Controlled generation of luminescent centers in hexagonal boron nitride by irradiation engineering

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Luminescent centers in the two-dimensional material hexagonal boron nitride have the potential to enable quantum applications at room temperature. To be used for applications, it is crucial to generate these centers in a controlled manner and to identify their microscopic nature. Here, we present a method inspired by irradiation engineering with oxygen atoms. We systematically explore the influence of the kinetic energy and the irradiation fluence on the generation of luminescent centers. We find modifications of their density for both parameters, while a fivefold enhancement is observed with increasing fluence. Molecular dynamics simulations clarify the generation mechanism of these centers and their microscopic nature. We infer that \( V_0 C_6 \) and \( V_6 \) are the most likely centers formed. Ab initio calculations of their optical properties show excellent agreement with our experiments. Our methodology generates quantum emitters in a controlled manner and provides insights into their microscopic nature.

INTRODUCTION
Quantum emitters are the cornerstones of many applications such as quantum telecommunication (1), quantum sensing (2), and quantum metrology (3). Therefore, quantum emitters in solid-state systems such as semiconductor quantum dots (4), nitrogen-vacancy (5), and silicon-vacancy (6) centers in diamond have become rapidly growing research fields. Recent experiments at cryogenic temperatures have demonstrated that two-dimensional (2D) materials can host quantum emitters (7–9) even with site selectivity on the submicrometer scale (10). Achieving site-selective and on-demand quantum emitters (11) at room temperature is an experimental challenge. Achieving this would be useful to mature emerging technologies such as quantum computing and communications (12) without cryogenic cooling systems.

The 2D material hexagonal boron nitride (hBN) can host luminescent centers deep within the large, indirect bandgap of \( 6 \text{ eV} \) (13). These centers showed room temperature quantum emission (14) making hBN a promising platform to achieve site-selective quantum emitters at room temperature. The 2D nature of hBN enables placing quantum emitters in close proximity to optical cavities (15) and coupling of quantum emitters to plasmonic structures (16) for optimized light-matter interactions (11, 17). Recent studies show complex photophysics of quantum emitters (18) as well as multiple-emitter contributions (19). The origin of these luminescent centers is ascribed to several defects in the hBN lattice (20–22), but their microscopic nature is still under debate because the generation mechanism remains poorly understood.

Except for bottom-up techniques such as chemical vapor deposition, at least one further method is required to generate quantum emitters in hBN. The most commonly used method is to dropcast a solution of low-quality hBN flakes on a substrate followed by thermal annealing in argon at 850 °C (23). Hereby, usually low-quality hBN flakes are used, which are known to host many intrinsic defects. This was manifested by the fact that standard furnace annealing generated a large number of luminescent centers in this low-quality hBN, while it was less efficient for high-quality hBN (24). Starting with fewer defects enables a highly controlled generation of quantum emitters required for applications in quantum photonics (12).

Besides thermal annealing of hBN of various qualities, oxygen plasma (24, 25) and high-energy oxygen irradiation (26, 27) have been used to generate quantum emitters in hBN. However, applying irradiation engineering, i.e., tuning both irradiation energy and irradiation fluence (defined as the number of atoms per area), remains unexplored on hBN, while this technique can create defects controllably in other 2D materials (28).

Here, we present a novel method to enhance the generation of luminescent centers in hBN via irradiation engineering with oxygen atoms and subsequent annealing. We tune the irradiation energy from 120 to 300 eV as well as the irradiation fluence by a factor of 10 to controllably generate luminescent centers in high-quality hBN with few intrinsic defects. We find a maximum density of luminescent centers at 240 eV and a remarkable, fivefold enhancement when increasing the irradiation fluence by 10. Furthermore, several of these luminescent centers are confirmed to be quantum emitters.

The results of our irradiation engineering in combination with molecular dynamics (MD) simulations strongly suggest that irradiation-induced amorphization followed by recrystallization creates two groups of luminescent centers in the topmost layers. Furthermore, we demonstrate that irradiation with oxygen atoms controls the density of generated luminescent centers in hBN. The presented method is wafer-scalable and could be extended to other gapped 2D materials as well as other irradiating atoms or ions. Our experimental and theoretical findings indicate that the two groups of luminescent centers are related to \( V_6 C_6 \) and \( V_6 \) defects, as evident in particular from an excellent agreement of the experimental photoluminescence (PL) line shapes with the results of ab initio calculations.
RESULTS AND DISCUSSION

Generation of luminescent centers in hBN

Our irradiation-based generation process is illustrated in Fig. 1A. We mechanically exfoliate high-quality hBN flakes onto SiO$_2$/Si substrates. The samples are subsequently irradiated with oxygen atoms at controlled kinetic energies between 120 and 300 eV in a reactive ion etch (RIE) reactor where the irradiation fluence is selected by the irradiation time. Here, the oxygen atoms are mostly neutral with a small fraction of positively charged oxygen (see Materials and Methods). This irradiation is carried out at low pressure providing a narrow energy distribution as well as a small angular dispersion (29). After irradiation, the samples are annealed at 850 °C in nitrogen (details in Materials and Methods). We monitor the evolution of the optical properties of our samples during the generation process by a customized confocal microscope with a lateral resolution of 1 μm (see Materials and Methods and section SI). All spectra shown in this work are not background-corrected. We take PL counts normalized to each map. (Fig. 1). Unnormalized PL maps are shown in section SII.

By taking PL maps after each step, the evolution of individual luminescent centers is monitored. A typical evolution of one luminescent center is shown in Fig. 1D. After exfoliation, a flat PL spectrum is observed (blue curve), indicating no luminescent center. The sharp peak at 2.235 eV is the Raman-active $E_{2g}$ phonon in hBN (30) for a 2.37-eV excitation laser (see Materials and Methods). The PL spectrum remains unchanged after irradiation, but a clear PL peak around 2.17 eV appears after subsequent annealing. This luminescent center appeared at the edge of the flake, although other centers appeared away from the edge (see section SIII). Both irradiation and annealing are crucial steps to achieve many luminescent centers per area, as discussed below.

Luminescent centers generated by our process can be classified into two main groups depending on the shape and intensity of their zero-phonon line (ZPL) and phonon side bands (PSBs). Representative spectra of these groups of luminescent centers are shown in Fig. 1C, while more spectra are shown in section SIV. The first group (group I) is characterized by a narrow ZPL followed by two marked PSBs red-shifted by 160 to 200 meV from the ZPL, corresponding to phonon-assisted PL involving bulk optical phonons (31, 32). We find a second group (group II) that displays a broader and less pronounced ZPL associated with a series of red-shifted, overlapping PSBs of acoustic and optical nature. These PSBs are less marked than in group I. We note that this classification of luminescent centers is specific to this work and cannot be directly compared to the nomenclature presented in previous studies (23, 33).

Studying different irradiation energies and irradiation fluences

In our studies, we use three different bulk crystals for exfoliation of multiple hBN flakes resulting in three different batches (batches 1, 2, and 3), all from the same manufacturer (see Materials and Methods). To quantify the efficiency of generating luminescent centers in hBN, we define the density per unit surface

$$S = N/A$$

Here, $N$ is the number of generated centers and $A$ is the area of all hBN flakes. Details on the number of generated centers and the flake areas are given in section SV.

First, we focus on the density after each process step (Fig. 2A). For batch 1, we find no luminescent centers in untreated flakes after exfoliation and only a few after irradiation. After subsequent annealing of batch 1, the density increases up to 0.012 centers/μm$^2$. For reference, we also investigate the density of batch 1 after annealing without prior irradiation and find a density of 0.005 centers/μm$^2$. Since this density is well below 0.012 centers/μm$^2$, both irradiation and annealing are crucial steps to achieve high densities. In contrast to batch 1, a small, nonzero density was observed in batch 2 before treatment. While both batches are from the same supplier and nominally comparable, batch 1 and batch 2 were taken from different crystals. Such differences in crystallinity and purity are typical between crystals. After irradiation of batch 2, the density decreases close to zero because most of the centers present after exfoliation do not withstand the irradiation. Subsequent annealing increases the density up to 0.005 centers/μm$^2$, which is higher than in batch 1. For both batches, the density is small after exfoliation because high-quality...
Photophysical properties of luminescent centers

To analyze the photophysics of our luminescent centers, we choose the most stable emitters for intensity correlation measurements, also called $g^{(2)}$ measurements (see section SI). In Fig. 3A, PL spectra from localizing the centers and during the $g^{(2)}$ measurements are shown. These spectra show good agreement, and thus, only small spectral wandering is observed. We fit our experimental correlation functions with theoretical curves of a three-level system

$$g^{(2)}(\tau) = 1 - b \cdot e^{-|\tau|/T_1} + c \cdot e^{-|\tau|/T_2}$$

where $b$ is the antibunching amplitude, $c$ is the bunching amplitude, and $T_1$ and $T_2$ are the lifetimes of the antibunching and bunching process, respectively. By convoluting Eq. 1 with our instrument response function (see section SI), we obtain the antibunching dips given in Fig. 3B. For 240 eV, we measure the $g^{(2)}$ function of a PSB, which is a reliable test of the quantum nature of luminescent centers (31). A value of $g^{(2)}(0)$ below 0.5 means that the single-photon contribution is nonzero, but not necessarily high (34). For 200-eV irradiation, we find a luminescent center with $g^{(2)}(0) = 0.069 \pm 0.403$, indicating clear quantum emission. Further centers show $g^{(2)}(0) = 0.553 \pm 0.087$ and $g^{(2)}(0) = 0.876 \pm 0.149$ after 240 and 270 eV, respectively. More experimental data of extended $g^{(2)}$ functions and stability measurements are shown in section SIX.

**MD simulations of oxygen irradiation**

To get insights into the microscopic processes taking place under oxygen irradiation, we carried out MD simulations. We studied the irradiation with oxygen ions onto a six-layer hBN target under normal incidence (Fig. 4A and section SX). The average number of boron ($V_B$) and nitrogen vacancies ($V_N$) per incident oxygen atom was calculated for different irradiation energies (Fig. 4B and movies S1 and S2). The numbers of both $V_B$ and $V_N$ increase almost linearly with increasing irradiation energy while we obtained an overall higher number for $V_N$. This is in agreement with the lower formation energy of 7.3 eV for $V_N$ compared to 10.4 eV for $V_B$ reported by extended Tersoff potential (ExTeP) (35) and density functional theory (DFT) (21). This lower vacancy formation energy makes it easier to displace a nitrogen atom in the hBN lattice and to form $V_N$.

For two batches of hBN, our experiments showed a slight increase in the density of generated luminescent centers when increasing the irradiation energy from 120 to 240 eV and a slight decrease...
or saturation from 240 to 300 eV (see Fig. 2B). Within our measurement uncertainties, one valid interpretation is a linear increase of the density with irradiation energy. This linear increase is not as large as the vacancies concentration increase predicted by our MD simulations (see Fig. 4B). One possible reason is the annihilation of \( V_N \) by the subsequent annealing in nitrogen atmosphere via breaking nitrogen molecules (see section SXI). Another possible reason is that the empirical MD cannot differentiate between ions and atoms while we irradiate with a small contribution of positively charged oxygen (see section SXII).

As described above, we also experimentally studied the influence of the irradiation fluence on the density of generated luminescent centers in hBN. We observed a remarkable, fivefold enhancement in the density when increasing the fluence by a factor of 10. To get an understanding of this observation, we carried out MD simulations for high-fluence irradiation (see movies S3 and S4). An additional annealing at 100 °C was performed after ion impact simulations with the main goal to remove metastable configurations, but not to mimic the experimental annealing process, as macroscopic times cannot be achieved even in analytical potential MD simulations. In Fig. 4C the first two hBN layers after a fluence of \( 1 \times 10^{15} \text{cm}^{-2} \) are shown. Both layers are very amorphous and show large distortions both in and out of plane. The third and fourth layers remain crystalline after irradiation with only slight deformation out of the plane (see section SX). To quantify the observed amorphization of hBN, we calculated the radial distribution function (RDF) for the top three layers of hBN (Fig. 4D). The RDFs were calculated for fluences from \( 1 \times 10^{14} \) to \( 1 \times 10^{15} \text{cm}^{-2} \), which are around our experimental fluences (see Materials and Methods). The RDFs for a monocrystalline material are Dirac delta functions corresponding to constant atom-to-atom distances in the crystal (black dashed lines in Fig. 4D).

After high-fluence irradiation, the first three hBN layers show broad peaks in the RDF, indicating an amorphous material. The boron-boron distance (blue curves in Fig. 4D) is a broad peak for a fluence of \( 1 \times 10^{14} \text{cm}^{-2} \) and becomes even broader when increasing the fluence up to \( 1 \times 10^{15} \text{cm}^{-2} \). Hence, the higher the irradiation fluence, the more amorphous the hBN becomes, as expected from our experiments.

To get further insights into the optical properties of our amorphous hBN after irradiation, we analyzed the electronic structure of the top four irradiated layers (see section SXIII). Defects lead to
important changes in the electronic structure of the two topmost layers by introducing a large number of midgap states. The defect-associated states cover the entire bandgap region and stem from both valence band and conduction band orbitals, as both types of elements are removed from the lattice. For the third and fourth layer, however, the electronic structure changes only slightly, while a few strongly localized states are obtained for the third layer.

The results of our experiments and MD simulations indicate strongly that amorphization of the two topmost layers takes place under irradiation with oxygen ions. Thus, we propose the following mechanism for the generation of luminescent centers in hBN. The irradiation amorphizes the topmost layers and erases luminescent centers previously present. This is supported by the experimental observation that luminescent centers present beforehand are erased after irradiation (see batch 2 in Fig. 2A). Thermal annealing recrystallizes the amorphous layers, so that a few defects remain in the topmost layers. The recrystallization is experimentally supported by bulk phonon-assisted PL (31, 32) observed in group I emitters (see Fig. 1C). We note that the very amorphous topmost layer can also evaporate during thermal annealing and that the annealing step cannot be simulated by using MD, as macroscopic time scales cannot be achieved in practice.

**DFT calculations of PL line shapes of defects**

To get insights into the microscopic origin of our luminescent centers, we consider both the irradiation and annealing steps in our generation process (Fig. 1A). Irradiation with oxygen atoms forms $V_B$ and $V_N$ (see Fig. 4B) but can also create the double vacancy $V_{BN}$ and oxygen atoms on nitrogen sites ($O_N$). Note that oxygen atoms on boron sites ($O_B$) are less likely (36). Subsequent annealing in a nitrogen environment provides nitrogen atoms (by breaking nitrogen molecules) leading to the annihilation of $V_N$ and $O_N$ as well as transforming $V_{BN}$ into $V_B$ (see section SXI). Thus, $V_B$ is the only irradiation-induced defect withstanding annealing in nitrogen.

Besides irradiation-induced defects, impurities can be incorporated in the hBN lattice during our process (Fig. 1A). The carbon substitutes $C_B$ and $C_N$ can be incorporated into the hBN lattice from ubiquitous hydrocarbons (37). Since carbon is present in our experiments both intrinsically in the hBN and in the annealing environment (see Materials and Methods), $C_B$ and $C_N$ are likely to be formed.

All in all, we have $V_B$, $C_B$, and $C_N$ formed during our process. During annealing, these defects become mobile and new defects can be formed; in particular, $V_B$ and $C_N$ can merge into $V_{NC_B}$. Theoretical investigations predict $C_B$ and $C_N$ to be optically inactive in our spectral regime (38). Furthermore, $V_{NC_B}$ has been ascribed to quantum emission (39) and $V_B$ (negatively charged $V_B$) has been ascribed to optically detected magnetic resonance (40, 41). Therefore, we choose $V_{NC_B}$ and $V_B^-$ (Fig. 5A) to calculate PL line shapes via DFT.

Figure 5B shows the PL line shapes of $V_{NC_B}$ and $V_B^-$ obtained from DFT calculations (details in Materials and Methods and section SXIV). Pronounced PSBs are observed for $V_{NC_B}$, while the calculated spectrum of $V_B$ shows a broad ZPL with less pronounced PSBs. In Fig. 5C we compare two representative luminescent centers of groups I and II (also shown in Fig. 1C) to the calculated spectra. This qualitative comparison is done by matching the ZPLs of experimental and calculated line shape. Furthermore, the calculated line shapes were rescaled in intensity such that the PSBs fall on top of each other. Excellent agreement of group I and $V_{NC_B}$ as well as group II and $V_B$ is found. A small deviation is that the calculated $V_B$ spectrum vanishes above the ZPL, whereas the group II centers show a ZPL on top of a broad background. Possible reasons for deviations between calculated and experimental spectra are effects of edges, layers, material distortion, and strain on the luminescence properties of defects (39, 40, 42). Nevertheless, our excellent agreement outstands previously reported comparisons of experiments with ab initio calculations.

In this work, we have studied the generation of luminescent centers in hBN via an irradiation-based process. The versatile processes in our RIE reactor allow irradiation engineering by tuning both the irradiation energy and the irradiation fluence. This is novel compared to previous studies of high-energy irradiation (26, 27) and oxygen plasma (24, 25) processes, since highly directional ions with a narrow energy distribution were used in the present work. The density of generated luminescent centers changes with both irradiation energy and fluence, while increasing the irradiation fluence shows a substantial enhancement of the density. Within our luminescent centers, we find two groups, named groups I and II, which show

![Fig. 5. Comparison of PL line shapes to ab initio DFT calculations.](http://advances.sciencemag.org/content/7/17/eabe7138/F5)

**Fig. 5. Comparison of PL line shapes to ab initio DFT calculations.** (A) Schematics of the $V_{NC_B}$ and the $V_B^-$ defects. (B) Calculated PL line shapes of $V_{NC_B}$ and $V_B^-$. (C) Comparison of calculated and experimental PL line shapes obtained after 10-s irradiation at 240 eV and subsequent annealing. The calculated PL line shapes are shifted to the ZPL of each emitter and rescaled. The colors of the spectra in (B) correspond to the ones in (C).
photophysical properties similar to previously reported quantum emitters in hBN. We propose that both groups of luminescent centers are formed by amorphization of hBN via irradiation, followed by recrystallization via annealing where the luminescent centers are created in the topmost layers. This mechanism of generating luminescent centers highlights the necessity of both irradiation and annealing, confirmed by experimental findings. Furthermore, the proposed mechanism of generating luminescent centers is strongly supported by MD simulations of oxygen irradiation of hBN as well as experimental observations of bulk–phonon assisted PL. All in all, the combination of experimental and theoretical findings allows us to rule out defects unlikely to be formed during our process and to focus on the most likely defects to understand the microscopic origin of our luminescent centers. Ab initio calculations of PL line shapes show excellent agreement of group I centers with \( V_{\text{N,\text{C}}B} \) and of group II centers with \( V_{\text{B}} \). Our comparison is qualitative and further spectroscopic methods would be needed to unambiguously identify the nature of these luminescent centers \((43–45)\). Nevertheless, our excellent agreement of experimental and theoretical PL line shapes is outstanding compared to previous reports.

Our irradiation-based method relies on inexpensive and widely used equipment and therefore enables low-cost and large-scale generation of luminescent centers in hBN with controlled densities. Site-selective quantum emission at room temperature might be achieved by combining our depth-selective generation of luminescent centers with standard nanolithographic techniques. Furthermore, the irradiation engineering presented in this work could be adapted to other gapped 2D materials for generating typical defects such as vacancies or substitutional defects based on impurities intrinsic to the 2D material itself or originating from the annealing environment. Different irradiation energies and fluences, as well as different annealing environments, might be required to optimize the density of these typical defects, which could be known or even previously unknown types of quantum emitters.

**MATERIALS AND METHODS**

**Sample fabrication**
We used bulk hBN crystals from HQGraphene and mechanically exfoliated them with tape (low-adhesion release and ultraviolet release tape, EPL BT-150E–KL, Nitto Denko) onto a SiO\(_2\)/Si chip with an oxide thickness of \( \sim 100 \) nm. The chip was priorly rinsed in acetone and isopropyl alcohol (IPA), as well as oxygen plasma ashed for 5 min. The area of each hBN flake was determined by counting the number of pixels in the PL map showing the Raman-active \( E_{2g} \) phonon of hBN at 1366 cm\(^{-1}\) \((14)\). Multiplying this number of pixels by the pixel area gives the area of each hBN flake with a precision of 5 \( \mu \)m\(^2\). By their optical contrast with respect to the substrate, we could estimate a thickness range from 3 to 64 nm after irradiation. We note that irradiation is thinning out the flakes slightly (see section SXV), as observed for oxygen plasma treatment \((46)\).

Afterward, the exfoliated hBN flakes were irradiated with oxygen atoms in an RIE reactor with parallel plate geometry. A high-frequency generator operating at 13.56 MHz is capacitively coupled to the bottom electrode. We use \( O_2 \) inlet gas at a constant flow of 40 sccm. The pressure in the reactor during the process is kept low at 30 mTorr to minimize the angular dispersion of the ions. Ions in the generated plasma acquire a kinetic energy \( E_{\text{kin}} = qV_{\text{DC}} \) given by the ion charge \( q \) and the DC bias \( V_{\text{DC}} \) [sum of the DC self-bias, the main contribution, and the plasma potential; \((47)\)]. Because of the composition of our plasma (see section SXII), we assume \( q = 1 \), as well as irradiation with mainly neutral oxygen atoms and a small contribution of positively charged oxygen. Furthermore, the irradiation is carried out in the collisionless regime (or close to it) since the mean-free path of oxygen ions in plasma is 1 cm \((48)\) which is similar to the plate separation in our RIE reactor but larger than the sheath thickness for oxygen ions at our working pressure \((49, 50)\). This collisionless regime ensures a narrow energy distribution as well as a small angular dispersion, thus making our process well controlled and easy to model.

Our samples were irradiated at different kinetic energies by running processes at various \( V_{\text{DC}} = 120, 200, 240, 270, \) and 300 V. We measured fluctuations of \( V_{\text{DC}} \) in our reactor during the processes below \( \pm 5 \) V. Two batches (batch 1 and batch 2) are used for studying different irradiation energies. Here, the irradiation time is kept constant at 10 s, which results in a fluence of \( 1 \times 10^{14} \) to \( 1 \times 10^{15} \) atoms/cm\(^2\). One batch (batch 3) is used to study the irradiation fluence. Here, the irradiation time varies from 100 to 1000 s, resulting in fluences from \( 1 \times 10^{15} \) to \( 1 \times 10^{16} \) atoms/cm\(^2\).

Subsequently, the chips were annealed inside a graphite box at 850 °C in nitrogen (99.999%) for 30 min with a ramp of 20 °C/min for heating and cooling. The pressure in the chamber was 80 mbar when cold and 170 mbar when hot.

**Optical spectroscopy**
All PL measurements were performed with a customized scanning microscopy setup (details in section SI). All spectra are obtained at room temperature and are shown without background correction. All PL maps and spectra shown in Fig. 1, 3, and 5 are obtained with a 2.37-eV laser except the blue spectra for 240 and 270 eV in Fig. 3A where a 2.40-eV laser was used. The \( g^{(2)} \) measurements in Fig. 3B were carried out with a 2.37-eV laser for samples irradiated at 200 eV and with a 2.40-eV laser for irradiation at 240 and 270 eV.

**DFT calculations of PL line shapes**
For our calculations of PL spectra of \( V_{\text{N,\text{C}}B} \) and \( V_{\text{B}} \) defects, the planar configurations of ground and excited states involved in the transitions were considered. While the planar configuration is the most stable one for all other cases, only for the excited state of \( V_{\text{N,\text{C}}B} \) (i.e., \( 2^3\text{B}_1 \)) does the carbon atom of the defect relax out of plane. The out-of-plane configuration is stable compared to the planar configuration by 0.23 eV for monolayer hBN, while the energies differ by 0.036 eV in a trilayer hBN with a \( V_{\text{N,\text{B}}C} \) defect embedded in the central hBN layer. A very small barrier of 0.036 eV for trilayer hBN is consistent with the fact that only the planar configuration has a very good qualitative agreement with experimental PL spectra.

We used DFT calculations using HSE06 for exchange and correlation, since the PBE functional fails for defect states \((51)\). We implemented our calculations in versions 5.3.3 of the Vienna Ab Initio Simulation Package \((52, 53)\) and the DSCF method described in \((20, 54)\). For the detailed theory and for details on the calculation of the PL line shapes, we refer to \((39)\).

**Molecular dynamic simulations**
We used the LAMMPS computational package \((55)\) and defined the interaction between B and N atoms with an ExTep \((35)\) and at small separations with the Ziegler–Biersack–Littmark potential \((56)\).
51. J. R. Reimers, A. Sajid, R. Kobayashi, M. J. Ford, Understanding and calibrating density-functional-theory calculations describing the energy and spectroscopy of defect sites in hexagonal boron nitride. J. Chem. Theory Comput. 14, 1602–1613 (2018).

52. G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993).

53. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).

54. A. Sajid, J. R. Reimers, M. J. Ford, Defect states in hexagonal boron nitride: Assignments of observed properties and prediction of properties relevant to quantum computation. Phys. Chem. Theory Comput. 14, 1602–1613 (2018).

55. S. Plimpton, Fast parallel algorithms for short-range molecular dynamics. J. Comput. Phys. 117, 1–19 (1995).

56. J. Ziegler, J. Biersack, U. Littmark, The Stopping and Range of Ions in Solids (Pergamon Press, 1985), vol. 1, p. 321.

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The PDF file includes:

- Supplementary Text
- Figs. S1 to S12
- Tables S1 to S4
- Legends for movies S1 to S4

Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/7/8/eabe7138/DC1)

- Movies S1 to S4
I. OPTICAL CHARACTERISATION

All PL measurements were performed with a customised scanning microscopy setup based on an inverted microscope (Eclipse Ti-U, Nikon). A continuous wave (CW) laser was used, either with a photon energy of 2.37 eV (0520L-13A, Integrated Optics) or 2.40 eV (CW mode of LDH-IB-520-B, PicoQuant GmbH). The laser was focused onto the sample with a 50X objective (NA = 0.6, Nikon) which resulted in a spot size diameter of 1 µm, which is our spatial resolution. The collected light was extracted with the same objective. For PL maps, the sample was scanned using a X-Y stepper-motor driven stage (MCLS03408, Mad City Labs GmbH). The collected light was filtered by a 550 nm long pass filter (FELH0550, Thorlabs Inc.) and directed to a spectrometer (Shamrock 303i, Andor) which is equipped with a 150 lines/mm grating. For PL measurements, the diffracted light was sent to an EMCCD (Newton 970, Andor). All spectra shown in this work are not corrected for background luminescence which is usually done by subtracting a PL spectrum next to a luminescent centre. This holds also for spectra taken during correlation measurements. A pixel-by-pixel analysis of spectra revealed locations of luminescent centres.

For correlation measurements, we used one of our CW lasers (given in Methods) to excite luminescent centres. Furthermore, the PL was sent to a variable output slit of the spectrometer. By changing the incident angle of the grating and the width of the output slit, our spectrometer acts as a variable spectral filter. Thus we can select a narrow spectral part of the PL for correlation measurements. After the PL passed this variable filter, it was coupled into a custom-made fiber splitter (TM105R5F1B with angled physical contact (APC) connectors, Thorlabs Inc.) with its outputs connected to two single-photon counting modules (SPCM-AQRH-15-FC, Excelitas Canada Inc.). The temporal correlation was given by a time-correlated single-photon counting module (Time Tagger 20, Swabian Instruments GmbH). The obtained $g^{(2)}$ functions are fitted with a theoretical curve (see main text) which is convoluted with our system response function. We used a Gaussian function for our system response with a variance of 0.5014 ns, given by the detectors and the time correlator. Due to thermal re-emission of our single-photon counting modules we got additional coincidence counts at ±20 ns. We suppressed most of these coincidence counts by using our customised fiber splitter with APC connectors, but we could not remove them completely. Since this thermal re-emission is spectrally broad it can not be filtered out with a spectral filter.
II. PROCESS OF EMITTER GENERATION

FIG. S1. PL maps after each process step showing the evolution of one hBN flake. The color scales show the absolute integrated PL counts instead of the normalised PL counts in the main text. All PL maps are taken with a 2.37 eV laser.
III. EXAMPLE OF A LUMINESCENT CENTRE GENERATED AWAY FROM THE EDGE

FIG. S2. Example of a luminescent centre generated away from the edge of a hBN flake. The spectrum of the luminescent centre is shown in the left panel while the right panel shows the integrated PL map with the location of the centre. The hBN flake is from Batch 3 after 1000 s irradiation at 240 eV (Irr.) and subsequent annealing at 850°C. Here, an excitation laser at 2.37 eV is used. Note that this flake is different to the one presented in Fig. S12.
Besides Group I and Group II centres (discussed in the main text), we also find a third group of luminescent centres. Due to a spectral gap between the excitation laser and the long pass filter, we observe PL peaks which could be either PSBs of a hidden ZPL or a ZPL itself. Those line shapes are classified as luminescent centres of Group III. For both lasers (2.37 eV and 2.40 eV) we assign PL peaks above 2.037 eV to Group III centres.

FIG. S3. A selection of Group I, Group II and Group III luminescent centres. All data is obtained from Batch 1 after 10 s irradiation at 240 eV and subsequent annealing. Here, an excitation laser at 2.37 eV is used.
V. DETAILS OF GENERATED LUMINESCENT CENTRES AND TREATED FLAKES

| Batch 1 | Group I | Group II | Flakes | Area(µm²) |
|---------|---------|---------|--------|-----------|
| Untreated | 0       | 0       | 18     | 1359      |
| 200 eV   | 7       | 0       | 15     | 922       |
| 240 eV   | 0       | 0       | 13     | 1002      |
| 270 eV   | 0       | 0       | 14     | 880       |
| 200 eV + 850 °C | 8   | 0       | 14     | 827       |
| 240 eV + 850 °C | 20  | 7       | 29     | 2324      |
| 270 eV + 850 °C | 4   | 2       | 13     | 732       |

TABLE S1. Number of Group I and Group II luminescent centres, number of flakes treated and area of all flakes for each process step of Batch 1.

| Batch 2 | Group I | Group II | Flakes | Area(µm²) |
|---------|---------|---------|--------|-----------|
| Untreated | 7       | 0       | 13     | 1191      |
| 120 eV   | 2       | 1       | 13     | 1131      |
| 240 eV   | 0       | 0       | 5      | 441       |
| 300 eV   | 1       | 0       | 14     | 1194      |
| 120 eV + 850 °C | 12  | 9       | 13     | 1048      |
| 240 eV + 850 °C | 15  | 5       | 14     | 725       |
| 300 eV + 850 °C | 21  | 8       | 14     | 1099      |

TABLE S2. Number of Group I and Group II luminescent centres, number of flakes treated and area of all flakes for each process step of Batch 2.

| Batch 3 | Group I | Group II | Flakes | Area(µm²) |
|---------|---------|---------|--------|-----------|
| 100 s   | 4       | 1       | 13     | 837       |
| 500 s   | 11      | 3       | 13     | 610       |
| 1000 s  | 12      | 8       | 13     | 764       |

TABLE S3. Number of Group I and Group II luminescent centres, number of flakes treated and area of all flakes for each process step of Batch 3.
VI. DETAILED DENSITIES OF BATCH 1 AND 2

FIG. S4. Total densities of luminescent centres in untreated, after 10 s irradiation (Irr.), and subsequent annealing (Irr. + Ann.). (a) Densities of Batch 1 for individual irradiation energies (colored curves) as well as the density for all irradiation energies (black curves), presented in the main text. (b) Densities of Batch 2, labelled as in (a). The relatively high density after 200 eV irradiation in (a) is due to seven luminescent centres found on a single hBN flake.
VII. ERROR BAR OF DENSITIES OF LUMINESCENT CENTRES

The density $S$ of generating luminescent centres is defined (see the main text) as

$$S = \frac{N}{A}$$

where $N$ is the number of generated centres and $A$ is the sum of all flake areas. Applying standard propagation of uncertainty gives an error for the density of

$$\Delta S = |\frac{\partial S}{\partial N}| \cdot \Delta N + |\frac{\partial S}{\partial A}| \cdot \Delta A = \frac{\Delta N}{A} + \frac{N \cdot \Delta A}{A^2}$$

Here, the first term gives an error arising from the uncertainty $\Delta N$ and the second term the uncertainty arising from $\Delta A$. We use the following uncertainties in our data analysis

$$\Delta A = M \cdot 5 \, \mu m^2 \text{ and } \Delta N = \begin{cases} 1 & \text{if } N < 4 \\ \text{round}(N/10) & \text{if } N \geq 5 \end{cases}$$

with $M$ being the number of flakes mapped and $\text{round}(x)$ rounding off $x$ to an integer.

The error $\Delta A$ stems from the uncertainty of determining the area of one flake (see Materials and Methods). The error $\Delta N$ originates from the non-perfect counting of luminescent centres. We established a pixel-by-pixel analysis to reveal the locations of luminescent centres (LCs) which consists of two steps. The first step is a fit analysis which provides likely candidates for LCs. However, not all of these locations fulfill the requirements for being a LC, i.e. showing strong ZPL or the presence of PSBs. Some of these candidates are too noisy and we discard them, but they could still be single or multiple LCs with low brightness. This gives the estimated error $\Delta N$ shown above.
VIII. FRACTIONS OF EMISSION INTO ZPLS

The fraction $\alpha$ of ZPL emission is given by

$$\alpha = \frac{C_{\text{ZPL}}}{C_{\text{complete}}}$$

with $C_{\text{ZPL}}$ and $C_{\text{complete}}$ being the PL counts integrated over the spectral ranges given in Tab. S4.

| Column in Fig. 3 | ZPL fraction | ZPL range       | Complete PL range |
|------------------|--------------|-----------------|-------------------|
| 200 eV           | 0.39906      | 2.176 eV - 2.210 eV | 1.5 eV - 2.262 eV |
| 240 eV           | 0.04927      | 2.207 eV - 2.221 eV | 1.5 eV - 2.262 eV |
| 270 eV           | 0.09509      | 1.985 eV - 2.020 eV | 1.5 eV - 2.262 eV |

TABLE S4. The ZPL counts divided by the PL counts (ZPL fraction), the ZPL range and the PL range for all luminescent centres shown in Fig. 3A.
FIG. S5. Detailed photophysics of luminescent centres after 10 s irradiation and annealing (Batch 1). (a) Both the spectrum from localising the centres (red) and the spectrum during the $g^{(2)}$ measurement (blue) is shown. (b) The $g^{(2)}$ functions of selected emitters. The collected spectral region is shaded blue in (a). (c) Stability of the emitters during $g^{(2)}$ measurements. The relative fluctuations (i.e. the standard deviation divided by the mean value) from top to bottom panel are 0.1365, 0.0385 and 0.0259. The centre in the top panel blinked during our measurements which causes a higher relative fluctuation. Here, the counts are acquired from one detector of our Hanbury Brown and Twiss setup with a bin width of 0.1 s. (d) Extended $g^{(2)}$ functions shown in (b). The corresponding irradiation energy is given by the inset in (a).
X. MOLECULAR DYNAMICS SIMULATIONS

A. Simulation setup

We performed analytical potential molecular dynamics (MD) simulations using the LAMMPS computational package as detailed below. The simulation setup for oxygen ion irradiation of hexagonal boron nitride (hBN) is presented in Fig. S6. The nearest neighbor distance (B – N) in the optimised structure using the potential is 1.4457 Å and was used in the RDF figure in the main text. The system shown in Fig. S6a (70 × 70 Å²) was used for high-fluence O ion irradiation, while the studies of single-ion impacts were carried out with a smaller system with a size of 25x26 Å². The atomic geometry of the structure was initially optimised using the analytical potentials to be described in section X B below. The target systems were then irradiated with O ions (the empirical MD cannot differentiate between ions and atoms, so that we use word ”ion” to emphasise that this is an energetic projectile). The initial absolute temperature of the system was zero, and periodic boundary conditions were employed. As for the high-fluence irradiation, following each impact and before the next one, the target system was allowed to evolve with time and then slowly quenched to absolute zero temperature.

The outermost atomic layers were kept fixed during irradiation simulations, as schematically shown in Fig. S6a, so that the entire system was not displaced under O ion impacts. To avoid the unrealistic reflection of heat and pressure waves from the borders of the system, the velocities of the atoms were scaled down in the border areas using the Berendsen thermostat thus mimicking the energy dissipation in an infinitely large system. In fact, three thermostat regions near the supercell boundaries were defined with a different dissipating power in order to precisely dissipate the outgoing energy waves. Free MD was carried out in the central region.

The number of atoms in the simulation cell under single ion and high-fluence O irradiations were 1441 and 10753 respectively. To assess the influence of irradiation fluence on amorphisation of hBN layers three different irradiation fluences, $1 \times 10^{14}$, $5 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm² were simulated. We sampled over the impact points in the irreducible area (Fig. S6c) in the hBN primitive cell and averaged the results. For each incident energy 1000 impacts per irreducible area were simulated. The incident O ion energies were in the range of 100 eV to 300 eV, close to the experimental values, and the incident angles were fixed to normal.

FIG. S6. Simulation setup for O ion irradiation of hBN. (a) Top view of the system. This system size was used for high-fluence irradiation, while a smaller target size of 25x26 Å² was employed for the simulations of single-ion impacts. The outermost atoms (blue) were kept fixed during the irradiation simulations. The kinetic energies of the atoms were scaled down in the areas indicated by red. (b) Side view of the hBN structure. Six stacked hBN layers were simulated. (c) An irreducible area (orange triangle) was taken to consider various impact possibilities in a systematic way for the pristine material.
B. Interatomic potentials

The interactions between B and N atoms were defined with an ExTeP. This potential accurately describes the main low energy B, N, and BN structures and yields quantitatively correct trends in the bonding as a function of coordination. The vacancy formation energies reported by the developers of ExTeP show a good agreement with the DFT results. A potential to describe O-B and O-N interactions is not available. However, O and N, being next to each other in the periodic table, have a rather similar subatomic structure, meaning that a well-tuned interatomic potential for one of them could reasonably describe the interactions of the other one as well. Thus, in our simulations, we modelled O as N atoms but with the mass of oxygen. In order to describe the interaction of atoms at small separations, the Ziegler-Biersack-Littmark (ZBL) potential was used.

C. High-fluence oxygen irradiation

![High-fluence oxygen irradiation](image)

**FIG. S7.** Top and side view of the first four hBN layers after 100 eV oxygen irradiation and subsequent annealing at 100 °C. The irradiation fluence is $1 \times 10^{15}$ atoms/cm$^2$. L stands for Layer and L1 is the top-most layer.
The energetics of a $\text{N}_2$ molecule interacting with a defective hBN sheet. (a) A $\text{N}_2$ molecule interacting with a hBN sheet with two nitrogen vacancies $\text{V}_\text{N}$. (b) The $\text{N}_2$ molecule attaches to one of the $\text{V}_\text{N}$. Hereby, one of the $\text{V}_\text{N}$ is annihilated. DFT calculations show that configuration (b) is higher in energy by $\Delta E = 2.91 \text{ eV}$. (c) Migration of the N adatom to the remaining $\text{V}_\text{N}$. Here, the migration energy barrier and the interaction of the N adatom with $\text{V}_\text{N}$ were neglected. (d) The annihilation of a N adatom with vacancy gives rise to an energy release of 10.41 eV.
We undertook optical emission spectroscopy measurements (OES) to probe the composition of the plasma generated in our reactor. Fig. S9 shows OES data for a 40 sccm oxygen process at $P = 36\,\text{W}$. It clearly shows a main peak at 777 nm, corresponding to atomic oxygen $\text{O}$, as well as a smaller $\text{O}^+$ peak at 559 nm and Si peak at 635 nm. The Si peak stems from the silicon wafer present in the chamber while measuring the OES spectra. This result justifies that our irradiation is mainly with oxygen atoms.

For clarity, we note that the main oxygen peak at 777 nm is related to excited oxygen atoms $\text{O}^*$ decaying with emissions at 777 nm and 845 nm: $\text{O}^* \rightarrow \text{O} + h\nu$. In our setup, we are only able to detect the peak at 777 nm; the peak at 845 nm is out of the range of our spectrometer. Those excited states $\text{O}^*$ can be explained as a mutual neutralization between positive $\text{O}^+$ and negative $\text{O}^-$ oxygen ions ($\text{O}^+ + \text{O}^- \rightarrow \text{O}^* + \text{O}$) created and accelerated at the initial stage of the plasma. The latter justifies the choice of an ion charge $q = 1$ to determine the kinetic energy $E_{\text{kin}}$ in our different irradiation processes.

![Optical emission spectrum of the plasma in our RIE reactor.](image_url)
XIII. BAND STRUCTURE CALCULATIONS OF IRRADIATED STRUCTURES

Density functional theory calculations on irradiated structures were carried out in the plane-wave basis and within the projector-augmented wave description of the core regions, as implemented in the VASP code. The calculations have been done using GGA/PBE functional. The structures were fully relaxed using the maximum force on each atom being less than 0.01 eV/Å. The electronic structure calculations for irradiated structures including 965 to 1663 atoms, corresponding to $11 \times 19$ supercells of hBN, have been done using 300 eV energy cutoff. The Brillouin zones of the supercells were sampled using $2 \times 2 \times 1$ Monkhorst-Pack grid points.

![Side and top views of the optimised top bilayer structure of hBN after irradiation](image1)

**FIG. S10.** *The optimised top bilayer structure of hBN after irradiation in side and top views.* Boron and nitrogen atoms are shown in yellow and indigo, respectively.

![Electron density of states (DOS) for different layers of the irradiated hBN](image2)

**FIG. S11.** *The electron density of states (DOS) for different layers of the irradiated hBN.* The filled green areas represent the occupied electronic states. The midgap states are clearly seen in DOS from the two top-most layers.
Calculated are performed for periodically replicated defects in a two-dimensional hBN monolayer. For the calculation of the total energy, the electronic structure and the ground state geometry we used version 5.3.3 of the Vienna Ab Initio Simulation Package (VASP). We utilised the standard PAW-projectors provided by the VASP package (projector augmented wave, PAW). Pristine single-layer hBN was first geometrically optimised using the conventional cell and a 27x27x1 Monkhu-Pack reciprocal space grid. A large vacuum region of 30 Å width was used to separate a single layer of hBN from its periodic images and to ensure that interaction between periodic images is negligible. The optimised bond length of pristine hBN is 1.452 Å, only slightly different to the one used in Supplementary Note X. All the defects were then realized in a 9x9x1 supercell and allowed to fully relax using a plane wave cut-off of 700 eV for a maximum force of 0.001 eV Å$^{-1}$. K-point convergence was checked and finally a K-point mesh of 3x3x1 was used for all calculations. The normal modes and dynamical matrices were calculated at the Γ point of the Brillouin zone. The total energies of the excited states were calculated within the ΔSCF method that provides accurate zero-phonon-line (ZPL) energy and Stokes-shift for the optical excitation spectra for triplet manifold.
FIG. S12. Optical microscope images of one flake from Batch 3 before (Untreated) after 1000 s irradiation at 240 eV (Irr.).
MOVIES OF OXYGEN IRRADIATION

Movie S1. Single oxygen irradiation at 200 eV, side view.
Movie S2. Single oxygen irradiation at 200 eV, top view.
Movie S3. High-fluence irradiation at $1 \times 10^{15}$ cm$^{-2}$, side view. The irradiation energy is 100 eV.
Movie S4. High-fluence irradiation at $1 \times 10^{15}$ cm$^{-2}$, top view. The irradiation energy is 100 eV.
