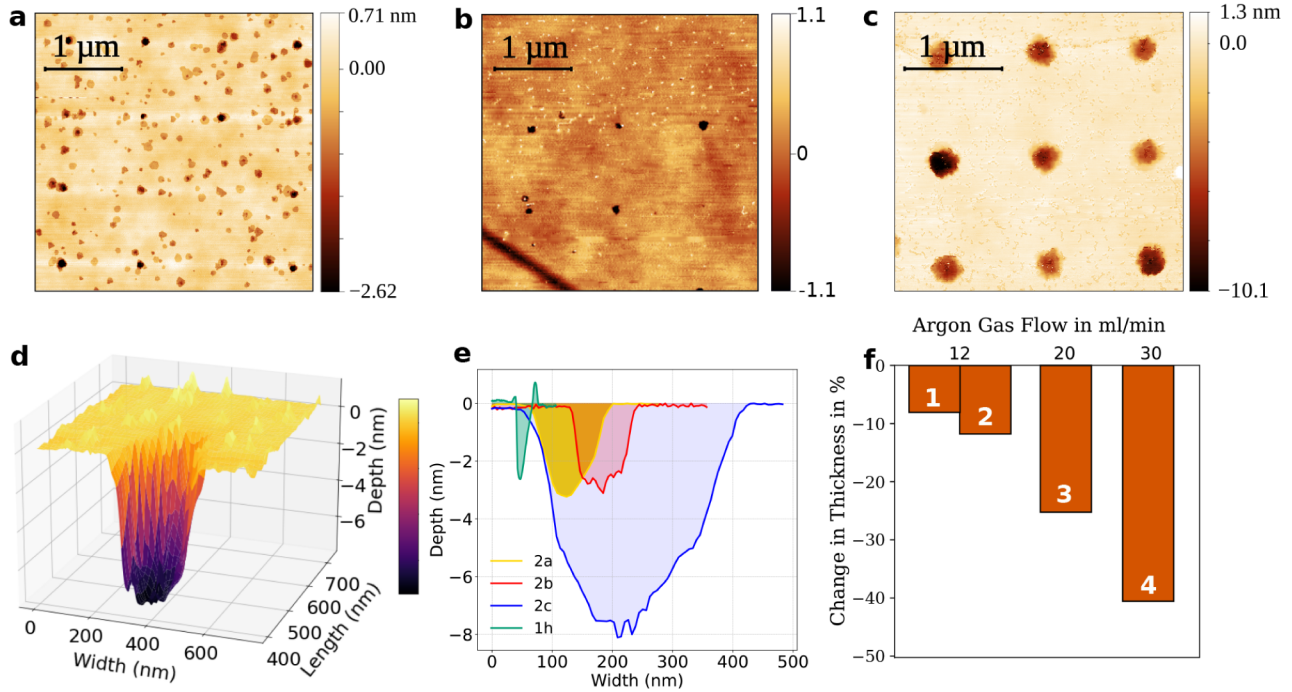


Figure 2. (a,b) AFM image (tapping mode) of indentations in an hBN flake after annealing in an Ar atmosphere. In (b), the area was cleaned by AFM contact scans prior to the fabrication of the indentations. (c) Indents annealed in air. (d) Three-dimensional representations of AFM scans of an indent annealed in air. (e) Cross-sectional profiles of sample indentations prepared with different annealing recipes, cf. Figure 2a–c, and an unannealed indentation X from Figure 1h. (f) Average thickness change of multiple hBN flakes after annealing at different Ar flows. Numbers indicate the parameter set of annealing; see Table 1.

possible across flakes of varied thickness, as seen in Figure 1a. Figure 1b–e represents variations of the debris protruding around each indentation. In Figure 1b,c, the debris accumulates at the upper and lower sides of the indentation, attributed to the back-and-forth motion of the tip. In contrast, the insets in Figure 1d,e reveal different debris patterns, highlighting variations in the response of the material to the indenting tip despite identical parameters and indentation angles. Although the AFM tip is extremely hard, it is subject to wear during the indentation process. This erosion is evident when comparing the tip before and after use for indentation (Figure 1f,g). The degradation of the tip’s carbon coating likely contributes to the debris around the indentations. This suggests that AFM nanoindentation transfers carbon into hBN, thereby enabling the formation of carbon-containing defects at the indented sites. By performing an AFM contact-mode cleaning,^{22–25} the indentations appeared cleaner, i.e., without surrounding debris, as shown in Figure 1h. If the debris would exclusively consist of hBN, the morphology of the indentation would remain unchanged or show only torn edges after contact cleaning (Figure S1). Instead, the debris is largely removed by contact-mode cleaning, and the indentation becomes clearly visible, indicating that the debris was originally loosely bound material. We conclude that the debris around the indentations is a mixture of nanoscale hBN fragments and carbon residues from the AFM tip.

Effect of Annealing on the Topography. The optical properties of emitters in hBN can be improved by thermal annealing.^{23,26} This step is essential not only for activating emitters but also for modulating the surface topography. In order to gain insight into the detailed effects that thermal treatment has on the surface topography of the indented hBN flakes, we analyzed the influence of AFM contact-mode

cleaning, oxidation conditions, and the flow of argon (Ar) gas into the furnace during annealing.

Figure 2 illustrates a comparison of AFM scans obtained in the tapping mode after annealing under various conditions. The hBN flake shown in Figure 2a was indented without subsequent contact-mode cleaning and annealed under an Ar atmosphere at 850 °C (Table 1). This process results in the

Table 1. Parameters for the Thermal Annealing of hBN in Ar or Air

Set	T_A (°C)	t_A (min)	P_A (mbar)	Gas flow (sccm)	Exfoliated from	Thickness reduction (%)
Figure 2a	850	30	6	15	single crystal	—
Figure 2b	850	30	6	15	powder	—
Figure 2c	850	30	1000	in air	single crystal	—
1 ^a	1000	30	20	12	single crystal	8.1
2 ^a	1000	15	16	12	powder	11.5
3	1000	30	6	20	powder	25
4	1000	30	14	30	powder	40.5

^aDegassed at 400 °C for 15 min before raising to the activation temperature; the oven was purged before these annealing sequences.

formation of widespread and randomly distributed pits, in addition to the intentional indentations produced in a square-like pattern, which appear as wider and deeper features. These additional and randomly arranged pits appear distinct, without any surrounding coagulation of hBN as seen from the AFM scans. A sample that was first cleaned with an AFM contact-mode scan before producing indentations (Figure 2b) followed

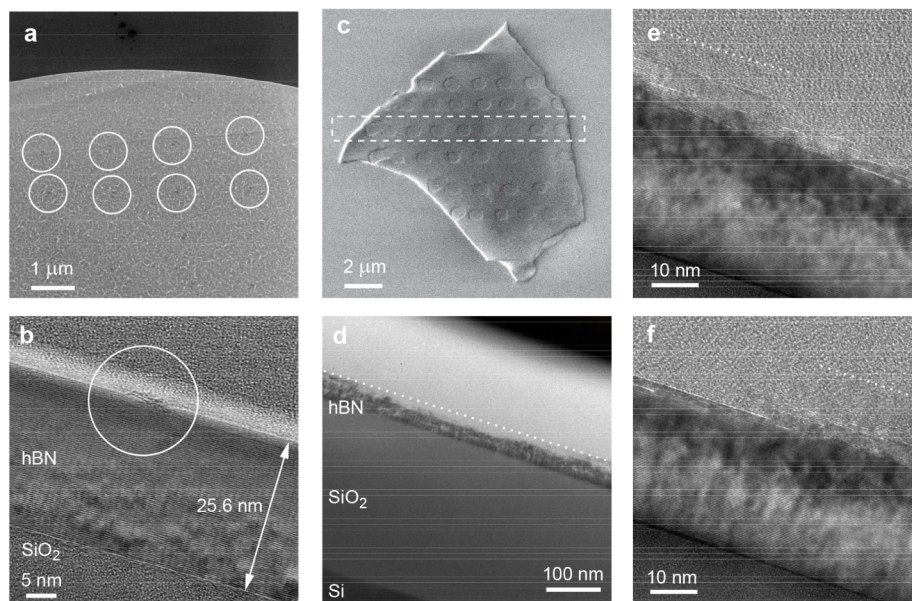


Figure 3. Electron micrographs of AFM-induced nanoindentations in hBN. (a) Scanning electron microscope (SEM) top view of an as-prepared sample before annealing with some nanoindentations indicated by circles. (b) TEM cross-sectional view in high resolution of a potential indentation (circle) in the near-surface region of the hBN flake shown in (a). (c) SEM top view of an hBN flake with clearly widened indentations as a result of annealing the sample at 1000 °C in an Ar atmosphere. The dashed rectangle indicates the area from which the FIB lamella was extracted. (d) TEM cross-sectional view of an individual indentation in the hBN flake shown in (c). The dotted line indicates the uppermost surface of the flake. (e,f) TEM cross-sectional view in high resolution of the left and right edge of the indentation, respectively. Dotted lines indicate the topmost layer up to which lattice planes are resolved.

by the same Ar annealing process demonstrates a significant reduction in the number of random etching pits. This suggests that atomic clusters, hBN fragments, or other debris on the surface of a noncleaned but indented hBN flake act as nucleation centers for the formation of additional pits by high-temperature annealing. In the upper region of Figure 2b, the small protrusions (white color) on the surface are indicative of upturned BN flakes, assumed to be caused by some etching but much less compared to Figure 2a. A sample which was not contact-cleaned and was annealed in air (Figure 2c) exhibits substantially deeper, wider, and more isotropic etching,²⁷ which is more clearly visible in the 2D cross-sectional profile, Figure 2d. It shows several atomic layers of hBN being thoroughly etched and that the bottom of the pit has a rough surface. To summarize the effect of annealing on the indentations in hBN, Figure 2e shows cross sections of an indentation obtained from AFM scans. While annealing in Ar has more effect on the diameter of the indentations than on their depths, annealing in air strongly increases their lateral size as well as their depths. In the latter case, the air constituents (N_2 and O_2) seem to have a stronger detrimental effect on the chemical stability of hBN. Furthermore, the area surrounding the indented hole is uniform, unlike the protrusion observed prior to annealing, Figure 1.

In addition to the gas species, the effects of gas flow, pressure, and annealing time on the morphology of the hBN flakes were also investigated. Measurements of thickness variations before and after annealing were conducted on three flakes per set for different parameter sets of annealing (Table 1), and their average thickness changes are depicted in Figure 2f. The results indicate that in the pressure range of 6–20 mbar Ar, pressure fluctuations had a minimal impact, while the Ar flow rate significantly affected the thickness reduction, that is, etching. They further suggest that the flow of Ar has a

dominant effect on the process of physical etching possibly by a combination of enhanced hBN sublimation and the physical impact of Ar molecules. This is best seen by comparing sets 1 and 3 (Table 1), where the latter was performed at a much higher flow but at a lower Ar gas pressure.

Despite inert gas conditions, hBN starts to decompose at around 850 °C. An increased Ar flow accelerates sublimation by promoting the ablation of disintegrated surface molecules at a higher rate. Additionally, collisions with Ar atoms contribute to the enlarged indentation features observed after annealing. This is consistent with the formation of pillar-like roughness following substantial etching, which removes multiple hBN layers. Such structures can be eliminated by AFM contact-mode cleaning (Figures S2 and S3).

Preannealing surface treatment, such as AFM contact-mode cleaning (Figure 2b), effectively removes contaminants and intrinsic defects, thereby mitigating etching. Although moderate etching can enhance the emitter yield, excessive etching, especially under high Ar flow, introduces surface roughness and promotes structural irregularities as well as various energy landscapes. We observed that while etching does not reduce SPE yield, overetching leads to dim SPEs and emitter ensembles, obscuring deterministic patterns.

Therefore, ensuring surface cleanliness and precise annealing conditions is essential for consistent SPE formation in hBN. Our final protocol involves exfoliation of hBN, followed by cleaning in AFM contact mode and subsequent annealing in low Ar flow (≈ 10 sccm) at 13 mbar. Experimental details are provided in the section Experimental Methods.

Imaging the Cross Section of an Indentation. The cross section of individual indentations was investigated by TEM on thin lamellae prepared by focused-ion beam (FIB) milling. Figure 3a shows a top view of a flake with tiny AFM-induced indentations before annealing. Although it is difficult

to hit these indentations in the lamella prepared by FIB, an extended defect at the surface of the flake is resolved in the cross section in Figure 3b. We attribute this region of appropriate size to a potential individual AFM-induced nanoindentation, where some material is pulled out of the hBN flake due to the back-and-forth motion of the tip, as mentioned above; cf. Figure 1. In contrast to the well-ordered hBN lattice planes resolved underneath the defect region, the latter seems to be strongly disordered. From the number of lattice planes and the measured thickness of this and other flakes, an interlayer spacing of 0.329 ± 0.004 nm along the hBN c axis is determined.

After annealing at 1000 °C in an Ar atmosphere, the indentations in Figure 3c appear much wider and deeper compared to the indentations in the as-prepared flake, in agreement with the AFM images (Figure 2c). The increase in width and depth after annealing in Ar environment seems to also depend on the size of the indentation produced prior to annealing. The cross-sectional view in Figure 3d shows an individual indentation of ≈ 300 nm lateral size and ≈ 10 – 20 nm depth in the hBN flake on the SiO_2/Si substrate. The left and right edges of the indentation were resolved with high resolution, again clearly showing hBN lattice planes stacked along the c axis; see Figure 3e,f. In contrast to the dark-appearing lower part of the flake where the lattice planes extend through the whole lamella thickness, the faint lines in the upper 10–20 nm represent the decreased hBN-to-carbon ratio within the lamella, leading to a lower contrast due to cutting through the circular crater. The most important result is that the lattice planes of the upper part of the hBN flake where the indentation occurs appear to be continuous up to the edge of the indent without major interruptions or larger defects. We stress that the maintenance of continuous layers in the upper regions up to the edge of the crater was observed for a number of different indentations on a flake.

Comparison with the highly disordered surface region shown in Figure 3b suggests that the indentation created before annealing acts as a nucleus for the breaking of atomic bonds in a limited region, which then grows during annealing, as the disordered material is removed. As a result, the atomic order in the near-surface region of the flake appears to remain intact up to the edge of the crater, where the thickness increases. The fact that indentation preferentially grows in the lateral dimension parallel to the hBN lattice planes than in the perpendicular direction indicates that a well-ordered hBN plane is more resilient to damage than broken bonds at the side of lattice planes. This is supported by our finding that the bottom of the final crater seems to be flat.

Activation of Quantum Emitters. In the following, we demonstrate the importance of annealing for the activation of quantum emitters in nanoindented hBN flakes. Figure 4a shows an AFM image of an hBN flake with a regular array of intentionally created indentations before annealing. However, fluorescence is not observed at or near the indented sites (Figure 4b). After the sample is annealed at 850 °C in Ar, several quantum emitters appear (Figure 4c), which are not stable over time and tend to bleach or blink. In contrast, annealing at 1000 °C yields a high concentration of activated stable SPEs near indented locations and also some distance away from any indentation, as shown in Figure 4d.

The confocal excitation volume in our measurements (approximately 300 nm lateral diameter and 900 nm depth) is much larger than the size of an individual indentation.

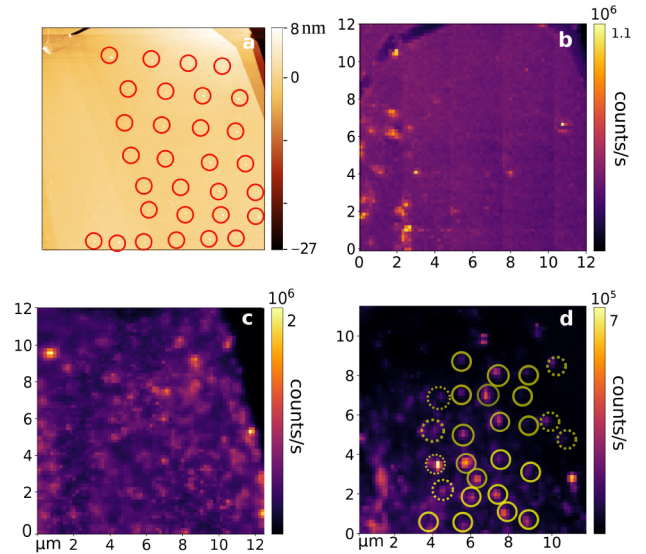


Figure 4. Comparing topography and fluorescence of nano-indented hBN in the same region. (a) AFM scan after indentation before annealing. Each indentation has been circled as a guide to the eye. (b) Fluorescence intensity map before annealing. (c) Fluorescence intensity map after annealing at 850 °C. (d) Fluorescence intensity map after annealing at 1000 °C. Activated SPEs near indented locations are marked by solid circles, while emitters that appear at some distance away from any indentation are marked by dashed circles.

Therefore, we cannot pinpoint the exact subdiffraction location of an emitter within an indentation from the far-field image alone. Given that a nanoindentation produces a crater on the order of tens of nanometers, it is unlikely that a point defect is created exactly at the center of the indentation. Instead, we observe that emitters tend to form around the periphery of the indented sites, predominantly near the edges of the indentations observed in TEM, Figure 3e,f. It is possible that defects initially created at the indentation bottom migrate to the flake surface or to nearby regions during high-temperature annealing and eventually settle in energetically favorable locations.^{28–30} Importantly, annealing the indented regions at 1000 °C in Ar activates a dense accumulation of emitters within an area of roughly $11 \times 11 \mu\text{m}^2$, underscoring the effectiveness of this fabrication technique in producing SPEs. The fact that these emitters are more or less deterministically fabricated and observed in close vicinity to the AFM-produced indentations rules out that they arise from organic molecules or organic residues from cleaning solvents, which could appear at the hBN/substrate interface.³¹

Optical Properties of SPEs in Nanoindented hBN.

Figure 5a shows the distribution of emitters recorded from 12 different flakes that were nanoindented and annealed. With 41% probability, we observe emitters with a ZPL within the 565–590 nm wavelength range, which are referred to as class A emitters. This suggests that our nanoindentation and annealing approach reproducibly forms a specific type of defect. Other emitters that also exhibit exceptionally sharp features and high brightness are detected within the wavelength range of 540–560 nm and are classified as class B emitters. They have been linked to carbon-related defects with electron-spin characteristics.¹⁴ Additional emitter classes are found in the 620–640 nm range (class C) and around the 700 nm wavelength (class D). The latter appear less frequently and tend to appear more

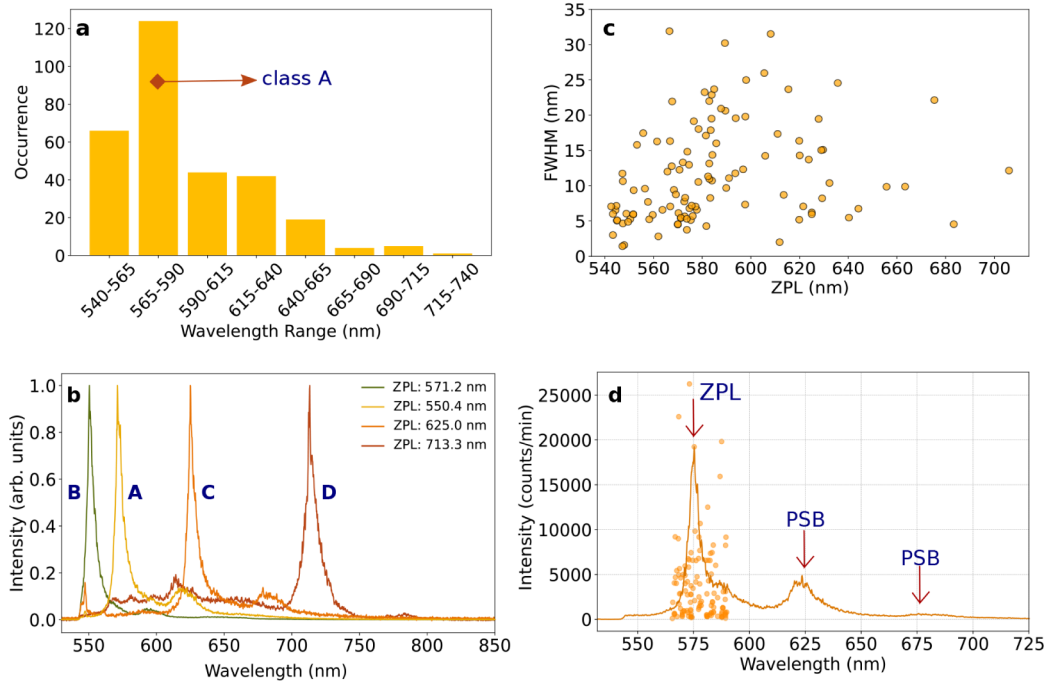


Figure 5. (a) Distribution of occurrences of a total of 305 SPEs from 12 different flakes with different emission wavelengths. The most reproducible SPEs are in the 565–590 nm wavelength range, denoted as emitter class A. (b) Photoluminescence spectra (maximum intensity normalized) of representative emitter classes. (c) Line width of isolated SPEs extracted from their experimental spectrum vs their ZPL wavelength. (d) A representative photoluminescence (PL) spectrum of type A, showing a sharp ZPL at 575 nm and phonon sidebands at 625 and 680 nm, respectively. The dots represent ZPLs of other class A emitters.

in samples subjected to extensive etching. Figure 5b provides representative photoluminescence spectra for each of these emitter classes with a distinct ZPL, each accompanied by its PSB.

The emitters can also be categorized by the number of distinct SPE lines observed within a single confocal volume, as shown in Figure S5. An isolated SPE corresponds to a single sharp emission line within this volume. Our fabrication process yields emitters of which 70% can be individually resolved and about 47% are isolated SPEs rather than emitter ensembles. This distinction is important because isolated SPEs exhibit well-defined coherent optical transitions that can be probed at room temperature, allowing one to observe spectral shifts and other properties without the interaction effects from a nearby emitter. Furthermore, the isolation of individual emitters improves the signal-to-noise ratio by minimizing background fluorescence, an advantage for techniques such as ODMR and optical and magnetic manipulation of defect states.

The line widths of isolated SPEs vs their ZPL wavelength are plotted in Figure 5c. Most isolated emitters belong to class A and exhibit line widths between 10 and 20 nm. Consequently, we focus on this predominant class in the remainder of this section. Figure 5d shows a representative PL spectrum with a dominant peak near 575 nm (2.16 eV), together with ZPL positions and their corresponding spectral intensities of isolated class-A emitters (dots). Here, the intensity is the photon count detected by the spectrometer over 1 min integration time. Figure 5d also portrays that several emitters display ZPL spectral intensities well above the typical intensity of ≈ 3000 counts/min recorded on our emitters, with some exceeding it up to six times. While small spectral shifts can arise from strain and electron–phonon interactions, such intensity variations might be tunable after fabrication by external

strain.^{32,33} At room temperature, the narrowest reported inhomogeneous line width for hBN is ~ 9 nm^{13,26} supporting the idea that our class A emitters likely originate from a single defect species, as their line widths are comparable or broader.

Previous studies have reported SPEs around 575 nm (2.16 eV),^{16,34} which have been attributed to carbon-related defects in hBN.^{12,35} Theoretical calculations indicate that multiple carbon-based defect configurations in hBN are energetically favorable and emit across a broad range of wavelengths (≈ 540 – 650 nm, or 2.30–1.90 eV).^{36–39} This wide range of possible emission energies makes the precise identification of the defect challenging. Moreover, local effects such as strain and charge states can shift the emission of a given defect, meaning that even a single defect type may produce a range of ZPL positions under different conditions. To further probe the nature of the dominant emitters, we examined their spectral line shape, phonon sideband energy (PSE), and excited-state lifetime. The PSE is the energy difference between the ZPL and the primary PSB.⁴⁰ A characteristic time τ_0 for the excited state is derived from a fit $g^{(2)}(\tau) = 1 - a \times \exp(-|\tau|/\tau_0)$ of the second-order correlation measurement $g^{(2)}(\tau)$, where τ is the measured delay time between detection of two consecutive photons. Here, τ_0 is an estimate of the excited-state lifetime. A more accurate determination of the latter would require an analysis of its dependence on the laser intensity⁴¹ and time-correlated single-photon counting (TCSPC) technique, which were not done in the present work.^{42–44}

From the individual PL spectrum of 11 emitters in one flake and their second-order autocorrelation data $g^{(2)}(\tau)$ (Figure S6), we determined $\tau_0 \approx 2 \pm 1$ ns; see Figure 6a. The $g^{(2)}(\tau)$ data were acquired over ≈ 15 s with the same laser power that was used for the fluorescence and spectral data (approximately 80 μ W). Due to the brightness of the emitters, antibunching is

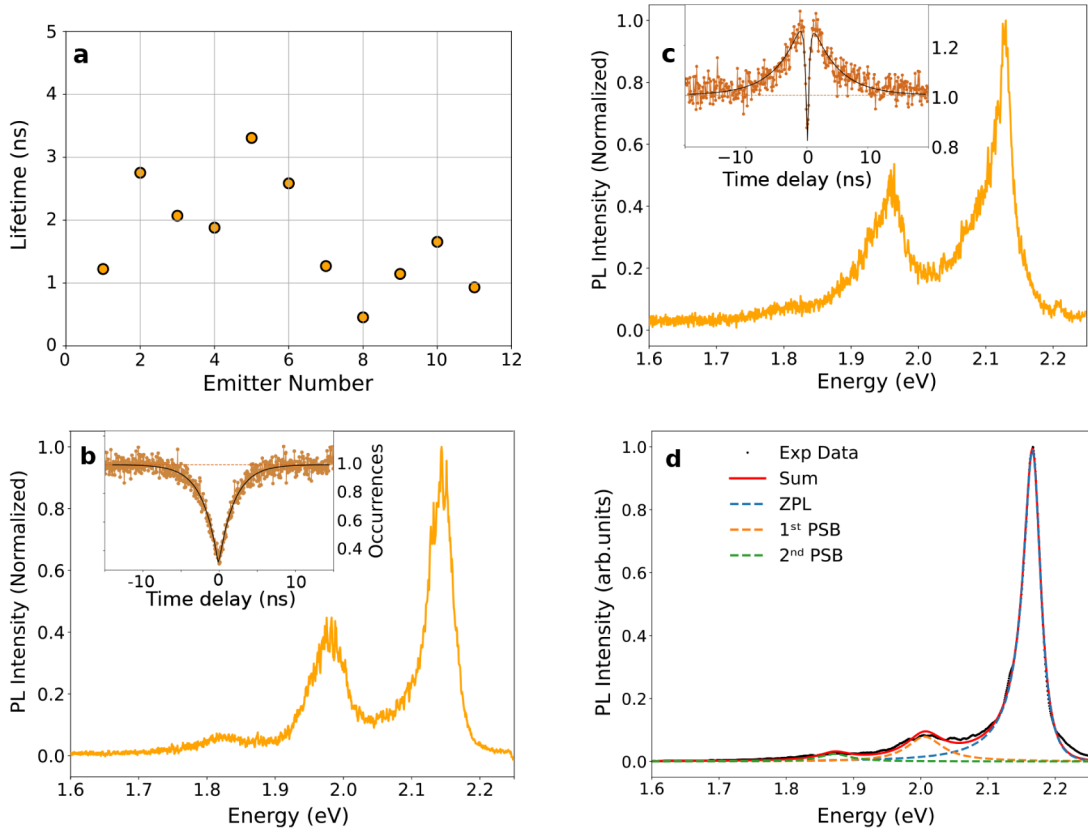


Figure 6. (a) Characteristic time of class A emitters from the same flake. (b) PL intensity spectrum in the energy domain. The inset shows the second-order autocorrelation function $g^{(2)}(\tau)$ of this emitter, characteristic of a two-level system, confirming the single-photon nature of the emission. (c) PL spectra of another class A emitter. The inset shows $g^{(2)}(\tau)$, characteristic of a three-level system. (d) Spectral fit to obtain the Debye–Waller factor $W = 0.80$, phonon sideband energy PSE = 162 meV, and Huang–Rhys factor $S = 0.22$ for an isolated emitter. Average values for class A emitters are given in Table 2.

Table 2. Parameters of Class A Isolated Single Emitters Compared with Theoretical Results⁴⁰

	ZPL (eV)	ZPL (nm)	PSE (meV)	S	W	Time τ_0 (ns)
C_2C_N (calc.) ⁴⁰	2.13	582	180	1.35	0.26	2.19
Class A (this work)	2.15 ± 0.03	577 ± 7	179 ± 2	0.475 ± 0.030	0.631 ± 0.018	2 ± 1

clearly visible within a few seconds. Figures 6b and 6c show PL spectra of two representative emitters along with their $g^{(2)}(\tau)$, see insets, with ZPLs at 2.14 and 2.13 eV, respectively. In the first case, we obtain a characteristic time $\tau_0 \approx 2.07$ ns and a $g^{(2)}(0) \approx 0.31$, indicating a single-photon emitter with $g^{(2)}(0) < 0.5$. In contrast, the second emitter shows an asymmetric line shape, a narrower line width, and bunching behavior. A three-level fit $g^{(2)}(\tau) = 1 - (a + b) \times \exp(-|\tau|/\tau_1) + b \times \exp(-|\tau|/\tau_2)$ reveals fast and slow components with two characteristic times $\tau_1 \approx 0.34$ ns and $\tau_2 \approx 4.26$ ns, respectively, indicating that the system sometimes remains in an excited shelving state. However, the observation of a bunching behavior is rare.

For a more quantitative analysis, we fitted the spectra of class A emitters to obtain the Debye–Waller factor, $W = I_{\text{ZPL}}/I_{\text{total}}$, i.e., the ratio of the integrated emission intensity of the ZPL to the total integrated emission intensity, and the Huang–Rhys factor, $S = \ln -W$.⁴⁵ A representative spectrum of an isolated SPE is shown in Figure 6d, where the ZPL accounts for $W = 0.80$ (80% of the total emitted photons are in the ZPL), and the primary PSB appears at an energy of 162 meV, yielding a Huang–Rhys factor of $S = 0.22$. The best fit was obtained with a skewed Voigt function for the asymmetric ZPL line shape

and with Lorentzian and Gaussian functions for the first and second PSBs, respectively.

Table 2 summarizes the optical parameters obtained for isolated class A emitters and compares them with the theoretical values predicted for the carbon trimer defect (C_2C_N) in hBN.⁴⁰ We find excellent agreement between our experimental values obtained for the ZPL energy (≈ 2.16 eV), PSE (≈ 179 meV), and spectral line shape and those calculated for the C_2C_N defect. One notable difference is that our experimental Debye–Waller factor W is significantly higher than the theoretical value, as also reported in other experimental works.^{10,45,46} Consequently, the extracted Huang–Rhys factors in the experiment are smaller than those predicted by the theory. Minor discrepancies between the experimental and theoretical values are expected, as the calculations do not fully account for interlayer defects or strain effects that can vary with flake thickness and the local environment. Furthermore, mixing different charge states of the defect can affect the ZPL energy. While the ZPL position, PSE, and the lifetime provide substantial information, they may not alone conclusively characterize the exact configuration of the defect. However, the strong correspondence between our

results and the carbon trimer model (C_2C_N) strongly suggests that this defect is responsible for the SPEs we observe. Narrowing down the defect to the carbon trimer is an important step toward delving into its energy-level scheme and spin properties.

Emission polarization measurements were taken on twenty-two different emitters from one of the fabricated samples. Photon counts from a single APD were recorded by rotating a polarizer in the emission line. Results of four emitters are shown in a polar plot in Figure 7, with more information on

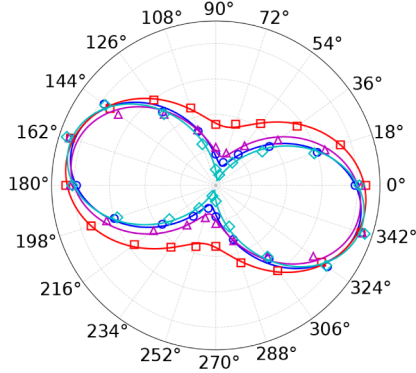


Figure 7. Polar plot of normalized intensity vs polarizer angle θ for four different emitters. Solid lines indicate $\cos^2(\theta)$ behavior fitted to the data.

the fitting parameters and data of the remaining 18 emitters presented in Figure S7. Remarkably, almost all emitters show similar emission of highly linearly polarized light^{2,47} along a common direction; see Figures 7 and S7. From the $\cos^2(\theta)$ fit shown in Figure 7, the common orientation of the four dipoles is found to be pointing along $167^\circ \pm 3^\circ$. Almost all the other emitters (Figure S7) had a similar dipole orientation. A rare case of an emitter with a different polarization orientation along the 90° and 270° axes was found, which was located close to another emitter.

While many of the emitters exhibit a highly in-plane polarization, some emitters have shown out-of-plane polarization features, as can be seen for the emitter represented by red data points, where the intensity does not completely vanish at $\theta = 77^\circ$ and $\theta = 257^\circ$, as one would expect from the $\cos^2(\theta)$ behavior, because of a nonzero out-of-plane component.⁴⁸

The inclination toward a certain polarization axis indicates that the defects are likely part of the crystal structure and chemically bonded within the hBN lattice. This polarized emission likely originates from the particular anisotropic structure of the defect center in the lattice. It also proves that after annealing, the defects are not formed on deformed structures of the flake, as could be expected from the nanoindentation. This consistent polarization pattern among most of its emitters provided an added advantage of this method for the integration of quantum emitters onto waveguides and photonic circuits.

CONCLUSIONS

AFM nanoindentation followed by thermal annealing provides a controlled route to generate stable high-quality single-photon emitters in hBN. The method yields a high density of isolated carbon-related defects, mainly attributed to the C_2C_N carbon trimer^{40,49} with narrow line widths, dominant emission in ZPL,

and excellent spectral stability. The defects exhibit a common dipole orientation, emitting linearly polarized light, suggesting that they all are part of the lattice structure, with similar chemical interactions in the defect environment consistent with the crystallographic symmetry of the lattice. Further investigation of their electron-spin properties (e.g., via ODMR) and atomic-scale characterization of the indented regions^{50,51} will deepen our understanding of these color centers.

The properties of the emitters are strongly influenced by the annealing conditions. Excessive etching due to elevated Ar flow or air exposure^{50,51} increases the clustering of defects and surface roughness. Optimizing Ar flow and surface cleanliness are crucial for precise emitter formation in a structurally well-ordered atomic environment and removes surface adsorbates and trapped bubbles.⁵² Because quantum emitters in hBN are sensitive to their local atomic environment, even slight modifications in fabrication can affect their deterministic formation. However, once formed, the emitters fabricated by nanoindentation are robust and are often observed to be stable for more than a year under ambient conditions. For example, the polarization analysis of the emitters was carried out more than 1.5 years after their production and activation. Hence, our results and process insights contribute to a scalable, charge-neutral pathway for SPE engineering, advancing the integration of hBN emitters into quantum photonic and sensing technologies.

EXPERIMENTAL METHODS

Before exfoliation, diced 5×5 mm SiO_2/Si chips were sequentially cleaned using hot acetone, acetone ultrasonication, ethanol, IPA, and weak O_2 plasma and then baked at $200^\circ C$. Twelve flakes from which the analysis has been presented were prepared by exfoliating hBN powdered crystals, which were purchased from the Graphene Supermarket. The crystals were first placed on a crylic adhesive tape (Nitto SPV 224PR-MJ) and then cleaved six times using a fresh tape each time to obtain thin flakes, which were then finally exfoliated onto SiO_2/Si chips. hBN was exfoliated onto the heated chips following a postplasma treatment baking process while they were still warm. After preselecting flakes with thicknesses between 40 and 70 nm, they were scanned in the tapping mode with Bruker's Dimension Icon Atomic Force Microscope system with a scan range of $90 \mu m$ to confirm thickness and surface cleanliness. For flakes that exhibit surface contaminants, contact cleaning was performed using Multi75DLC AFM tips from Budget Sensors. This was followed by AFM nanoindentation using a force curve technique.

Indentations were created using Tap300DLC tips (Budget Sensors). The tip was replaced after approximately 200 indentations were made. Topography scans before and after indentation were conducted using HQ:NSC15/Al BS tips from MikroMasch. High-resolution scans of the indentations were performed using HiRes-C15-Cr-Au-5 tips, also from MikroMasch. The use of a sharp tip was essential to obtain a good profile of the depth of the indentations because the indentation and scanning tip radius were too large to obtain enough resolution for the detection of surface vacancies at room temperature. For each indentation, a trigger voltage of 1.6 V was applied for 2 s each for approach and dwell time, using a relative displacement setting. Before automated force curves were initiated for indentation, the tip was brought into contact with the surface. When scanning in the contact mode, a feedback set point voltage of 1 V was used. If the set point voltage was too low, surface contaminants could remain, while excessive voltage could cause strain or tears.

For annealing, the chips were placed in a glass tube inside a ceramic furnace, which was connected to the mass flow controller (MFC) on one side and to the vacuum pumps (Scroll and Turbo) on the other. A high vacuum of 2×10^{-5} mbar was achieved before annealing

commenced. The sample was allowed to degas at 400 °C for 15 to 30 min until the pressure stabilized. After this, the temperature was set to 1000 °C, the Ar flow rate was adjusted to 10 sccm, and the turbo pump was turned off while keeping the rough pump running. It took approximately 45 min to reach 1000 °C. A pressure valve was used to reach and maintain a pressure of 13 mbar or higher. The samples were then annealed for 30 min at 1000 °C. This annealing method was used for the 12 flakes, some of which were double-annealed by first being heated to 850 °C.

Cross-sectional TEM lamellae were prepared by using a Helios 5 UX FIB system operated with Ga ions. To protect the hBN surface, a two-step electron-beam-induced carbon deposition was carried out, first with 2 kV and 0.40 nA to obtain an ≈ 100 nm layer, followed by 0.80 nA to increase the thickness by an additional layer of ≈ 200 nm. Subsequently, an ≈ 3 μ m ion-beam-induced tungsten capping layer was deposited. Final thinning of the lamellae on the TEM grid was performed stepwise by reducing the accelerating voltage from 30 to 2 kV, lowering the beam current from 0.44 nA to 17 pA, and increasing the stage tilt from 1.5° to 4.0°.

Due to the electron beam sensitivity of the hBN layers, the TEM investigations were performed at an acceleration voltage of 80 kV using a Cs-corrected FEI Titan 80–300 electron microscope at magnifications between 245,000 and 320,000. Images were recorded with a Gatan US1000 CCD camera (2048 $\times$ 2048 pixels) at exposure times of a few seconds.

Fluorescence measurements were conducted at ambient temperature by using a confocal setup with an excitation laser at 532 nm. The power of the excitation laser for all measurements shown in this work was set to around 80 μ W on the sample. Utilizing the Hanbury–Brown–Twiss (HBT) experiment, we verified that all of the emitters documented in this study are single-photon emitters (SPEs). The piezoelectric system was calibrated, facilitating the location of flakes from the markers. The atomic force microscopy (AFM) scans and corresponding fluorescence images matched in size. The shape and edges of the flake allowed to identify the indented regions, as the SiO₂ substrate exhibits fluorescent contrast. In the confocal setup, the fluorescence signal from the sample was filtered through a 532 nm notch and edge filters and directed through the pinhole to an automated flip mirror. This setup controls the light pathway to either the spectrometer or avalanche photodiodes (APDs). Before reaching the APDs, a nonpolarizing 50/50 beam splitter was used to divide the emission beam for correlation statistics. The optical components mentioned were obtained from Thorlabs. The photon counts presented in this paper represent the total photon counts from both APDs. A PI Acton SP2 500 spectrometer and a Pixis/Pylon 2K instrument were used for spectral acquisition.

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Notes

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