

The origin of deep-level impurity transitions in hexagonal boron nitride

X. Z. Du, J. Li, J. Y. Lin, and H. X. Jiang^{a)}

Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, Texas 79409, USA

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Deep ultraviolet photoluminescence (PL) emission spectroscopy has been employed to investigate the origin of the widely observed deep level impurity related donor-acceptor pair (DAP) transition with an emission peak near 4.1 eV in hexagonal boron nitride (*h*-BN). A set of *h*-BN epilayers were grown by metal-organic chemical vapor deposition (MOCVD) under different ammonia (NH₃) flow rates to explore the role of nitrogen vacancies (V_N) in the deep-level transitions. The emission intensity of the DAP transition near 4.1 eV was found to decrease exponentially with an increase of the NH₃ flow rate employed during the MOCVD growth, implying that impurities involved are V_N. The temperature-dependent PL spectra were measured from 10 K up to 800 K, which provided activation energies of ~ 0.1 eV for the shallow impurity. Based on the measured energy level of the shallow impurity (~ 0.1 eV) and previously estimated bandgap value of about 6.5 eV for *h*-BN, we deduce a value of ~ 2.3 eV for the deep impurity involved in this DAP transition. The measured energy levels together with calculation results and formation energies of the impurities and defects in *h*-BN suggest that V_N and carbon impurities occupying the nitrogen sites, respectively, are the most probable shallow donor and deep acceptor impurities involved in this DAP transition.

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Hexagonal boron nitride (*h*-BN) has been under intensive investigation in recent years due to its unique physical properties including wide bandgap energy (~ 6.5 eV), high emission efficiency, large thermal conductivity, high chemical and temperature stability, as well as large neutron capture cross-section of the isotope boron-10.^{1–15} It is a very promising material for deep ultraviolet photonic devices^{1–12} and neutron detector applications.^{13–15} However, the development of epitaxial growth of wafer-scale semiconducting *h*-BN, which is a prerequisite for practical device fabrication, is still in the early stage and will benefit from a better understanding of its fundamental properties. The physical origins of various commonly observed deep level impurity related emission lines in *h*-BN are not yet fully understood due to the lack of tunability in growth parameters in synthesizing bulk and powder-like *h*-BN in the past. A comprehensive study on the properties of the impurity transitions in *h*-BN grown under controlled conditions is necessary to provide not only a better understanding of its optical properties but also input for approaches towards the improvement of material quality and elimination of undesired impurities or defects as well as the design of particular device structures.

There have been several studies focusing on the optical transitions in *h*-BN. A series of sharp emission peaks above 5.77 eV corresponding to the free exciton transitions in *h*-BN have been observed in high crystalline quality bulk crystals of very small size, from which a large exciton binding energy ($E_B \approx 740$ meV) has been deduced.^{1,2,16–18} In other *h*-BN materials (powder-like *h*-BN, pyrolytic *h*-BN, *h*-BN thin films, and deformed *h*-BN bulk crystals), the dominant emission bands are near 5.5 and 5.3 eV, which were ascribed to bound exciton (or trapped excitons) and quasi-donor-acceptor pair (q-DAP) transitions,^{4,9,16,17} respectively.

Another widely observed emission line is near 4.1 eV (Refs. 4 and 19–21), and there are solid evidences supporting that this is a DAP type of transition.^{4,19,20} However, the nature of the impurities or defects involved in the DAP transition as well as their energy levels have not been experimentally determined.

In this work, a set of *h*-BN epilayers were grown by metal organic chemical vapor deposition (MOCVD) under different ammonia (NH₃) flow rates to allow the investigation of the role of nitrogen vacancies (V_N) in the deep impurity level related DAP transition in *h*-BN. Based on our experimental results and theoretical insights on the formation energies and the calculated energy levels of the V_N related impurities including V_N and carbon impurities occupying the nitrogen sites (C_N) in *h*-BN, we attribute V_N as the shallow donor and C_N as the possible deep acceptor.

The *h*-BN epilayers employed in this study were synthesized on *c*-plane sapphire substrates using MOCVD. Triethylboron (TEB) and NH₃ were serving as B and N sources, respectively.^{8–12} The excitation source in the photoluminescence (PL) measurement system is a frequency-quadrupled Ti-sapphire laser (197 nm lasing wavelength, 76 MHz repetition rate, 100 fs pulse width, and average optical power of ~ 1 mW). A monochromator (1.3 m) collects and disperses the PL signal, which was then detected by a microchannel plate photomultiplier tube.^{9,12}

Figure 1 shows the room temperature PL spectra of *h*-BN epilayer samples grown under varying NH₃ flow rates from 0.2 to 1.5 standard liters per minute (SLM) during the MOCVD growth. All other growth conditions of these samples were identical. The PL spectra of the samples were measured side-by-side. Three emission peaks around 4.1 eV region are clearly resolved at 4.12, 3.92, and 3.72 eV from the PL spectrum of the *h*-BN sample grown under an NH₃ flow rate of 0.2 SLM. These three peaks are equally spaced

^{a)}hx.jiang@ttu.edu

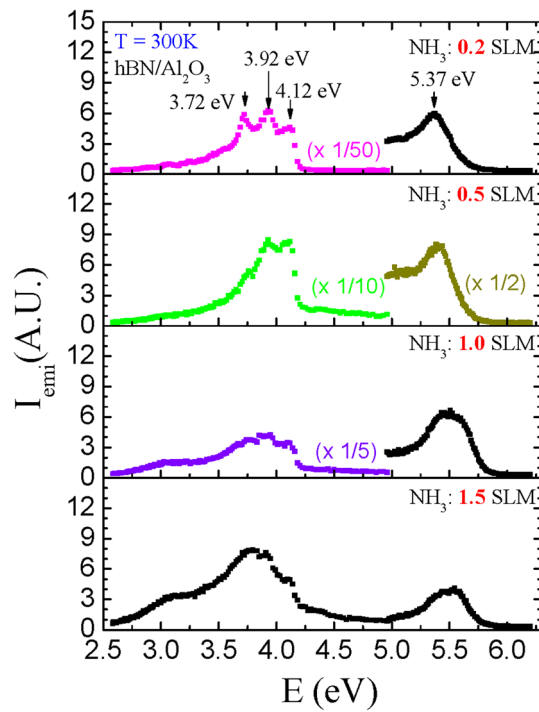


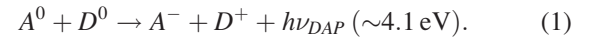
FIG. 1. Room temperature PL spectra of *h*-BN epilayers grown under different NH_3 flow rates.

with an energy separation of 200 meV. We attribute the three peaks to the same impurity related zero-phonon emission line at 4.12 eV and its phonon replicas. The phonons involved in these transitions are ascribed to the longitudinal optical (LO) phonon mode based on the observed energy separation of ~ 200 meV, which is close to the known value of LO phonons (~ 200 meV) in *h*-BN.²² A similar feature has been observed in *h*-BN polycrystalline samples, in which four emission peaks were detected near 4.1 eV with an identical energy separation of ~ 186 meV,²⁰ attributed to the impurity related main peak at ~ 4.10 eV and its phonon replicas, where the energy of the involved phonons was ~ 186 meV, which lies between the E_{2g} (169 meV) and LO phonon (200 meV) modes at the Γ point in *h*-BN.²² The phonon involved in the optical emission lines was suggested to be a local phonon mode around the involved impurities.²⁰ It is interesting to note that the phonons involved in the impurity transition observed in *h*-BN epilayers here are LO phonons, while those in *h*-BN polycrystalline samples were local phonon mode around the impurities. This may be due to the fact that our *h*-BN epilayers are single crystals as confirmed by the x-ray diffraction measurements.^{8,11}

The most striking feature exhibited in Figure 1 is that the intensity of the 4.1 eV emission line decreases rapidly with an increase of the NH_3 flow rate. The integrated emission intensity decreased by a factor of 50 as the NH_3 flow rate was increased from 0.2 to 1.5 SLM. During MOCVD growth, NH_3 serves as the source of nitrogen atoms during the formation of *h*-BN epilayers. As the NH_3 flow rate increases, more N atoms are supplied to the reaction zone, and hence, the concentrations of V_N and its related defects in the samples are decreased. The results shown in Fig. 1 provide a clear evidence that the DAP transition near 4.1 eV is associated with the presence of V_N or its related defects.

Other emission lines shown near 5.3–5.5 eV have been attributed to *g*-DAP and bound (or trapped) exciton transitions in *h*-BN.^{4,9,16,17} The emission intensity of these transitions depends weakly on the NH_3 flow rate.

The optical processes of the DAP emission line near 4.1 eV can be described by the following equation:



Its emission intensity is proportional to the product of the concentrations of the donors $[D^0]$ and acceptors $[A^0]$ according

$$I_{\text{emi}}(\text{DAP}) \propto [D^0][A^0]. \quad (2)$$

If the chemical species of D^0 is nitrogen vacancies, then we have $[D^0] = [V_N]$ and the donor concentration ($[D^0]$ or $[V_N]$) as well as the DAP emission intensity is expected to decrease with an increase of the NH_3 flow rate. On the other hand, to the first order, the rate of decrease in $[V_N]$ with increasing the NH_3 flow rate is also proportional to the total number of available V_N , or equivalently

$$d[V_N] \propto -[V_N]d(R_{\text{NH}_3}), \quad (3)$$

where R_{NH_3} is the NH_3 flow rate employed during the MOCVD growth. Note that for simplicity Eq. (3) does not take into account of other processes during the material growth such as interface chemistry and species adsorption. Deduced from Eq. (3), the concentration of V_N is expected to decrease exponentially with increasing the NH_3 flow rate

$$[V_N](R_{\text{NH}_3}) \propto e^{-\frac{R_{\text{NH}_3}}{R_0}}, \quad (4)$$

where R_0 is a proportionality constant. Figure 2 plots the integrated emission intensity of the 4.1 eV transition line, I_{emi} (~ 4.1 eV), as a function of the NH_3 flow rate (R_{NH_3}), which clearly demonstrates that the measured emission intensity decreases exponentially with increasing R_{NH_3} . The solid line is a least square fit of data with Eq. (4) with the fitted value of R_0 of around 0.28 SLM. The results shown in Fig. 2 thus strongly support the assignment that V_N is the

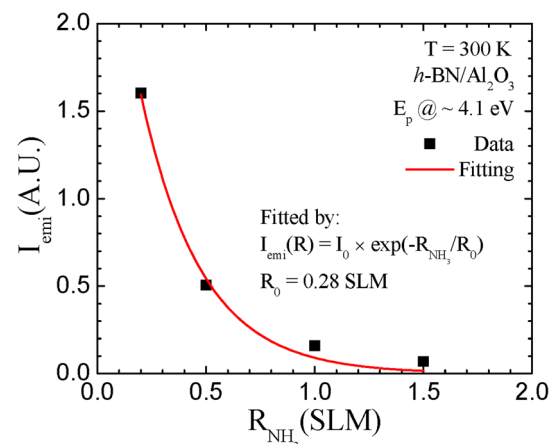


FIG. 2. Integrated PL emission intensity of the DAP transition near 4.1 eV in *h*-BN as a function of the NH_3 flow rate (R_{NH_3}).

impurities involved in the DAP transition at ~ 4.1 eV. Previous theoretical and experimental studies suggested that the formation energies of V_N and C_N in h -BN are relatively low^{19,23–27} and hence they are relatively easy to incorporate during the crystal growth of h -BN.

To determine the energy levels of the impurities involved in the DAP transition near 4.1 eV, the temperature-dependent PL spectra of the h -BN epilayer sample grown under a 1.5 SLM NH_3 flow rate were measured from 10 K to 800 K and the results are shown in Fig. 3. As shown in Fig. 3, the integrated PL emission intensity near 4.1 eV, I_{emi} (~ 4.1 eV), decreases continuously with an increase of temperature and I_{emi} (4.1 eV) at room temperature is about 1/5 of that at 10 K. Figure 4 is an Arrhenius plot of I_{emi} (4.1 eV), from which an activation energy of ~ 0.1 eV can be extracted. This energy corresponds to the shallow impurity involved in this DAP transition. Note that the energy level (~ 0.1 eV) of the shallow impurity measured from the thermal dissociation of bound impurity states alone (Arrhenius plot) may be slightly underestimated. The energy level of the deep impurity involved in this DAP transition can be deduced from $E_g - E_{shallow} - h\nu_{emi} = 6.5 - 0.1 - 4.1 = 2.3$ eV. In deriving this value, Coulomb interaction between ionized donors and acceptors has been neglected and $E_g = 6.5$ eV is used.^{1,18}

The results shown in Figs. 1 and 2 provide direct evidence that V_N is the impurity involved in the DAP transition near 4.1 eV. Local density approximation (LDA) and G_0W_0 calculation methods have provided the energy level of V_N in

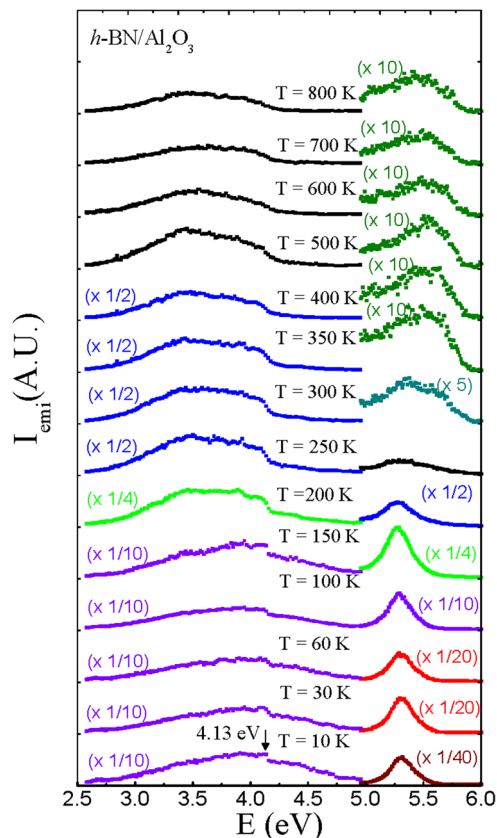


FIG. 3. Temperature dependence of the PL spectra of an h -BN epilayer grown under 1.5 SLM NH_3 flow rate measured between 10 and 800 K.

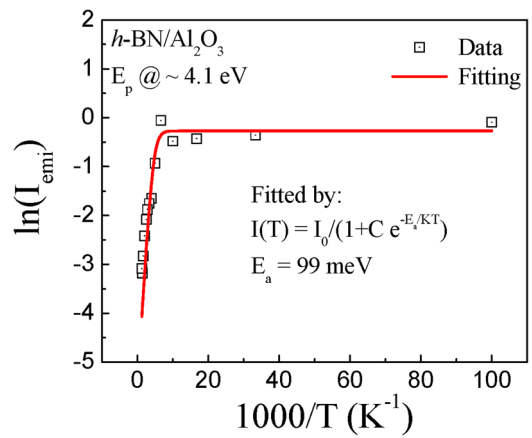


FIG. 4. Arrhenius plot of integrated PL emission intensity of the DAP transition near 4.1 eV of an h -BN epilayer grown under 1.5 SLM NH_3 flow rate.

h -BN of around 0.15 eV and 0.4 eV below the conduction band, respectively.²⁸ Other calculations also indicated that V_N is a shallow donor in h -BN.^{27,29} We therefore assign V_N to be the shallow donor involved in the DAP transition near 4.1 eV with an activation energy of ~ 0.1 eV. Our measured energy level of V_N agrees reasonably with those calculated values considering a large uncertainty among the calculated values. Among the impurities and defects in h -BN, C_N is the most probable acceptor.^{27,29} Its calculated energy levels are around 1.1 eV and 3.2 eV obtained by LDA and G_0W_0 methods, respectively,²⁸ which are in reasonable agreement with our measured value of ~ 2.3 eV for the deep impurity level involved in the DAP transition. Therefore, the assignment of the acceptor involved in the DAP transition near 4.1 eV to C_N is very plausible. The low formation energies of V_N and C_N in h -BN agree with the fact that the transition near 4.1 eV is widely observed in h -BN. Most likely, carbon impurities were originated from the boron precursor (TEB source). Both the V_N and C_N concentrations are related with the nitrogen atom supply (the NH_3 flow rate) since the concentration of C_N directly correlates with the available V_N sites. Our results suggest that both V_N and C_N impurities can be eliminated (or minimized) by growing h -BN in N-rich conditions.

It is interesting to note that the behavior of V_N in h -BN bears some similarity with V_N in AlN ,³⁰ GaN ,^{30,31} and InN .^{32,33} The DAP impurity transition in h -BN also resembles the widely observed deep-level transitions in other III-nitride semiconductors,³⁴ such as the yellow line (YL) at ~ 2.2 eV in GaN ³⁵ and the violet line (VL) in AlN at ~ 3.4 eV,^{36,37} which are also due to DAP transitions between shallow donors and deep acceptors and the elimination of these deep level impurity related transitions normally translates to enhanced material quality.³⁴ With the assignment of the involved impurities and determination of their energy levels, we are able to construct the energy diagram of the DAP transition with emission peak near 4.1 eV in h -BN, as shown in Fig. 5. In Fig. 5, V_N and C_N are attributed to the shallow donor and deep acceptor involved in this DAP transition, respectively.

In summary, we have studied the deep level impurity related DAP transition near 4.1 eV in h -BN epilayers. By

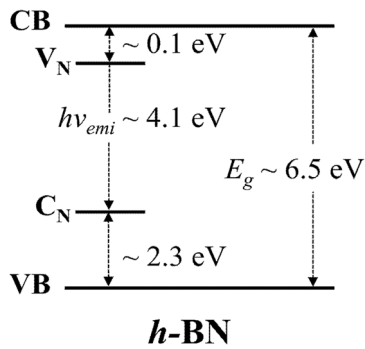


FIG. 5. Energy diagram showing the impurities and their energy levels involved in the DAP transition near 4.1 eV in *h*-BN.

comparing the PL emission spectra of a set of *h*-BN epilayers grown under different NH_3 flow rates during MOCVD growth, it was evident that V_N and C_N are the impurities involved in this transition. The temperature dependent PL spectra revealed an activation energy of the shallow impurity of ~ 0.1 eV. The energy level of the deep acceptor impurity was deduced to be ~ 2.3 eV. Based on the energy levels and theoretical insights on most probable impurities and defects in *h*-BN, we tentatively assign the shallow and deep impurities involved in this DAP transition, respectively, to the nitrogen vacancies and carbon impurities occupying the nitrogen sites. Our results indicate that by monitoring the impurity related emission peaks in *h*-BN, while varying the growth conditions, epilayers with improved optical qualities can be obtained.

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