Carbon dimer defect as a source of the 4.1 eV luminescence in hexagonal boron nitride

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We propose that the carbon dimer defect C_BCN in hexagonal boron nitride gives rise to the ubiquitous narrow luminescence band with a zero-phonon line of 4.08 eV (usually labeled the 4.1 eV band). Our first-principles calculations are based on hybrid density functionals that provide a reliable description of wide band-gap materials. The calculated zero-phonon line energy of 4.3 eV is close to the experimental value, and the deduced Huang-Rhys factor of $S \approx 2.0$, indicating modest electron-phonon coupling, falls within the experimental range. The optical transition occurs between two localized $\pi$-type defects states, with a very short radiative lifetime of 1.2 nanoseconds, in very good accord with experiments.

Layered materials with inter-layer van der Waals (vdW) bonding have recently attracted a lot of interest due to their distinct chemical and physical properties. Among this class of systems hexagonal boron nitride (hBN) stands out because of its large band gap of 6.08 eV, which quantifies electron-phonon coupling during optical transitions usually leads to marked non-exponential decay dynamics with very long tails, at odds with the single-exponential decay of the 4.1 eV line. Regarding radiative free-to-bound transitions, these occur on a millisecond time scale at typical decay of the 4.1 eV line. For DAP transitions, the variation in donor-acceptor pair distance is inconsistent with the measured lifetime of $\tau = 1.1 – 1.2$ ns, while the wide band exhibits multi-exponential dynamics with the slowest components having decay times of a few 100 ns. All these results indicate a very distinct origin of the two bands, and from now on we will only discuss the structured 4.1 eV band.

Recently, single-photon emission associated with the 4.1 eV band has been reported. Fast electrons in a transmission electron microscope were used to excite luminescence at $T = 150$ K. Measurement of the second-order correlation function confirmed that photons originate at a single emitter. The lineshape and the lifetime of the CL band were identical to those in ensemble measurements, confirming that in both experiments luminescence was caused by the same defect. These experiments have renewed the interest in the 4.1 eV band due to its potential use in quantum optics.

Despite the ubiquity of the 4.1 eV line, the microscopic nature of the defect that causes the luminescence is still not known. The intensity of the band increases drastically in both bulk crystals and epitaxial layers when carbon is purposely introduced during growth. Therefore, the involvement of carbon has been naturally assumed. It has been suggested that the 4.1 eV emission is caused by a transition from either a shallow donor (a so-called donor-acceptor pair or DAP transition) or from the conduction band (free-to-bound transition) to the neutral carbon acceptor on the nitrogen site, C_N. There are strong arguments against these scenarios. First, the time dynamics of DAP and free-to-bound transitions are inconsistent with the measured lifetime of $\tau = 1.1 – 1.2$ ns. For DAP transitions, the variation in donor-acceptor pair distances usually leads to marked non-exponential decay dynamics with very long tails, at odds with the single-exponential decay of the 4.1 eV line. Regarding radiative free-to-bound transitions, these occur on a millisecond time scale at typical
excitation conditions (carrier densities ~10^{17} \text{ cm}^{-3}) significantly slower than the dynamics of the 4.1 eV line. An additional argument comes from our recent first-principles study\cite{23}, where the acceptor level of C_N was found to be at 2.9 eV above the valence band maximum (VBM). Since the band gap of hBN is ~6.1 eV, DAP and free-to-bound transitions should therefore have energies smaller than 3.2 eV, i.e., they should not appear in the UV at all. The fast nanosecond radiative decay dynamics of the 4.1 eV line\cite{16,24} indicates that this is a transition where the ground state and excited state are localized in close proximity, likely on the same defect. Recently, Korona and Chojnacki used quantum chemistry calculations to suggest that carbon clusters made from two to four atoms give luminescence in the range from 3.9 to 4.8 eV in monolayer hBN. However, different UV lines were not discriminated in this study, and neither the stability of clusters nor parameters (lifetimes and electron-phonon coupling) of optical transitions were investigated.

In this Letter we use first-principles density functional theory to show that the C_BCN complex, in which two carbon atoms substitute on nearest-neighbor sites in the hBN lattice, accounts for all known experimental facts about the 4.1 eV luminescence: the involvement of carbon, the energy of the transition, the very short radiative lifetime, and moderate electron-phonon coupling.

Our calculations are based on the hybrid density functional of Heyd, Scuseria, and Ernzerhof. In this approach, a fraction $\alpha$ of screened Fock exchange is admixed to the short-range exchange potential described by the generalized gradient approximation of Perdew, Burke and Ernzerhof. We use $\alpha = 0.40$, for which calculations yield a band gap of 6.42 eV, consistent with the experimental gap. When zero-point renormalization due to electron-phonon interactions is accounted for. We used the projector-augmented wave approach with a plane-wave energy cutoff of 500 eV, and van der Waals interactions were included via the Grimme D3 empirical correction scheme. With these settings the calculated lattice parameters of hBN ($a = 2.49$ Å and $c = 6.51$ Å) and the enthalpy of formation for hBN (2.96 eV per formula unit) are in very good agreement with experimental values. Defect calculations have been performed in orthorhombic supercells containing 240 atoms and with lattice vectors $5(a + b)$, $3(a - b)$, $2c$, where $a$, $b$, $c$ are vectors of the primitive hBN lattice. The Brillouin zone was sampled at the $\Gamma$ point. Ionic relaxation was carried out until Hellmann-Feynman forces were less than 0.005 eV/Å. Calculations have been performed using the Vienna Ab-initio Simulation package (VASP).

We start by calculating the formation energy of the carbon dimer $E_f(C_BCN)$, which is given by:

$$ E_f(C_BCN) = E_{tot}(C_BCN) - E_{tot}(BN) + \mu_B + \mu_N - 2\mu_C + q(E_F + E_V) + \Delta_q, \tag{1} $$

where $E_{tot}(C_BCN)$ is the total energy of the supercell containing one dimer, and $E_{tot}(BN)$ is the total energy of a pristine supercell. $\mu_N$ and $\mu_B$ are chemical potentials of nitrogen and boron; $\mu_N + \mu_B = E_{BN}$, where $E_{BN}$ is the total energy of bulk BN per formula unit. $\mu_C$ is the chemical potential of carbon, set to the per-atom energy of a diamond crystal. In  

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Calculated formation energies vs the Fermi level for C_BCN, C_B, and C_N defects under (a) N-poor and (b) N-rich conditions.}
\end{figure}
occupied, while the $b_2^*$ state is empty, resulting in the electronic wave function $|b_2 b_2^*\rangle$ (symbols without a bar are for spin-up electrons, symbols with a bar for spin-down). This is a singlet state $^1A_1$. In the ground state the length of the C–C, C–N, and C–B bonds are 1.361, 1.391, and 1.497 Å, respectively (cf. the nearest-neighbor distance of 1.435 Å in bulk hBN). The excited state is obtained when one $b_2$ electron is promoted to the $b_2^*$ state, yielding the wave function $\frac{1}{\sqrt{2}}(|b_2 b_2^*\rangle - |b_2^* b_2\rangle)$, also a $^1A_1$ state. We calculate the energy and the resulting geometry of the defect in the excited state using the so-called delta self-consistent field approach (ASCF)\textsuperscript{29} with constrained orbital occupations, as explained in the Supplementary Material. In the excited state there is a slight geometry rearrangement: the C–C bond elongates by 7% to 1.456 Å, while C–N and C–B bond lengths change by less than 1.5% (to 1.372 and 1.499 Å, respectively).

The calculated one-dimensional configuration coordinate diagram\textsuperscript{11} is shown in Fig. 3(a). We obtain a ZPL energy of $E_{ZPL} = 4.31$ eV. The Franck-Condon shifts are 0.22 eV in the excited state and 0.24 eV in the ground state. To quantify electron-phonon coupling, we calculate\textsuperscript{29} the Huang-Rhys factor $S$, which is a measure of the average number of phonons emitted during the optical transition\textsuperscript{11}. We find an effective phonon frequency of $\hbar \Omega = 120$ meV, yielding the Huang-Rhys factor $S = 0.24/0.12 = 2.0$, which is consistent with the experimental estimate $S = 1.2$ reported in Ref.\textsuperscript{12}. The Huang-Rhys factor is related to the Debye-Waller factor $w_{ZPL}$ (the fraction of light emitted into the ZPL) via $w_{ZPL} \approx e^{-S}$. Our calculated value of $w_{ZPL} \approx 0.14$ is smaller than the experimental value of 0.26 reported in Ref.\textsuperscript{30}. However, note that due to the exponential dependence of $w_{ZPL}$ on $S$ small errors in the latter can lead to large errors in the former.

Apart from the excited-state singlet $^1A_1$, there is also a triplet state $^3A_1$ with configuration $|b_2 b_2^*\rangle$. $^3A_1$ is 3.22 eV above the ground state, i.e., 1.09 eV lower than the excited-state singlet due to the exchange interaction between the two electrons. The energy-level diagram of the neutral C\textsubscript{6}BN dimer is shown in Fig. 3(b).

The rate of the radiative transition between the two singlet states is given by (in SI units)\textsuperscript{11}.

\begin{equation}
\Gamma_{rad} = \frac{1}{\tau_{rad}} = \frac{n_D E_{ZPL}^3 \mu^2}{3 \pi \varepsilon_0 c^2 n^2}.
\end{equation}

Here $\varepsilon_0$ is vacuum permittivity, $n_D$ is the refractive index of the host ($n_D \approx 2.6$ for energy $E \approx 4$ eV\textsuperscript{31}), and $\mu = 1.06$ eÅ is the computed transition dipole moment for the transition $b_2 \rightarrow b_2^*$. Using the calculated value of $E_{ZPL} = 4.31$ eV, we obtain the rate $\Gamma_{rad} = 8.6 \times 10^8$ s$^{-1}$, corresponding to $\tau_{rad} = 1.2$ ns.

The $b_2 \rightarrow b_2^*$ transition is a strong dipole transition (so-called $\pi \rightarrow \pi^*$ transition) with the polarization along the C–C bond. Experimental measurements of polarization would be really valuable but have not yet been performed so far. The calculated $\tau_{rad} = 1.2$ ns is in good agreement with the experimental value of 1.1–1.2 ns\textsuperscript{22}, but one should exercise caution comparing the two. The lifetime of the excited state $^1A_1$ is governed by two decay mechanisms [Fig. 3(b)]: the radiative transition to the ground state $\Gamma_{rad}$ and the inter-system crossing (ISC) to the triplet state $\Gamma_{ISC}$: $\tau = 1/(\Gamma_{rad} + \Gamma_{ISC})$. However, in the Supplementary Material we show that $\Gamma_{ISC} \ll \Gamma_{rad}$, and this justifies the comparison of the calculated rate with the measured one. Since $\Gamma_{ISC} \ll \Gamma_{rad}$, we also conclude that the quantum efficiency of the radiative transition is close to unity.

Our results show that the calculated optical properties of the C\textsubscript{6}BN defect are in very good agreement with the known properties of the 4.1 eV line. In fact, carbon dimers have been observed by annular dark field (ADF) electron microscopy in boron nitride monolayers\textsuperscript{22} exfoliated from bulk hBN. Carbon atoms have distinct intensity in ADF images, and this allows a direct identification of C–C pairs\textsuperscript{22}. This experimental proof of the existence of C\textsubscript{6}BN defects in bulk hBN is in excellent agreement with our conclusions regarding the stability of carbon dimers.

In summary, we have reported the results of hybrid functional calculations for the carbon dimer in hexagonal boron nitride. Those calculations allow us to conclude that C\textsubscript{6}BN is the defect which is responsible for the 4.1 eV emission in hBN. The carbon dimer is expected to form whenever carbon...
is present during growth, explaining the observed correlation between the presence of carbon and the 4.1 eV line. The calculated zero-phonon line of the intra-defect optical transition of 4.31 eV is close to the experimental value. Moreover, the theoretical Huang-Rhys factor of $S = 2.0$ is consistent with the experimental estimate $S = 1 - 2$, and radiative lifetime $\tau_{\text{rad}} = 1.2$ ns is close to experimental value $\tau_{\text{rad}} = 1.1 - 1.2$ ns. Identification of the chemical nature of the defect will enable more controlled experiments involving the 4.1 eV line, in particular using the $\text{C}_3\text{B}_6\text{N}$ defect as a single photon emitter.\[13\] Our analysis shows that the quantum efficiency of this emitter should be close to unity. Combined with a very short radiative lifetime this results in a very high photon yield. Together with a modest value of the Huang-Rhys factor (large weight of the ZPL) and a well-defined polarization axis, this makes the carbon dimer a very interesting quantum emitter in the near UV.

SUPPLEMENTARY MATERIAL

See Supplementary Material for the calculation of the excited state singlet and the inter-system crossing crossing rate from the excited-state singlet $^1\text{A}_1$ to the $^3\text{A}_1$ state.

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