3.1 Introduction

Gallium nitride and other III-V nitride materials are under active research nowadays because of their applications in short wavelength light emitting and high power transport devices. Very rapid development has been made in the development of blue laser diodes, which has been commercialized recently. In spite of spectacular technological achievements in last few years, there still exists, substantial lack in our understanding of the basic physical properties of these materials. Of particular importance is the origin of omnipresent yellow luminescence band (YLB), which affects the efficiency and longevity of optoelectronic devices. The YLB, commonly observed in undoped and doped n-type GaN, is a broad luminescence band centered around $\sim 2.2$ eV. The intensity of YLB varies widely depending on the quality of epitaxial film. The origin of YLB is highly debated subject. YLB was first observed by Ogino and Aoki[1] and assigned to a donor-acceptor pair (DAP) recombination from a shallow donor to deep acceptor. Recently, from a optically detected magnetic resonance (ODMR) study[2], it is concluded that YLB is due to a two step process, a non-radiative but ODMR active transition from a shallow donor to a deep double donor followed by a radiative but not ODMR active transition from deep donor to a shallow acceptor. Using time resolve photoluminescence and ODMR, Hofmann et al.[3] have claimed that YLB arises from a transition from a shallow donor to a deep donor. Further investigations[4-6], using hydrostatic pressure, photocapacitance spectroscopy and positron annihilation proposed all possible transitions involving different kind of donors and acceptors. Several models have been proposed for the microscopic origin of YLB. In the beginning it was believed[7,8] to be
due to dislocation or grain boundary, but it seems to be established experimentally[3,6,9-13] and theoretically[14-17] that YLB is due to intrinsic point defect. But, so far, no clear correlation between growth conditions and YLB intensity has been identified. Generally, vacancies, interstitial, antisite and/or complexes of these native point defects, which can act as multiple donors and/or acceptors are abundant in GaN. It is therefore appalling to attribute these native point defects as a source for the ubiquitous YLB. Indeed, recent first principle calculations[14-17] show strong evidence that Ga vacancy($V_{Ga}$) or complex involving $V_{Ga}$ is the origin of YLB.

Recently, another luminescence band centered around $\sim 2.9$eV, known as blue luminescence band (BLB), is often observed[18-23] in undoped(nominally n-type) and Mg-doped p-type GaN. There is also ongoing debate regarding the origin of BLB. Several recombination models involving different kind of donors and acceptors have been proposed for BLB. Kaufmann et al[18,20] proposed a deep donor and shallow acceptor recombination model for BLB. Recently, Shahedipour and Wessel[23] have explained the origin of BLB by a model whereby the concentration of luminescent centers depend on the Fermi level position. Already, there are several suggestions regarding the microscopic origin of BLB, but it is commonly believed that like YLB, the origin of BLB is related to point defect, not to extended defect[18-23]. Two principal mechanisms have been proposed for the origin of BLB in GaN. One of them comprises transition from the shallow donor to a deep acceptor, which was assumed to isolated $V_{Ga}$ or $V_{Ga}$-complex[24,25]. In an alternate model, BLB has been attributed to transition from the deep donor N-vacancy($V_N$)-Mg complex to Mg acceptor[20].

Hence, it is evident that the issue of the microscopic origin of YLB and BLB and the recombination mechanism giving rise to these luminescence bands are much less settled. To contribute to the clarification of the situation we have performed detailed study on these luminescence bands using different optical spectroscopic techniques. Our experimental results reveal that YLB and BLB are due to same native defect or same complex involving native point defect. We have proposed that $V_{Ga}$-O$_N$ complex is responsible for BLB and
YLB. $V_{Ga-O_N}$ is a double acceptor defect and gives rise to two levels $E_1(-/-)$ and $E_2(-/0)$ with negative-U ordering[26].

3.2 Experimental Details

The samples were undoped n-type wurtzite GaN epitaxial layers grown at Kansas State University, Kansas by metal organic chemical vapor epitaxy(MOCVD) on (0001) sapphire substrates in a vertical RF-heated, rotating disk quartz reactor operated at 76 Torr. The crystalline quality of the GaN epitaxial films was evaluated by X-ray double crystal diffraction using the GaN symmetrical(002) and asymmetrical(104) reflections. Details about the samples are given in Appendix C.

The electron concentrations were measured by Hall measurements. Four Ohmic contacts in the Van der Pauw geometry were made by evaporating Al and then annealing at 600° C for 30 minutes for Hall experiments. The resistivity and Hall measurements were performed at a magnetic field of 0.4T in the temperature range of 10-300K. We have chosen two sets of samples with maximum and minimum electron concentration. The electron concentration in the first set of samples was $1-3 \times 10^{18}$ cm$^{-3}$ and $1-5 \times 10^{16}$ cm$^{-3}$ in second set of samples. Details about Hall and resistivity measurements are given in Appendix F.

The samples were housed in optical cryostat and front surface excitation was used and emitted radiation was collected for PL spectroscopy. The PL spectra were collected in the wavelength region of 340-900nm. An filter was used to block any light shorter than 340nm. The samples were kept in a closed cycle He refrigerator and were excited by 325nm laser line of Kimmon He-Cd laser. The PL signal was collected into a Jobin-Yvon grating monochromator and detected with a UV-enhanced Si detector. The excitation density was varied from 10mWcm$^{-2}$ to 1Wcm$^{-2}$. The PL data were collected with lock-in-technique using lock-in-amplifier and desktop computer. Details about PL measurements are given in Appendix G.
For photoconductivity (PC) measurements, two coplanar Ohmic contacts were made by depositing Al and subsequently annealing the samples at 600°C for 10 minutes. The Ohmic contacts have been confirmed by I-V characteristics. A quartz-tungsten halogen lamp dispersed with monochromator was used for monochromatic source at each wavelength. The intensity of light at each wavelength was kept constant using closed loop control circuit. The sample was cooled to low temperature in dark in a closed cycle helium refrigerator and was then exposed to white light or monochromatic light from a tungsten-halogen lamp. Photocurrent at different temperatures were obtained in such a way that the sample was warmed up to 320K and equilibrated for an hour. The whole cycle ensures that the data taken at each temperature have the identical initial conditions. Details about photoconductivity measurements are given in Appendix H.

3.3 Experimental Results and Discussions

Fig.1 shows the PL spectra for two GaN samples with $5 \times 10^{16} \text{cm}^{-3}$ and $2 \times 10^{18} \text{cm}^{-3}$ electron concentration. PL spectra for both samples features band edge luminescence at 3.483eV due to donor bound exciton, known as I$_2$ bound exciton[27]. The split valence band free excitons, known as A, B and C exciton can be observed in our samples at relatively high temperature (50K) and high laser power. In both samples, shallow DAP emission with zero phonon line at about 3.283eV was observed, which was followed by several phonon replicas. All samples revealed broad YLB peak centered at about 2.25eV. In addition to YLB, in the visible part of the PL spectrum another broad peak, known as BLB centered at about 2.98eV appeared either as dominant peak (in the sample with $5 \times 10^{16} \text{cm}^{-3}$ electron concentration) or as a weak shoulder to the shallow DAP peak (in the sample with $10^{18} \text{cm}^{-3}$ electron concentration). It should be remembered that both the samples are grown under identical conditions. We have observed that BLB is always dominant in nominally n-type ($n<10^{17} \text{cm}^{-3}$) samples. In highly doped ($n>10^{17} \text{cm}^{-3}$) samples, the intensity of BLB is always very weak. There are
reports that BLB can be observed either nominally n-type or p-type GaN samples[18-23]. Recently, Shahedipour and Wessel[23] have explained the origin of BLB by a model whereby the concentration of luminescent centers depend on the Fermi level position. \textit{Hence, the point defect giving rise to BLB depends on the background electron concentration i.e. on the Fermi level position. and we can conclude that BLB becomes dominant in the PL spectra in those samples, where Fermi level lies far from the conduction band minima.} At this point, let us propose a model represented by Fig.2, which shows the transitions in terms of band diagram. We propose that the YLB involves a transition from deep level E₁ to valence band
or shallow acceptor level and BLB due to transition from deep level E₂ to valence band or shallow acceptor level.

We know develop a theoretical model which allows one to deduce the concentration of the native point defect giving rise to YLB and BLB. At low temperature, the band-edge transition is due to recombination involving bound exciton (BE). The ratio of the BE and YLB PL intensity can be obtained by dividing their individual rate and can be given by [10,28]

\[
\frac{I_{YLB}}{I_{BE}} = \frac{B N_T N_A}{A N_D n p} \propto \frac{N_T}{N_D^2}
\]  

where A and B are recombination coefficients for YLB and BE transitions respectively. Under low-density photoexcitation, the free electron and hole concentrations are \( n \sim N_D \) and \( p \sim N_A \). Similarly the ratio of BE and BLB PL intensity can be given by

\[
\frac{I_{BLB}}{I_{BE}} = \frac{C N_T N_A}{A N_D n p} \propto \frac{N_T}{N_D^2}
\]  

Figure 2: Sketches of the recombination model in terms of band diagram for BLB and YLB.
where $C$ is the recombination coefficient for BLB transition. At high temperature BLB and BE transitions cannot be observed, but YLB and band to band(BB) transitions can be observed easily. It can be shown that the ratio of PL intensity of YLB to that of BB transition is given by

$$\frac{I_{YLB}}{I_{BB}} = \frac{BN_TN_A}{Dnp} \propto \frac{N_T}{N_D} \quad (3)$$

where $D$ is the recombination for the BB transition. We can assume that $N_T$ does increases with $N_D$ or $n$, which will be justified latter. This dependency can be observed in III-V semiconductors with compensating defects whose abundance increases as doping concentration increases as shown by Baraff and Schluter[29]. It has been shown[14-17,30] that due to wide band gap of GaN, self compensation effect is stronger than other III-V semiconductors and reduces both n-type and p-type doping efficiencies due to formation of $V_{Ga}$ in n-type and $V_N$ in p-type GaN. If $N_T \propto N_D$, then and the $\frac{I_{YLB}}{I_{BB}}$ and $\frac{I_{BB}}{I_{BE}}$ ratios at low temperature should decrease with electron concentration and $\frac{I_{YLB}}{I_{BB}}$ at room temperature should be independent of electron concentration, as inferred by Eqn.1, 2 and 3. Fig.3 shows (i) the ratio of the PL intensity of bound exciton(BE) to that of YLB and BLB at 10K (ii) the ratio of PL intensity of band to band(BB) to that YLB at 300K as a function of electron concentration in GaN. Indeed, it is clear from Fig.3 that $\frac{I_{YLB}}{I_{BB}}$ and $\frac{I_{BB}}{I_{BE}}$ ratios at 10K decrease with electron concentration and $\frac{I_{YLB}}{I_{BB}}$ at 300K is independent of electron concentration. We can assume[10] that deep level concentration giving rise to BLB and YLB depends on the doping concentration according to power law

$$N_T \propto (N_D)^i \quad (4)$$

and we get from Eqn.1, 2 and 3

$$\frac{I_{YLB}}{I_{BE}} \propto N_D^{i-2} \quad (5)$$
Figure 3: (a) Intensity ratio of YLB and BB luminescence intensity as a function of electron concentration at room temperature. (b) Intensity ratio of YLB and BE luminescence intensity as a function of electron concentration at 10K. (c) Intensity ratio of BLB and BE luminescence intensity as a function of electron concentration at 10K.
\[ \frac{I_{BLB}}{I_{BE}} \propto N_{D}^{i-2} \]  \hspace{1cm} (6)

\[ \frac{I_{YLB}}{I_{BB}} \propto N_{D}^{i-1} \]  \hspace{1cm} (7)

Now, we can determine the exponent i from experimental results. Fig.3 shows that the electron concentration changes over more than three order of magnitude. Using the dependence of \( \frac{I_{YLB}}{I_{BE}} \) and \( \frac{I_{BLB}}{I_{BE}} \) on electron concentration, the exponent in Eq.5 and 6 can be determined from log-log plot and we have found \((i-2)=-1\) or \(i=1\) and hence, \( N_{T} \propto N_{D} \). The exponent in Eqn.7 can determined from log-log plot \( \frac{I_{YLB}}{I_{BB}} \) vs. electron concentration and we have found \((i-1)=0\) or \(i=1\) and hence,

\[ N_{T} \propto N_{D} \]  \hspace{1cm} (8)

Thus, our low temperature as well as room temperature PL data reveals that the deep level giving rise to YLB and BLB increases linearly with doping or electron concentration.

Hence, we can conclude the origin of YLB and BLB may be same. The dependence, \( N_{T} \propto N_{D} \) from room temperature and as well as from low temperature experimental data is a signature of compensating acceptor-type native defect, which was originally proposed by Longini and Greene[31] and confirmed by first principle calculation of Baraff and Schluter[29] in GaAs. Indeed, there are several first-principle theoretical calculations[14-17,30], which have provided evidences for \( V_{Ga} \) or \( V_{Ga}-O_{N} \) as self compensating acceptor centers in n-type GaN. It has been shown that the formation energy of these point defects decreases as electron concentration increases. \( V_{Ga} \) has been detected by positron annihilation studies[6] in bulk GaN, and their concentration was found to be related to the intensity of YLB. \( V_{Ga} \)-related defect complexes in GaN ware found to have electrical properties[14] dominated by the \( V_{Ga} \), i.e. they are acceptors and exhibit gap states arising from the N dangling bonds surrounding \( V_{Ga} \). As a triple acceptor the \( V_{Ga} \) is threefold negatively charged in n-type GaN and can attract up to three positively charged donors. Recent experimental[32,33] and
theoretical work[34] suggest that oxygen at a nitrogen site($O_N$) is the main cause if unintentional n-type conductivity in GaN. Secondary ion mass spectroscopy results on our undoped n-type GaN samples reveal high concentration($\sim 5 \times 10^{18} \text{cm}^{-3}$) of oxygen. Hence, complex involving $V_{Ga}$ and $O_N$ might be more favorable energetically, because complex formation is generally driven by electrostatic forces and it is possible to conceive that negatively charged acceptor($V_{Ga}$) and positively charged oxygen donor($O_N$)(abundant in undoped n-type GaN grown by MOCVD) attract each other and gain considerable amount of energy by forming complex. Indeed, it has been shown[14,17] that the formation energy of $V_{Ga}$-$O_N$ complex much less than that of $V_{Ga}$ and $V_{Ga}$-$O_N$ can have much larger binding energy($\sim 1.8$eV) and can be more stable than $V_{Ga}$. It has also been shown that equilibrium concentration of $V_{Ga}$-$O_N$ is almost two order of magnitude more than that of $V_{Ga}$ at growth temperature of 1300K(which is the growth temperature of our samples). Furthermore, it has been shown[35] that violet luminescence band(VLB) in AlN, which is believed to have essentially the same origin as the YLB in GaN. It has been found[35] that the VLB in AlN is correlated with the oxygen concentration. It has been shown[14,16,17] theoretically using first principle local-density-functional calculation that $V_{Ga}$-$O_N$, a double acceptor with two energy levels ($-$ /$-$) and ($-/0$) and $V_{Ga}$-$(O_N)_2$, a single acceptor with two energy levels ($-/0$) and $(+/0)$ in the gap are two stable defect complexes responsible for YLB in n-type GaN. Hence, it is suggested that YLB in n-type GaN is caused by $V_{Ga}$-$O_N$ related defect complexes.

The second issue is the metastability of YLB and BLB in sample with low electron concentration. Fig.4 shows the time dependent PL spectra of GaN samples with low electron concentration($5 \times 10^{16} \text{cm}^{-3}$). As the exposure time increases, PL intensity of BLB decreases and the intensity of YLB band increases, but the PL intensity of DAP and BE don’t change with exposure time. This fatigue behavior of BLB under constant illumination is the characteristics of metastable defect level in semiconductor. The slow decay of BLB PL intensity and gradual change of color of the emitting light from blue to yellow can be easily observed by naked eye. Not all GaN samples exhibit this metastable behavior. We observe
Figure 4: Time dependent PL spectra of the same GaN samples as shown in Fig.1 under constant excitation. (a) The PL intensity of BLB center at 3eV decreases with exposure time, whereas PL intensity of YLB centered at 2.25eV increases with exposure time in GaN sample with $5 \times 10^{16} \text{ cm}^{-3}$ electron concentration. But the PL intensity of BE at 3.48eV and DAP at 3.28eV don't change with exposure time. (b) The PL intensity of YLB does not change with exposure time in GaN sample with $2 \times 10^{18} \text{ cm}^{-3}$ electron concentration. PL spectra at different exposure time shifted upward equally for clarity.
this metastable behavior in samples with electron concentration \( \leq 5 \times 10^{16} \text{cm}^{-3} \). Fig.4 also shows the PL spectra of the sample with \( 2 \times 10^{18} \text{cm}^{-3} \) electron concentration for different exposure time and we don't observe the variation of relative PL intensity of YLB. In order to investigate this metastable behavior of BLB and YLB, we have performed time resolved PL for BLB and YLB using following sequence

(i) the sample was cooled in dark at 10K and illuminated with 325nm light from He-Cd laser and decay of BLB at 420nm was measured.

(ii) illumination was switched off and the sample temperature was raised to room temperature.

(iii) the sample temperature was again brought down to 10K in dark and the same area of the sample illuminated with He-Cd laser and decay of BLB was measured.

Fig.5 shows the time resolved luminescence of BLB and YLB. After the first illumination (procedure(i)) at 10K any further measurement does not show the decay of BLB and increase of YLB with time, rather starts immediately at I(\( \infty \)) in both cases. The same decay of BLB and increase of YLB, as for first illumination can be observed only after heating the sample at room temperature and cooling down in dark (procedure (i) and (ii)). Hence, the procedure (i) induces the transition of the defects giving rise to BLB from \( E_2 \) to \( E_b \) which results increase in PL intensity of YLB. The procedure (ii) induces the thermal deexcitation from YLB to BLB. Hence, we can conclude that YLB and BLB have common origin, which is also supported from the characteristic decay(\( \tau_{BL} \)) and growth(\( \tau_{YL} \)) time of BLB and YLB respectively. In Fig.5, solid lines represent the fit according to simple exponential decay \( I_{BL}(t) = I_1 + I_2 \exp(-t/\tau_{BL}) \) for BLB decay and \( I_{YL}(t) = I_3 - I_4 \exp(-t/\tau_{YL}) \) for YLB growth with \( \tau_{BL} = 2100 \text{ sec} \) and \( \tau_{YL} = 2020 \text{ sec} \). Hence, the rate of decay of BLB is equal to the rate of growth of YLB, which also signifies the common origin of YLB and BLB.

The metastability of BLB and its correlation with YLB can be explained by the negative-U nature of \( V_{Ga-O_N} \)[36]. An impurity or any other point defect in a semiconductor can introduce several stable charged states depending on the position of the Fermi level and
Figure 5: Evolution of BLB (at 420nm) and YLB (at 560nm) with time in GaN sample with $5 \times 10^{16} \text{cm}^{-3}$ electron concentration. Solid lines are the theoretical fit with exponential decay and growth for BLB and YLB respectively.

accredingly several defect energy levels can exist inside the band gap of the semiconductor. A defect has negative-U nature if it can trap two electrons (holes) with the second one more strongly bound than the first. The onsite Coulomb repulsion energy is defined as Hubbard correlation energy $U$[37], which is the difference between two energy levels. DX center[38,39] in n-type $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is the most extensively studied negative-U defect in semiconductor. In case of negative-U, energy levels due to defect are inverted[40,41] from their usual order and the ground state can have two electrons. $V_{\text{Ga}-O_N}$ has three charge states 0, - and – with two energy levels $E_1(-/-)$ and $E_2(-/0)$ inside the band gap, as shown in Fig.6 schematically. The normal positive-U ordering of levels mean that each charge state is thermodynamically stable depending on the position of Fermi level and $E_1$ will be closer to valence band compared to $E_2$. But negative-U properties of defect mean that the energy levels are inverted from their usual order and $E_2$, instead of $E_1$ will be close to valence band. In this case no position of Fermi
level can make negative charge state thermodynamically stable and if $E_F > (E_1 + E_2)/2$, then in thermodynamic equilibrium most of the defects will be in $- -$ charge state and when $E_F < (E_1 + E_2)/2$, most of the defects will be in $0$ charge state. Hence, in heavily doped n-type samples, $E_2$ will be populated and in p-type samples, $E_1$ will be populated and in case of nominally n-type samples it will be mixture of $E_1$ and $E_2$. At the heart of the support for this negative-$U$ model is the metastability of the luminescence bands. The crucial aspect of this work is the choice of samples with different electron concentration. The sample, with high electron concentration, Fermi level will lie close to conduction band and the occupancy of deep acceptor level in the ground state with two electrons will be high. It is proposed that YLB is observed when defect is in ground state with doubly negative charge state. But, in case of samples with low electron concentration, the Fermi level will lie far from conduction band and the occupancy of the defect in zero charge state which lies close to conduction band will be high and giving rise to BLB. In case of time dependent PL experiments, the YLB will be dominant in the samples with high electron concentration and BLB band will be dominant either in the samples with low electron concentration or in p-type samples. Hence, as the electron-hole pairs are generated with above band gap light(325nm), defects
Figure 7: The growth and decay transients of the photocurrent in GaN samples with (a) $5 \times 10^{16}$ cm$^{-3}$ electron concentration, (b) $2 \times 10^{18}$ cm$^{-3}$ electron concentration. The photocurrent was excited with He-Cd (325nm) laser line.

giving rise to BLB in the zero charge state capture photoexcited electrons from conduction band, and makes a transition to doubly negative charge state, because singly negative charge state is unstable due to negative-U nature of defect. As the photoexcitation is continued, the concentration of defect in the doubly negative charge state increases with time giving rise to the growth of YLB at the expense of BLB. Positive-U ordering of energy levels can not explain this transient behavior of YLB and BLB with time.

Further support for the metastability of BLB has been given by photo-quenching experiment. Fig.7 shows the growth of photocurrent with time under illumination from 325nm He-Cd laser in GaN samples. We observe that the conductivity increases after the light exposure to the sample. When the light is switched off after 2000 sec, the light induced conductivity persists, which is known as persistent photoconductivity (PPC) and will be discussed in detail in Chapter 4. It is clear that the photocurrent of the both samples in-
creases after the light exposure. However, photocurrent shows unusual quenching behavior in sample with low electron concentration, in which case BLB is dominant and the transient behavior of YLB and BLB can be observed, but the sample with high electron concentration does not show photo-quenching behavior. We have varied photon energy and found that the photocurrent-quenching can only be observed with above band gap light and with relatively high intensity of light. Same sequence(procedure (i) to (iii)) has been followed for this experiment. Photocurrent quenching can only be observed after the first illumination at low temperature(T<50K). It can be observed again after heating the sample at high temperature(T>200K) and cooling down in dark. When the sample is illuminated with photon energy higher than the band gap of the sample, the photocurrent increases and finally should saturate after a certain period of time, which is the case in sample with high electron concentration. When the light with above band gap energy is illuminated, free electrons and holes are created. In case of sample with low electron concentration, because of difference in electron and hole effective mass, Fermi level shifts upward and the occupancy of the defect in the ground state with two electrons increases and the defects make transition from higher lying level E₂ to lower lying level E₁. This is possible by capturing electrons from the conduction band. According to negative-U model, as the singly negative charged state of defect is unstable, the defects in the zero charged state make transition to doubly negative ground state after capturing two electrons from the conduction band resulting photo-quenching. Hence, the continued illumination provides the recombination between the photoexcited electrons and the defect level at E₂. Photoquenching in the sample with low electron concentration provides evidence for the existence of acceptor level at E₂ and metastable nature of the defect in the singly charged state. In order to investigate the energy levels involved in the YLB and BLB, we have performed the photoionization experiments with different photon energies, which is shown in Fig.8. These measurements were performed at 10K on same two samples with 5×10¹⁶cm⁻³ and 2×10¹⁸cm⁻³ electron concentration. All the points but open squares were obtained by scanning the photon energy upwards from 0.9
Figure 8: The photocurrent spectra with empty circles and with empty squares were scanned by decreasing photon energy and increasing photon energy respectively in same GaN samples (a) $5 \times 10^{16} \text{cm}^{-3}$ electron concentration, (b) $2 \times 10^{18} \text{cm}^{-3}$ electron concentration.

eV to 2.5 eV. The points represented as open squares were obtained by scanning the photon energy downward from 2.5 eV to 0.9 eV. For theoretical description of the photocurrent spectra it is assumed that photocurrent $I_{PC}$ is proportional to the intensity of the absorbed light $I_{abs}(\omega) = I_0(\omega) - I(d, \omega)$, where $I_0(\omega)$ is the spectral intensity of light illuminated on the sample, $I(d, \omega)$ is the transmitted intensity of light and $d$ is the thickness of the sample. According to Lambert-Beer law the photocurrent can be given by:

$$I_{PC}(d, \omega) = C_s I_0(\omega)(1 - e^{-\alpha(\omega)d})$$

where $C_s$ is the scaling factor related to the measured photocurrent with the number of the absorbed photons and $\alpha$ is the absorption coefficient. The expression for $\alpha$ as a function of $I_{PC}$ can be given by (from Eqn.9)
Figure 9: The absorption spectra derived from photocurrent spectra (Fig.7) using Eq.10 with empty circles and with empty squares were scanned by decreasing photon energy and increasing photon energy respectively in same GaN samples (a) $5 \times 10^{16}$ cm$^{-3}$ electron concentration, (b) $2 \times 10^{18}$ cm$^{-3}$ electron concentration.

$a(\omega) = -\frac{1}{d} \ln \left( 1 - \frac{S(\omega)}{C_s} \right)$ (10)

where $S(\omega) = I_{PC}(d, \omega)/I_0(\omega)$ is the normalized photocurrent and

$C_s = \frac{S(\omega)}{1 - e^{-\alpha(\omega)d}}$ (11)

$C_s$ is independent of photon energy and calculated at $\alpha(\hbar\omega = 3.81 \text{eV}) = 1.55 \times 10^4 \text{cm}^{-1}$[43].

Fig.9 shows absorption spectra of the two GaN samples, which are transformed (using Eqn.10) from photocurrent spectra shown in Fig.8. It is clear from Fig.8 and 9, that the photocurrent and optical absorption spectra don’t show the transitions involved for luminescence bands clearly, except a threshold for photoionization at 1eV. To get clear threshold for different deep level involved in the luminescence bands, we have applied Lucovsky formula[44], which is originally proposed for absorption due to deep level defect centers in
Figure 10: The plot of $[\alpha \times \text{Energy}^2]^{2/3}$ vs photon energy derived from absorption spectra (Fig.8) with empty circles and with empty squares were scanned by decreasing photon energy and increasing photon energy respectively in same GaN samples (a) $5 \times 10^{18}$ cm$^{-3}$ electron concentration, (b) $2 \times 10^{18}$ cm$^{-3}$ electron concentration.

semiconductor. According to Lucovsky model, the absorption co-efficient changes with photon energy by following relation

$$\alpha \propto \frac{(\hbar \omega - E_i)^{3/2}}{(\hbar \omega)^{3}} \tag{12}$$

where $E_i$ is the deep level energy. Eq.12 represents the transition from a deep localized state to conduction band. Fig.10 shows the transformed spectra of variation of absorption co-efficient with photon energy according to Eq.12. The deep level involved in the luminescence bands can be obtained by linear extrapolation of the $[\alpha(\hbar \omega)^3]^{2/3}$ as a function of photon energy $\hbar \omega$ as shown in Fig.10. When the sample is first excited with low energy photons ($\sim 0.9$ eV) and photon energy is scanned upward, we observe a threshold at 0.95 eV in both samples. But, when the sample is first excited with high energy photon ($\sim 2.5$ eV) and photon energy is scanned downward, we observe the same threshold at 0.95 eV and in addition to this
we observe another threshold at 0.5eV. The deep level responsible for YLB at $E_1$ transforms to metastable singly charged negative state and the excitation of electrons from the $E_2$ state with threshold energy at 0.5eV could be observed. But, when the sample is first excited with low energy photons ($\sim 0.9$eV) and scanned upward, it was not possible to transform the doubly negative stable charge state to metastable charge state and the threshold at 0.5eV could not be observed, instead the threshold at 0.95eV was observed. The threshold at 0.5eV can be observed only at low temperature (T<50K), but the threshold at 0.95eV can be observed at high temperature. Recently, from photoionization experiment a deep level at 0.55eV from the conduction band minima has been observed\cite{45} in unintentionally doped n-type GaN. We propose that the deep levels responsible for YLB and BLB lies 0.95eV and 0.5eV below the conduction band respectively.

### 3.4 Summary and Conclusions

(i) We have observed that BLB can be observed in nominally n-type undoped GaN samples with electron concentration $\sim 5 \times 10^{16}$cm$^{-3}$ and it has been reported\cite{18-23} that BLB can be observed in p-type GaN samples. Hence, observation of BLB in GaN depends on the position of the Fermi level in the system. Occupancy of the defect giving rise to BLB increases as Fermi level lies far from the minima of the conduction band.

(ii) The dependence of the near band-edge luminescence, YLB, BLB and BB transitions and their ratios on electron concentration has been investigated. Analysis of experimental data in terms of a theoretical model based on the rate equations reveals that the concentration of native defects giving rise to YLB and BLB increases linearly with doping concentration i.e. electron concentration. We have concluded from these experimental results that the microscopic origin of both YLB and BLB is same. $V_{Ga}$-related defect complex, most probably double acceptor $V_{Ga}$-$O_N$ is responsible for YLB and BLB.

(iii) We have observed in time dependent PL and time-resolved PL that as the photoexci-
tation starts at low temperature the PL intensity of BLB and YLB decreases and increases respectively, at the same rate. These experimental results have been explained by a negative-U model of defect center responsible for BLB and YLB, which also corroborates our earlier conclusion regarding microscopic origin of BLB and YLB.

(iv) Further support for negative-U nature of the defect causing BLB and YLB has been provided by photo-quenching experiment.

(v) Finally, energy levels involved for BLB and YLB have been identified by photocurrent spectroscopy.
References

36. D. J. Chadi(private communication).