Donor-Acceptor Pair Quantum Emitters in Hexagonal Boron Nitride

Qinghai Tan

Nanyang Technological University

Jia-Min Lai

Institute of Semiconductors, Chinese Academy of Sciences

Xue-Lu Liu

State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

Dan Guo

Institute of Semiconductors, Chinese Academy of Sciences

Yong-Zhou Xue

Institute of Semiconductors, Chinese Academy of Sciences

Xiu-Ming Dou

Institute of Semiconductors, Chinese Academy of Sciences

Bao-Quan Sun

State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

Hui-Xiong Deng

Institute of Semiconductors, Chinese Academy of Sciences <https://orcid.org/0000-0003-2155-8727>

Ping-Heng Tan

Institute of Semiconductors, Chinese Academy of Sciences <https://orcid.org/0000-0001-6575-1516>

Igor Aharonovich

University of Technology Sydney <https://orcid.org/0000-0003-4304-3935>

Weibo Gao

Nanyang Technological University <https://orcid.org/0000-0003-3971-621X>

Jun Zhang (✉ zhangjwill@semi.ac.cn)

State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083 <https://orcid.org/0000-0002-9831-6796>

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Donor-Acceptor Pair Quantum Emitters in Hexagonal Boron Nitride

Qing-Hai Tan^{1,2,3#}, Jia-Min Lai^{1,2#}, Xue-Lu Liu^{1,2}, Dan Guo^{1,2}, Yong-Zhou Xue^{1,2}, Xiu-Ming Dou^{1,2}, Bao-Quan Sun^{1,2}, Hui-Xiong Deng^{1,2}, Ping-Heng Tan^{1,2,4,5}, Igor aharonovich^{6,7*}, Wei-Bo Gao^{3*}, Jun Zhang^{1,2,4,5*}

¹ State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

² Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

³ Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore

⁴ Beijing Academy of Quantum Information Science, Beijing 100193, China

⁵ CAS Center of Excellence in Topological Quantum Computation, University of Chinese Academy of Sciences, Beijing 101408, China

⁶ School of Mathematical and Physical Sciences, University of Technology Sydney, NSW 2007, Australia

⁷ ARC Centre of Excellence for Transformative Meta-Optical Systems; Faculty of Science University of Technology Sydney, NSW 2007 Australia

[#] These authors contributed equally

*Email: igor.aharonovich@uts.edu.au, wbgao@ntu.edu.sg, zhangjwill@semi.ac.cn

Abstract:

Quantum emitters are needed for a myriad of applications ranging from quantum sensing to quantum computing. Hexagonal boron nitride (hBN) quantum emitters are the most promising solid-state platform to date due to its high brightness, stability, and the possibility of spin photon interface. However, the understanding of the physical origins of the single-photon emitters (SPEs) is still limited. Here, we present concrete and conclusive evidence that the dense SPEs in hBN, across entire visible spectrum, can be well explained by donor-acceptor pairs (DAPs). Based on the DAP transition generation mechanism, we have calculated their wavelength fingerprint, matching well with the experimentally observed photoluminescence spectrum. Our work serves as a step forward for the physical understanding of SPEs in hBN and their applications in quantum technologies.

Introduction

Layered van der Waals materials have received much attention not only for their novel optoelectronic properties¹ but also for the capability of hosting a wealth of

optically active defects that act as single-photon emissions (SPEs)^{2,3}. In particular, SPEs from two-dimensional (2D) hBN exhibit stable, bright, and efficient emission into the zero-phonon line (ZPL) even at ultra-high temperatures³⁻¹¹. Furthermore, the spin information of these emitters serves as a promising platform for fundamental research and potential applications in quantum technologies^{12,13}. However, the origin and the nature of the h-BN SPEs remain under debate¹⁴⁻¹⁷. The emission spectra of both intrinsic and engineered defects in hBN show broadband spectral range, distinct polarization profiles as well as different quantum efficiencies^{9,14,15,17}. Several bottom-up growth techniques as well as post-processing approaches such as ion implantation or electron irradiation have been aimed at identifying the sources^{12,13,18-20}. In addition, multiple theoretical calculations show that different types of atomic defects may exist, including nitrogen or boron vacancy complexes, antisite defects, or substitutional defects with carbon or oxygen^{14,15,17,21-24}, but a conclusive evidence for these prediction results is still lacking.

As one of the fluorescence mechanisms, the donor-acceptor pair (DAP) transition between the ionized donors and acceptors has been studied in traditional semiconductors, including silicon^{25,26}, silicon carbide^{27,28}, diamond²⁹ and other compound semiconductors³⁰⁻³³. Generally, the DAP transition is characterized by a series of sharp PL lines with a broadband wavelength range at low temperatures²⁶⁻²⁹. In particular, by designing the emitters with a well-defined donor-acceptor distance and orientation in covalently linked organic molecules, it can enable a promising avenue for manipulation and coherent control of spin states^{34,35}. Recently, the DAP induced emission has been theoretically predicted in hBN³⁶.

Here, we present experimental evidence for the existence of DAP quantum emitters in hBN. At low temperatures, we observe dense sharp photoluminescence (PL) lines over a broad range of wavelengths from blue (~ 440 nm) to red (~ 800 nm) color. Based on the DAP transition mechanism, we used DAP model to calculate the emission lines, matching the experimental results very well. We also give possible origin of DAP by comparing fitting results and density function theory (DFT) calculations. Our work indicates that the DAP transition mechanism may explain the broad distribution of observed quantum emitters in hBN and serve as a foundation for designing scalable quantum devices.

The DAP transition in hBN

The DAP transition describes a fluorescence mechanism that includes the Coulomb interaction between the ionized donors and acceptors. Considering the nature of deep levels in the wide bandgap of semiconductors (e.g., hBN), the DAP transition process can be simply described as following: the electrons (holes), created by laser excitations, can be trapped by the ionized donor sites (D^+) (or the neutral A^0) and acceptor sites (A^-) (or the neutral D^0) before the radiative recombination and the photon emissions, as shown in Fig. 1(a). In general, two types of DAP transitions exist considering the random distribution of D^+ and A^- sites: *Type 1*, where both donors and acceptors are located at the same atomic element species, as illustrated by the red arrows in Fig. 1(b); and *Type 2*, where the donors and acceptors occupy

different atom sites as indicated by the blue arrows in Fig. 1(b). This radiative recombination of DAPs in semiconductors can generate a series of sharp lines with a broadband distribution in the PL spectra, as reported for other semiconductors^{25-28,30-33}.

Fig. 1 | (a) The schematic diagram of the DAP transitions in large bandgap semiconductors. (b) The diagram of *type 1* (red arrow) and *type 2* (blue arrow) of DAP transitions in hBN. (c) PL spectrum of one typical hBN sample with 442 nm (2.81 eV) laser excitation at 4 K. (d) The measurement result of the second-order correlation function for one PL peak at 4 K. The inset shows the corresponding PL spectrum.

Figure 1(c) shows the typical PL spectrum of single-photon emitters from hBN sample at 4 K. The hBN samples are prepared on SiO₂/Si substrate from hBN flakes suspended in 50/50 ethanol/water solution (Graphene Supermarket). More experimental results can be found in Supplementary Materials Fig. S1. Interestingly, we find that the spectrum shows dense sharp emission lines, and covers a wide energy range from 2.80 eV (443 nm) to 1.544 eV (803 nm), confirmed on multiple samples (Fig. S1). Furthermore, these lines also show a narrow linewidth down to ~ 75 μeV , as shown in Fig. S1, which is close to the narrowest BN emitter linewidth currently reported⁸. Fig. 1(d) and Fig. S2 shows the $g^{(2)}(\tau)$ measurement results of two randomly selected PL lines, which prove that they are single-photon emitters. We also measured the stability of PL lines at different emission wavelengths and found that they are stable and bright, as shown in Fig. S3.

Fig. 2 (a) The calculated spectral distribution of *type 1* DAPs (color solid lines). The solid black line is the measured spectrum at 4 K. The labeled numbers of the peaks are the shell numbers for the neighboring DA pairs, and the dash lines are used to guide the eyes. Here 2.411 eV, *et al*, represent the energy levels for $|E_D - E_A|$. The bottom part shows a zoomed-in range in the upper one. (b) The calculated emitted-photon energies based on the DAP model as a function of R_m (the distance between the donors and acceptors, where m is the shell numbers). The solid symbols are experimental results and the solid curves are the calculated results of *type 1* based on equation 1. (c) The coincidence of experimental lines that match the calculated DAP lines overall measured PL lines in each range.

Based on the DAP transition mechanism, we use theoretical DAP model below to calculate the emission lines. In this model, the electrons, instead of relaxing from the valance band to donors or acceptors as reported in previous studies, such as in GaP³¹⁻³³, relax between defect levels within the large bandgap of hBN. Thus the energy of the emitted photons can be written as³¹:

$$E(R_m) = |E_D - E_A| + \frac{e^2}{4\pi\epsilon\epsilon_0 R_m} \quad (1)$$

where, E_A and E_D are the donor and acceptor levels, respectively. R_m is the m -th ($m=1, 2, 3, \dots$) nearest distance between the donors and acceptors as determined by the crystal structure and lattice constant, and m is the shell number, and $\frac{e^2}{4\pi\epsilon\epsilon_0 R_m}$ describes the Coulomb interaction between the donor and acceptor. The discrete R_m in the Coulomb term is responsible for the observed sharp lines in the emission spectra. For large R_m , the lines are closely located and barely distinguishable, resulting in a broad peak. Fig. 2(a) shows the calculated spectral distributions and the zoom-in result for type 1 DAPs based on five different $|E_D - E_A|$ values (other zoom-in results are shown in Fig. S4 in SI). To further confirm the rationality of the model, we used a series of values that slightly deviate from one $|E_D - E_A|$ to calculate the DAP lines, as shown in Fig. S5, and found that these calculated lines can not match well with the

experimental lines, especially for the small m numbers. Moreover, we also found that these calculated DAP lines based on the same $|E_D - E_A|$ values match well with the experimental results from other samples, as shown in Fig. S6. These results indicate that these sharp hBN PL lines here are indeed from the DAP process.

Figure 2(b) shows the calculated emitted-photon energies of the DAP as a function of R_m between the donors and acceptors. We found that the calculated results match most of the PL lines. Remarkably, we found that $\sim 70\%$ percent of the theoretically calculated emission wavelengths match precisely the experimental results, as shown in Fig. 2(c), indicating the truth of the DAP mechanism here. The unmatched lines can be attributed to the inhomogeneous distribution of the defects and the multipole term²⁷. In addition, the crystal structure of the hBN sample may be deformed with strains, which can also lead to small deviations³². Meanwhile, some of the emission lines may originate directly from the color centers without DAP effects. As shown in Fig. S7, our results suggest that both two types of DAP transitions may coexist in our hBN samples due to the random doping. The lifetimes of different DAP lines are also measured as shown in Fig. S8, which become longer as the shell number increases. These results can be understood by considering that the overlap between electrons and holes in DAP is reduced with R_m increase and thus, the lifetime is slightly changed³². The weak lifetime dependence on shell number can be understood by considering the deep level nature in hBN, and small varied R_m (0.7 nm to 1.6 nm) here, as well as the relatively large exciton Bohr radius (on the order of a few nanometers) of Wannier exciton type in 2D materials¹. More detailed discussions can be found in the SI.

Fig. 3 | (a) The calculated band structure of bulk hBN and the energy levels of different defect types. The blue lines indicate these defect states which are full-filled with electrons, the black straight lines represent these defect states which are half-filled with electrons, and these red lines denote the empty defect states. The energy of the host valence band maxima is set to zero. (b) The energy of different defect types. The superscript (F), (H), and (E) indicate the defect states are full-filled with electrons, half-filled with electrons, and empty, respectively. (An apostrophe (') is used to distinguish some substitutional atoms with the same electron occupancy two

energy levels). For example, $C_B^{(H)}$ denotes a C impurity substituting for a lattice B atom and half-filled with electrons. Anti-site denotes B_N and N_B , V_B and C_i denote boron vacancy and carbon interstitial, respectively. (c) The $|E_D - E_A|$ of different *type I* DAPs from our fitting result (red circle) and DFT calculation (black square).

To understand the origin defect of DAP, we calculated the electronic energy band structures of the bulk hBN and its possible defect states (Fig. 3) based on density function theory (DFT). At 4 K, the electron-phonon coupling is weak (almost no phonon sideband is observed in our spectra) and lattice relaxation hardly affects the calculation of defect energy levels, thus we did not consider the lattice relaxation¹⁴. The calculated band gap of bulk hBN is 5.98 eV, which is consistent with previous experimental results³⁷. We consider all possible transitions based on DFT calculated level of defects, i.e. electron transition from full-filled or half-filled level to half-filled or empty level, and get the transition energy by the energy difference between these levels. Comparing with the fitting results, we list the possible origin of DAPs in Fig. 3(c). For *type I* DAP spectra, where both donors and acceptors are located in the same lattice site, we infer the possible DA pairs here are $O_B^{(H)} - \text{anti}^{(E)}$ (~ 2.411 eV), $H_N^{(F)} - C_N^{(H)}$ (~ 2.18 eV), $H_N^{(F)} - O_N^{(H)}$ (~ 1.95 eV), $O_B^{(H)} - V_B^{(E)}$ (~ 1.708 eV), and $H_N^{(F)} - H_N^{(E)}$ (~ 1.430 eV). In *type 2* DAP spectra listed in Fig. S10, where donors and acceptors occupy the different lattice sites, the possible DA pairs are $H_N^{(F)} - V_B^{(H)}$ (~ 2.392 eV), $O_B^{(H)} - H_N^{(E)}$ (~ 2.215 eV), $\text{anti}^{(F)} - O_B^{(H)}$ (~ 1.978 eV), $\text{anti}'^{(F)} - O_B^{(H)}$ (~ 1.691 eV), and $V_N^{(H)} - O_B^{(H)}$ (~ 1.408 eV) (V denotes the vacancy defects). Here the SPE induced by the DAP transition mechanism in hBN provides a new way to understand the dense SPEs in layered semiconductors and opens a new way to produce single-photon sources for quantum technology.

Temperature dependence of the DAP lines

Next we investigate the behavior of DAP lines at higher temperatures. These dense SPE lines become weaker at elevated temperatures, as shown in Fig. 4(a). When the temperature increases to around 160 K, some of the dense peaks vanish and cannot be individually resolved from each other. This result may be explained by considering the thermal effects on the fine structures and the binding energies of the ground states of the donor/acceptor. At a higher temperature, phonons broaden the luminescent lines, i.e. when the energy difference between two peaks is smaller than the linewidth induced by thermal perturbation at the corresponding temperatures, they cannot be distinguished. On one hand, the thermal energy of the crystal may free the originally paired donor and acceptor with a large R_m and reduce the number of peaks at higher temperatures. On the other hand, with temperature increasing, the thermal energy is big enough to approach the binding energies of the DAP. As a result, the probability

of DAP transitions is greatly reduced and other mechanisms such as the transition between the excited states and the ground states of defects dominate the fluorescence process.

We fit one representative PL peak from 4 K to 160 K, and plotted the temperature dependence of the extracted linewidths and ZPL positions, as shown in Fig. 4(b). Because of the phonon effects in higher temperatures, the lineshape shows a change from Gaussian shape to Lorentzian shape, consistent with our following analysis. At low temperatures, the PL ZPL is usually dominated by inhomogeneous broadening induced by spectral diffusion, exhibiting a Gaussian shape; while as the temperature increases, homogeneous broadening induced by phonons starts to dominate leading to Lorentzian shape at higher temperatures^{38,39}. From 4 K to 160 K, the linewidths show a T^3 temperature dependence, consistent with the previous results^{9,40-42}. We find most of these DAP PL lines follow such a temperature dependence, as shown in Fig. S11. Furthermore, most of the ZPL positions can be well described by using the O'Donnell equation⁴³. It suggests the electron-phonon coupling plays an important role in the broadening and red-shift of the DAP lines.

Fig. 4 | (a) The temperature-dependent spectra of hBN SPEs excited by 442 nm (2.81 eV) from 4 K to 300 K. The peak at 1.9856 eV (the gray region) was zoomed as an example. (b) The temperature dependence of linewidth and energy of the PL peak at 1.9856 eV (4K). The red solid line in (b) is fitted by the function $aT^\alpha + b$, where $a = 2.21 (0.16) \times 10^{-10}$, $\alpha = 3.00 (0.02)$ and $b = 2.89 (0.07) \times 10^{-4}$ eV. The energy of ZPL is fitted by the O'Donnell equation (blue line) $E(T) = E(0) - S\langle\hbar\omega\rangle \coth[\hbar\omega/2k_B T]$, where S is an exciton-phonon coupling constant and $\langle\hbar\omega\rangle$ is the average phonon energy. Here $E_g(0)$, S and $\langle\hbar\omega\rangle$ is around 1.99 eV, 0.20 and 24.61 meV, respectively.

Conclusions

In conclusion, we demonstrated that the DAP transition mechanism could be one of the origins for the wide spectral viability of the SPEs in hBN. These results indicate that SPE on demand can be obtained by filtering the PL lines induced by DAP

transition or designing the distance of the donor-acceptor pair. Our work provides a fundamentally new understanding of the hBN SPEs and opens a door to achieve supercontinuum SPS on one monolithic hBN sample. Besides, it also hints that DAP mechanism should be an alternative way to produce quantum emitters in other semiconductors with efficient DAP emission, such as silicon, silicon carbide, diamond and other compound semiconductors.

Experiment Methods:

Photoluminescence (PL) measurement: PL spectra measurements were undertaken in backscattering geometry with a Jobin-Yvon HR800 system equipped with a liquid-nitrogen-cooled charge-coupled detector. The samples are cooled by the Montana cryostat system. A 50x long-working-distance objective lens (NA=0.5) and both 600 and 2400 lines mm⁻¹ gratings were used for the PL measurements at low temperatures. The highest resolution for our system with 2400 lines mm⁻¹ grating is around 40 meV.

The second-order correlation function measurement: The second-order correlation function measurement is carried out by using a home-built Hanbury-Brown-Twiss (HBT) setup. Two silicon Avalanche Photo Diodes (APD) are used to count photons. The 590 nm bandpass and 690 nm bandpass filters combined with a grating monochromator (1200 nm lines mm⁻¹) are used during the autocorrelation measurements.

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Author contributions Q.-H. T. and J.-M. L. contributed to this work equally. J.Z. and Q.T. conceived the ideas; Q.T., P.T. and J.Z. designed the experiments. Q.T., and X.L. prepared the samples. Q.T., Y.X., and X.D. performed experiments. D.G. and H.D. performed the DFT calculations. Q.T., J. L., W. G., I.A and Z.J. analyzed the data and wrote the manuscript with inputs from all authors.

Competing interests: The authors declare no competing financial interest.

Additional information Supplementary information is available in the online version of the paper. Reprints and permissions information is available online. Correspondence and requests for materials should be addressed to J.Z. (Email: zhangjwill@semi.ac.cn).

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