The origins of near band-edge transitions in hexagonal boron nitride epilayers

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Photoluminescence spectroscopy has been employed to probe the near band-edge transitions in hexagonal BN (*h*-BN) epilayers synthesized under varying ammonia flow rates. The results suggest that the quasi-donor-acceptor pair emission line at 5.3 eV is due to the transition between the nitrogen vacancy and a deep acceptor, whereas the 5.5 eV emission line is due to the recombination of an exciton bound to a deep acceptor formed by carbon impurity occupying the nitrogen site. By growing *h*-BN under high ammonia flow rates, nitrogen vacancy related peaks can be eliminated and epilayers exhibiting pure free exciton emission have been obtained. © *2016 AIP Publishing LLC*.
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Hexagonal boron nitride (*h*-BN) has attracted a considerable attention recently due to its unique physical properties including wide energy bandgap (~6.5 eV), high optical emission efficiency, high chemical and temperature stability, large in-plane thermal conductivity, and large thermal neutron capture cross-section of the isotope boron-10.[1–21] Prior studies have shown that *h*-BN is a promising material for the realization of deep ultraviolet emitters and detectors[1–18] as well as solid-state neutron detectors.[19–21] However, the development of epitaxial wafer-scale semiconducting *h*-BN with high crystalline quality and low defect densities, a prerequisite for practical device applications, is still in the early stage and will benefit from a better understanding of its fundamental optical properties. Among the myriad of material characterization techniques, one of the most effective approaches is to identify the physical origins of various commonly observed impurity and defect related emission lines in *h*-BN via photoluminescence (PL) studies. Comprehensive studies on the optical emission properties of *h*-BN for materials produced under controlled growth conditions are needed in order to provide insights into approaches towards the improvement of material quality and elimination of undesired defects and impurities.

There have been several studies concerning the optical transitions in *h*-BN. A series of free exciton (or quasi Frenkel exciton) transitions in *h*-BN at above 5.77 eV have been observed in high crystalline quality bulk crystals with very small size (tens to hundreds of μm), from which a large exciton binding energy (~0.7 eV) has been deduced.[3–10] On the other hand, in most *h*-BN materials (powder-like *h*-BN, pyrolytic *h*-BN, *h*-BN thin films, and deformed *h*-BN bulk crystals), the widely observed emission lines appear around 5.5, 5.3, and 4.1 eV.[7–17] The near band edge emission lines at 5.5 and 5.3 eV have been attributed to the recombination of an exciton trapped by a structural defect (or bound to an impurity) and quasi-donor-acceptor pair (*q*-DAP), respectively.[9–14] However, the origins of the impurities involved in these transitions as well as their energy levels are still not yet fully understood due to the lack of tunable growth parameters in synthesizing bulk and powder-like *h*-BN. More recently, we have studied the origin of the transition line near 4.1 eV in *h*-BN epilayers grown by metal organic chemical vapor deposition (MOCVD) by varying the ammonia (NH_3) flow rate up to 1.5 standard liters per minute (SLM) through which the nitrogen atoms supplied during the film deposition was controlled. Together with the previous experimental and theoretical insights,[22–29] our experimental results provided a strong evidence that the 4.1 eV emission line is due to a donor-acceptor pair (DAP) recombination involving the nitrogen vacancy (V_N) shallow donor and deep acceptor formed by carbon impurity occupying the nitrogen site (C_N).[30]

In this work, a set of *h*-BN epilayers of about 0.5 μm in thickness have been grown by MOCVD on *c*-plane sapphire substrates under varying NH_3 flow rates up to 20 SLM. Boron and nitrogen precursors were triethylboron (TEB) and NH_3, respectively.[14–17] A pulsed growth scheme (alternating flows of TEB and NH_3) was undertaken to minimize the prereaction between TEB and NH_3, which is important for obtaining epilayers in hexagonal phase. Prior to the *h*-BN epilayer growth, a low temperature BN buffer layer was first deposited on the sapphire substrate. The growth temperature for this buffer layer was ~800 °C. The growth rate was around 0.4 μm/h. The PL measurement system used consists of a pulsed (76 MHz repetition rate and 100 fs pulse width) frequency-quadruped Ti-sapphire laser with an excitation wavelength at 195 nm and average optical power of ~1 mW, a monochromator (1.3 m), a microchannel plate photomultiplier tube, and a closed-cycle He refrigerator with a temperature range between 10 and 850 K.[14] PL results revealed that the emission intensities of the 5.3 and 5.5 eV transition lines decrease systematically with an increase of the NH_3 flow rate, suggesting the involvement of nitrogen vacancy (V_N) or its related impurities. More interestingly, *h*-BN epilayers grown at very high NH_3 flow rates predominantly exhibit a single emission peak at 5.735 eV for which we assigned it to the free exciton transition in *h*-BN epilayers. An energy diagram pertaining to the 5.3 eV emission line has been

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constructed to provide a better understanding of as well as methods for eliminating the dominant impurities/point defects in *h*-BN epilayers.

Figure 1 shows the low temperature (T = 10 K) PL spectra of *h*-BN epilayers grown under different NH_3 flow rates ranging from 0.3 to 20 SLM with all other growth conditions being identical. The samples were placed side-by-side during the PL spectra measurements. As shown in Fig. 1, in the samples grown under low NH_3 flow rates (between 0.3 and 1.0 SLM), two dominant emission lines around 5.3 eV and 5.5 eV are clearly resolved, corresponding to the *q*-DAP transition and bound exciton transition, respectively. However, their emission intensities decrease continuously with an increase of the NH_3 flow rate. During the growth of *h*-BN epilayers, NH_3 serves as the source of the nitrogen atoms. The calculated formation energy of V_N in *h*-BN is quite low.[22] V_N and carbon impurities occupying the nitrogen sites (C_N) are known to be two of the most common impurities in *h*-BN.[22–30] V_N is a shallow donor[27–29] with an ionization energy of about 0.1 eV,[30] whereas C_N is a deep acceptor[23,27–30] with an ionization energy of about 2.3 eV.[30] The results shown in Fig. 1 infer that the *q*-DAP emission line near 5.3 eV involves V_N. With an increase of the NH_3 flow rate, more nitrogen atoms are supplied to the reactor and hence the concentration of V_N or impurities occupying the nitrogen sites is decreased. This assignment also corroborates the fact that the 5.3 eV emission line is widely observable in *h*-BN.[7–14] However, secondary ion mass spectrometry (SIMS) measurements revealed that the BN films have excellent stoichiometry.[15] Due to the detection limits, techniques such as SIMS are unable to probe the concentrations of V_N in the MOCVD grown films.

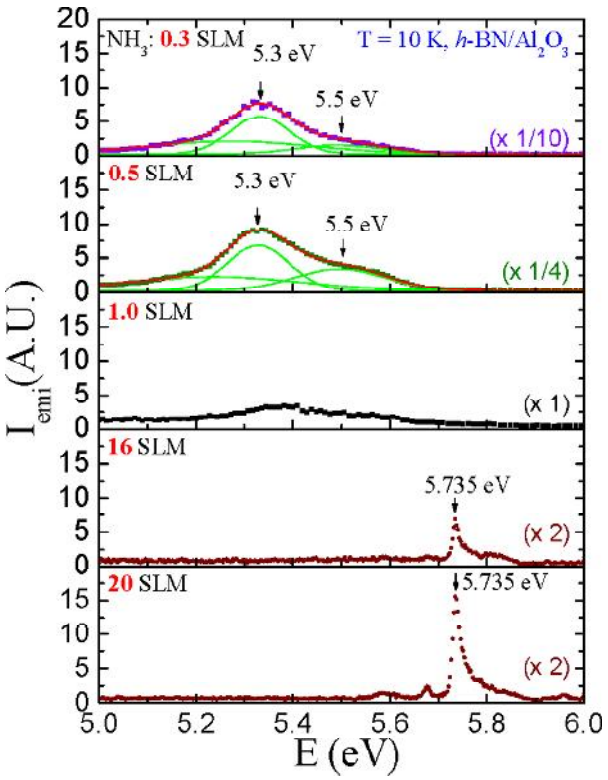

FIG. 1. 10 K PL spectra of *h*-BN epilayers grown under different NH_3 flow rates. The spectra are vertically shifted to provide a clearer presentation.

Another remarkable feature revealed in Fig. 1 is that the 5.3 and 5.5 eV emission lines disappear altogether and a sharp free exciton like emission line emerges at 5.735 eV when the NH_3 flow rate is increased to above 16 SLM. The complete elimination of the 5.5 eV emission line in *h*-BN epilayers grown under high NH_3 rates clearly speaks for the fact that the 5.5 eV emission is related to the recombination of an exciton bound to nitrogen vacancy (V_N) or to an impurity related to V_N. The results demonstrate that it is possible to completely eliminate V_N in *h*-BN epilayers by employing nitrogen-rich growth conditions. Our experimental observation is consistent with a recent first-principles calculation which suggested that the excess ammonia is expected to have a positive impact on the growth efficiency during *h*-BN deposition.[31] The free exciton emission line in *h*-BN epilayers has not been previously observed. It is interesting to note that the free exciton emission features in MOCVD grown *h*-BN epilayers are distinctly different from those of *h*-BN bulk crystals.[8–10] In *h*-BN bulk crystals, six sharp exciton emission lines (so-called S-series lines[9]) above 5.77 eV are simultaneously presented,[8–10] which have been thought to arise from the doubly degenerated dipole-forbidden (dark excitons with lower emission energies) and dipole-allowed (bright excitons with higher emission energies) exciton states, in which the dark exciton state can become allowed either due to the spontaneous or symmetry breaking caused by energy transfer from bright exciton as a result of the zero-point vibration of the lattice, or a strong spin-orbital interaction due to 2D layered structure.[3–6] On the contrary, the PL spectra of *h*-BN epilayers grown under high NH_3 flow rates (16 and 20 SLM) predominantly exhibit a single free exciton emission line above 5.7 eV. It is very likely that the mechanism to break the symmetry in *h*-BN epilayers is through the material imperfections introduced during the growth. Furthermore, the energy peak position of the exciton transition in *h*-BN epilayers is lower than those in *h*-BN bulk crystals, possibly attributed to different symmetry breaking mechanisms, strains, and material imperfections in epilayers versus in bulk crystals. Moreover, the 5.5 eV emission line can be resolved into multiple emission lines (referred as the D-series lines[9]) ranging from around 5.48 to 5.63 eV in Refs. 8–14, which are completely absent in *h*-BN epilayers grown under very high NH_3 flow rates. The D-series emission lines were believed to originate from the recombination of excitons bound to structural defects (e.g., stacking faults) or to impurities/defects.[9–14]

In the case of *h*-BN epilayers, the complete elimination of the 5.5 eV emission line in materials grown under high NH_3 rates points to the fact that the 5.5 eV emission line is related to the recombination of an exciton bound to nitrogen vacancy or to an impurity occupying the nitrogen site. Based on the energy peak positions of the exciton emission lines observed in *h*-BN epilayers here and in bulk materials (ranging from 5.7 to 5.8 eV),[8–10] the binding energy of the bound exciton (E_{BX}) related to the 5.5 eV emission line can be estimated to be around 0.2 to 0.3 eV. According to Haynes' rule, the binding energy of a bound exciton is about 10% of the impurity binding energy, neglecting the central cell correction.[32,33] This infers that the energy level of the impurity involved in the bound exciton transition at 5.5 eV is around

2 to 3 eV, which is very close to a value of ~2.3 eV for the energy level of C_N determined previously.[30] Therefore, it is highly plausible that the 5.5 eV emission line is due to the recombination of excitons bound to C_N deep acceptors (A^0,X), or I_1 type transition. We speculate that carbon impurities originate from the boron precursor (TEB source). An interesting point that is worth mentioning is that the I_1 transition (excitons bound to acceptors) is more readily observable than the I_2 type transition (excitons bound to donors) in *h*-BN epilayers, whereas in all other III-nitride semiconductors (AlN, GaN, InN), the I_2 type transition is more probable.[34,35] This is due to the fact that the Fermi level in undoped *h*-BN lies below the middle of the energy gap and undoped *h*-BN materials tend to be slightly p-type,[36] while undoped AlN, GaN, and InN tend to be n-type.[37] In this sense, *h*-BN is more like diamond[38] than other III-nitride semiconductors.

In *h*-BN epilayers grown under low NH_3 flow rates, it appears that the 5.3 eV *q*-DAP transition line involves V_N as a shallow donor. To determine the energy levels of impurities involved in the 5.3 eV transition, the temperature-dependent PL spectra for one representative *h*-BN epilayer grown under an NH_3 flow rate of 1.5 SLM were measured from 10 K to 500 K. As illustrated in Fig. 2(a), the emission intensity of the 5.3 eV emission line decreases continuously with increasing temperature, while the evolution of the emission peak position with temperature exhibits an onset temperature range in between 250 and 300 K in which the peak position hopped from 5.31 eV of *q*-DAP transition to 5.57 eV of acceptor bound exciton transition (I_1). The Arrhenius plot of the emission intensity around 5.3 eV is plotted in Fig. 2(b), in which the solid line is a least-squares fit of data with the following equation:

$$I(T) = I_0/(1 + Ce^{-E_a/KT}), \quad (1)$$

where I(T) and I_0 are the integrated PL intensities at temperature T and 0 K, respectively, C is a constant, E_a is the thermal activation energy of the PL intensity of the 5.3 eV *q*-DAP emission line, and K is the Boltzmann constant. The fitted activation energy is $E_a = 23$ meV. From our previous results,[30] V_N is a shallow donor in *h*-BN with an activation energy of $E_{shallow} \approx 0.1$ eV. Therefore, the measure E_a value of 23 meV is most likely related to the thermally activated carrier transfer process from *q*-DAP to I_1 transition. This interpretation is supported by the fact that the measured activation energy (23 meV) matches well with the onset temperature range where the PL spectral peak position change from *q*-DAP to I_1 occurred, which is between 250 K and 300 K, corresponding to a thermal energy of 21 to 25 meV. However, the energy level of the involved deep impurity can be deduced from $E_g - E_{shallow} - h\nu_{emi} = 6.5 - 0.1 - 5.3 = 1.1$ eV. In obtaining this energy level, $E_g = 6.5$ eV is used[3–8] and the Coulomb interaction between ionized donors and acceptors has been neglected. With the known presence of a deep level impurity with an energy level of about 1.1 eV, it should be possible to observe a band-to-impurity type transition by measuring the PL emission spectra in the near infrared spectral region near 1.1 eV. This is indeed the case. As shown in Fig. 3, a rather broad weak emission line with its peak energy around 1.2 eV was observed in the *h*-BN epilayer grown under an NH_3 flow rate of 1.5 SLM. This emission peak is most likely corresponding to a band-to-impurity transition between the deep acceptor involved in the *q*-DAP transition and the valence band. Previous theoretical studies have indicated that a substitutional carbon impurity on a nitrogen site could induce two deep defect levels localized on the carbon atom.[23,29] The observed deep acceptor with an energy level of 1.1–1.2 eV could also be related to the carbon impurities. With the origins being identified, it is therefore understandable that all the emission lines related to nitrogen vacancies at 4.1,[30] 5.3, and

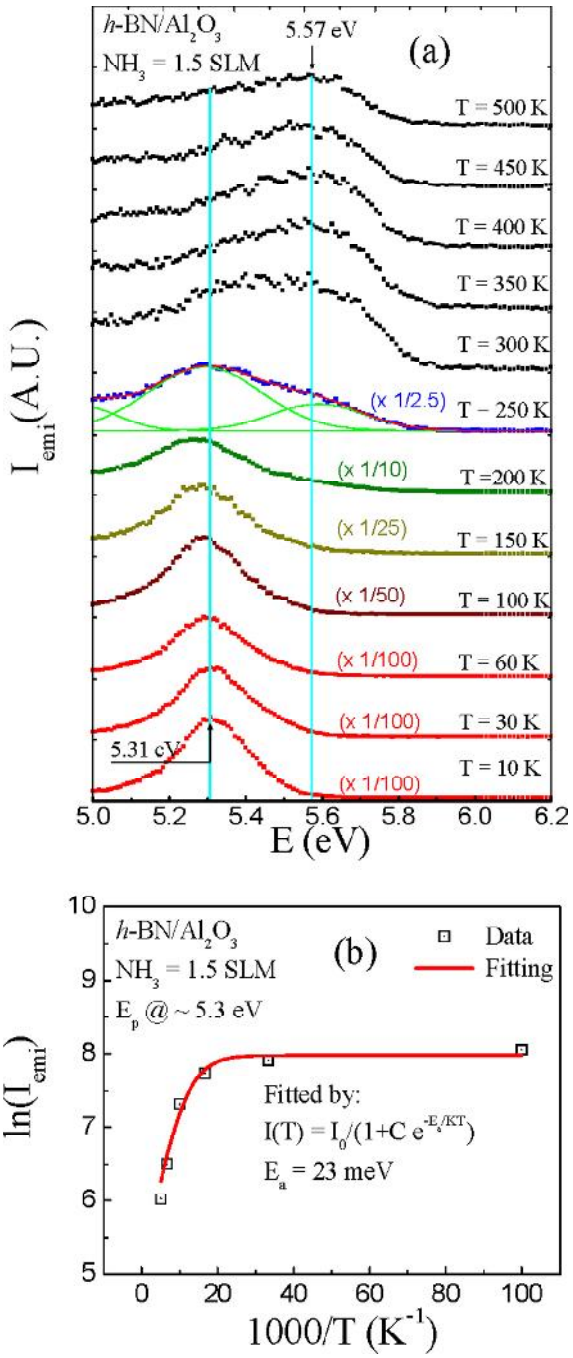

FIG. 2. Temperature dependent PL emission characteristics of an *h*-BN epilayer grown at an NH_3 flow rate of 1.5 SLM. (a) PL spectra measured between 10 and 500 K. The spectra are vertically shifted to provide a clearer presentation. (b) The Arrhenius plot of the integrated emission intensity of the *q*-DAP emission line (with a peak position at 5.31 eV at 10 K). The solid line is a least squares fit of data with Eq. (1).

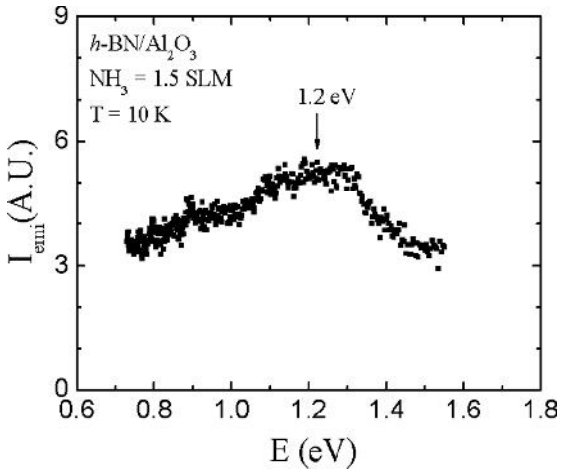

FIG. 3. A PL spectrum of an *h*-BN epilayer grown at an NH_3 flow rate of 1.5 SLM measured in the near infrared spectral region exhibiting an emission line at 1.2 eV.

5.5 eV can be minimized or completely eliminated by employing high NH_3 flow rates during the *h*-BN epilayer growth. With the determination of the energy levels involved, we have constructed an energy diagram to illustrate the optical process of the 5.3 eV transition line in *h*-BN epilayers, as depicted in Fig. 4. We believe that our results provide an improved understanding of the nitrogen vacancy related impurities/point defects as well as their effects on the optical emission properties of *h*-BN epilayers.

In summary, by controlling the NH_3 flow rate during MOCVD growth, we have observed a gradual elimination of the nitrogen vacancy and its related impurity emission peaks in *h*-BN epilayers and obtained *h*-BN epilayers exhibiting pure free exciton emission at 5.735 eV. Based on the low formation energies and the known energy levels of nitrogen vacancies (V_N) and carbon impurities occupying the nitrogen sites (C_N), we attribute the 5.3 eV *q*-DAP emission line to the transition between the nitrogen vacancy shallow donor and a deep acceptor with an energy level of 1.1 eV and the 5.5 eV emission line to the recombination of excitons bound to C_N deep acceptors. Our results demonstrate that it is possible to minimize the concentrations of V_N related impurities/point defects in *h*-BN epilayers by employing nitrogen-rich growth conditions.

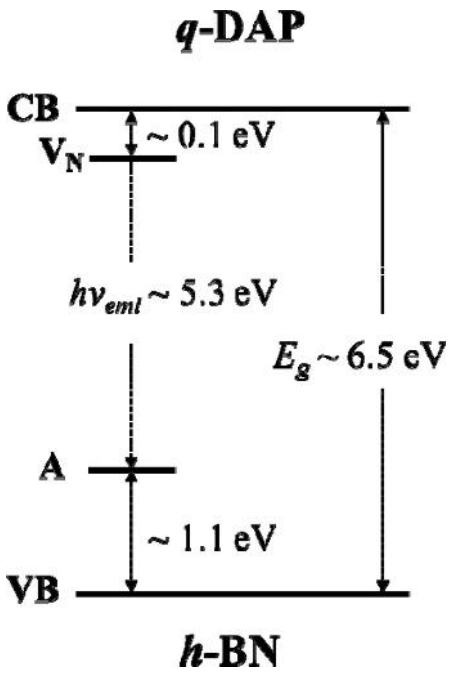

FIG. 4. Energy diagram illustrating the optical process of the widely observed 5.3 eV emission line in *h*-BN.

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