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# Free exciton transitions and Varshni's coeffecients for GaN epitaxial layers grown by horizontal LP-MOCVD

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**Abstract** – We have studied the photoluminescence properties of undoped epitaxial layers of GaN on sapphire substrate grown by horizontal low pressure metal organic chemical vapor deposition method in the temperature range of 9-300 K. At 9 K the spectra are dominated by the well resolved interband free excitons A and B as well as bound excitons. Temperature dependence of free exciton transitions was studied and Varshni's coefficients for the temperature variation of bandgap were determined.

## I. Introduction

Wide bandgap semiconductor materials have been the subject of intense research activity in the last decade, since they are the potential candidates for the development of several optoelectronic devices like blue LEDs, semiconductor lasers, UV sensors, field effect transistors, high density optical memory and digital video disc etc. Initial attempts were centered around the II-VI compounds ZnSe and ZnS with direct bandgap structure. However long device operating time could not be achieved based on these materials because of the crystallographic defects even at a lower density level of the order of $10^5$-$10^6$ $cm^{-2}$ [1]. Many breakthroughs were made recently in III-V semiconductor wide bandgap materials based on GaN which also has a direct bandgap. Recent highlights in this area include the demonstration of cw operation of InGaN laser diodes [2]. Dingle [3], Monemar [4] and Pankove [5] have done the early investigations on the electronic structure of GaN. Most of the studies on the optical properties of GaN are done by photoreflectance and few are related to photoluminescence [6-17]. In the photoluminescence generally only bound excitons are observed and it is rare to observe the well resolved free exciton luminescence. Only in high quality samples well resolved free exciton emissions can be observed. Since the photonic devices are based on the luminescence phenomena it is essential to understand the effects of various perturbations like crystal fields, spin-orbit interactions, lattice mismatch strains etc. on the emission properties. The basic understanding of the properties like bandgap and excitons is still in its infancy. Growth of high quality epilayers is still a challenge and various strategies are being explored even today. For example new substrates with multi domain structure like $LiGaO_2$ [18] and ZnO [19] were used in epitaxial growth in the latest reports. New source gases like triethyl gallium were tried in MOCVD growth [20]. We have successfully grown very good quality GaN epitaxial layers by horizontal metal organic chemical vapour deposition and observed very distinct free exciton A and free exciton B transitions. From the photoluminescence studies we infer that the quality of our epilayers is at least the same as that of the epilayers grown on the ZnO substrate which is supposed to have the best substrate properties because of its multi domain structure and closer lattice matching ($\varepsilon = 2\%$) to GaN. We have investigated the temperature dependence of free exciton transitions and Varshni's coefficients for bandgap variation were obtained for the first time from the photoluminescence spectra. The optical properties of donor bound excitons will be reported in a future communication.

## II. Experimental methods

The GaN films were grown on c-plane sapphire (0001) substrate by low pressure metal organic

chemical vapor deposition (LP-MOCVD) technique using horizontal reactor. The GaN buffer layer of 27 nm in thickness was grown at 560°C followed by undoped GaN epitaxial films at a higher temperature of 1080°C under a pressure of 100 Torr. The thickness of the epilayer is about 3.5 μm, and the film surface mirror-like, colorless, and transparent. For the cw photoluminescence experiments a He-Cd laser was used. The luminescence signal was dispersed by a McPherson 1-m monochromator and detected by Hamamatsu photomultiplier and a Lock-in amplifier of Princeton Applied Research. The samples were mounted on the cold finger of a closed cycle Helium cryostat and the sample temperature can be maintained at any desire value between 9 and 300 K.

## III. Results and discussion

The photoluminescence spectrum recorded at 9 K for GaN epilayer is shown in Fig. 1. The spectrum has four unresolved peaks which are deconvoluted into individual peaks by using a Lorentzian lineshape function. The dotted lines show the individual peaks,

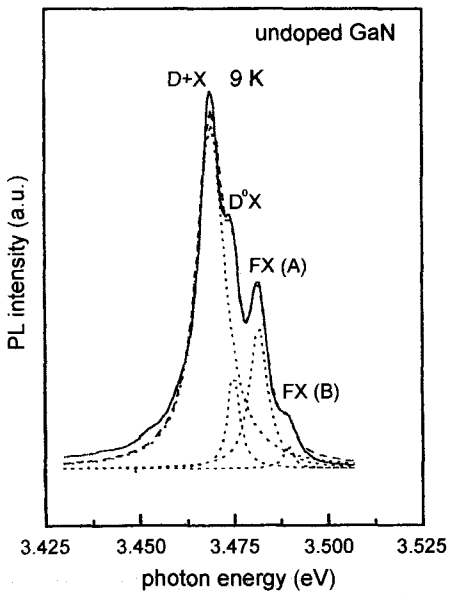


**Fig. 1.** PL spectrum at 9 K for the GaN epitaxial layer grown on (0001) sapphire substrate $D^+X$: ionized donor bound exciton, DX: donor bound exciton, FX(A): free exciton A, FX(B): free exciton B. The dotted lines show Lorentzian fitting to various transitions. The dashed line is the Lorentzian fitting of the experimental spectrum.

the dashed line shows the excellent fitting to the experimental spectrum to the Lorentzian function. The peaks are labelled as $D^+X$, DX, FX(A) and FX(B). The peak positions are 3.468, 3.474, 3.481 and 3.489 eV respectively. FX(A) and FX(B) are free exciton resonances, DX is the donor bound exciton and $D^+X$ is tentatively assigned to ionized donor bound exciton. The interpretation of these transitions was made on the basis of the values of the peak positions, halfwidths, temperature dependence and the peak separations. In this communication we will discuss only the free exciton transitions.

GaN grown on sapphire substrate has the wurtzite symmetry. The valence band is triply degenerate in the absence of any perturbations. But the wurtzite crystal field has hexagonal symmetry which lifts the degeneracy into a doubly degenerate state and a lower lying singlet state. The degeneracy is further removed because of the spin-orbit interaction and finally we have three valence bands called as A, B and C. These are also refered to as $\Gamma_9^v$, $\Gamma_7^v$ and $\Gamma_7^v$ in the order of decreasing energy. The radiative recombination of the electrons in the conduction band with the holes in these valence bands gives rise to free exciton transitions FX(A), FX(B) and FX(C), respectively. The free exciton transitions A and B observed at 3.481 and 3.489 eV are higher than those obtained from the strain free bulk GaN reported by Dingle [3] and Monemar [4]. Dingle *et al.* have performed the reflectance experiments and observed A, B and C excitons at 3.474, 3.481 and 3.501 eV, respectively. Both Dingle and Monemar have utilized bulk GaN samples. Hence these values represent the limit of strain free case. However, the epitaxial layers grown on sapphire substrate have large lattice mismatch of 13%, in addition to mismatch of thermal expansion coefficient, which develop a large amount of strain in the lattice. This is manifested as the deviation of the free exciton transition energies.

We make a very brief comparison of our exciton values with those reported in the literature. From the photoluminescence studies Volm *et al.* [7] observed A and B excitons at 3.4962 and 3.5050 eV, respectively, while Smith *et al.* [8] have given the corresponding values as 3.4857 and 3.4921 eV. Razeghi and co-workers [18] have achieved GaN epilayers on $LiGaO_2$ substrate, which has a very low lattice mismatch of only 0.9%. They have observed that the GaN thin

films grown at higher temperature of 1000°C peeled off as soon as they came in contact with the water vapor in the ambient air. They postulated that the peeling-off effect occurred because the $LiGaO_2$ substrate was damaged during the high temperature growth and became reactive with water, which reduces the adherence of the GaN epilayer. Hamdani *et al.* [19] have used (0001) ZnO substrate which has a lattice mismatch of only 2%. However in the photoluminescence spectrum they could observe only free exciton A. In the reflectance only they could resolve A and B excitons at 3.480 and 3.493 eV, respectively. The best method to remove the built in strain is to grow the epilayers on the GaN substrate. Such and attempt was recently made by Pakula *et al.* [11, 12]. However in the photoluminescence spectrum they could observe the free exciton lines only as weak lines and the spectrum was dominated by bound exciton lines. Amano *et al.* [16] investigated the connection between the strain and donor bound exciton luminescence. The deviation of the free exciton values from the strain free values in an indication of the magnitude of the strain. A comparison of the free exciton values reported by various workers obtained by different experimental methods is given in Table 1. The PL transition energies for our sample are closer to the strain free values compared to those reported by others. This means that the strain in our samples is much less and hence the misfit dislocations created must be minimum. Therefore the quality of our samples is very good.

The full width at half maximum (FWHM) of the FX(A) is 5.6 meV while that of FX(B) is 2.8 meV, which are quite narrow and again they signify the quality of our sample. These values are much smaller than those reported by Hamdani *et al.* [19] who have obtained PL and reflectance widths of the exciton transitions as 8 meV for GaN on ZnO substrate. In our case the energy separation between A and B exciton resonances is 8 meV which again is smaller than the A-B separation of 13 meV for GaN on ZnO [19]. The energy separation between A and B excitons is also an indication of the strain.

As the temperature increases the bound exciton

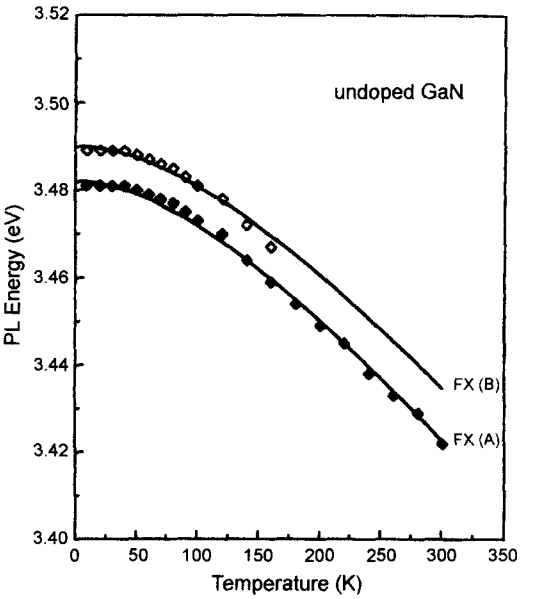


**Fig. 2.** Temperature dependence of free excitons for undoped GaN. Solid diamonds: free exciton A, open diamonds: free excition B. The solid lines are the theoretical fits to Varshni's equation.

**Table 1.** Values of free exciton transition energies, given in eV, for wurtzite GaN at low temperatures (around 10 K)

| FX(A) | FX(B) | FX(C) | Experimental method | Reference |
|---|---|---|---|---|
| 3.481 | 3.489 | – | Photoluminescence | Present work |
| 3.474 | 3.481 | 3.501 | Reflectance[a] | [3] |
| 3.4751 | 3.4815 | 3.4935 | Photoluminescence excitation[a] | [4] |
| 3.488 | 3.496 | – | Reflectance | [6] |
| 3.4962 | 3.5050 | – | Photoluminescence | [7] |
| 3.4857 | 3.4921 | – | Photoluminescence | [8] |
| 3.485 | 3.493 | 3.518 | Reflectance | [9] |
| 3.4903 | 3.4996 | 3.525 | Reflectance | [10] |
| 3.4780 | 3.4835 | 3.502 | Reflectance | [12] |
| 3.480 | – | – | Photoluminescence | [19] |
| 3.480 | 3.493 | – | Reflectance | [19] |

[a]Values are for strain free bulk GaN sample.

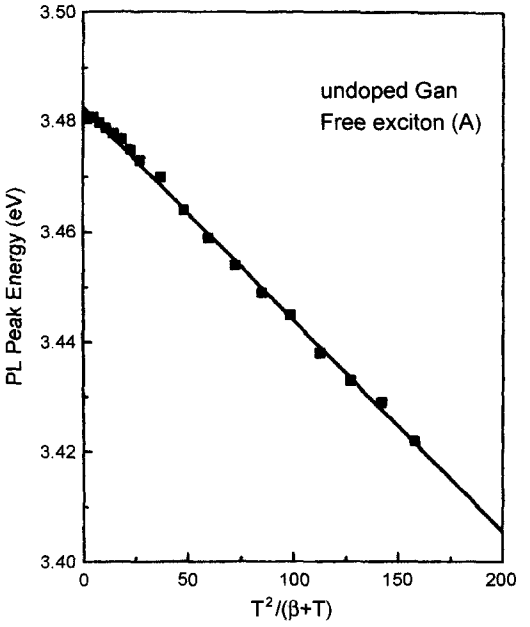


**Fig. 3.** Plot of PL peak energy as a function of $T^2/(\beta+T)$ for free exciton A.

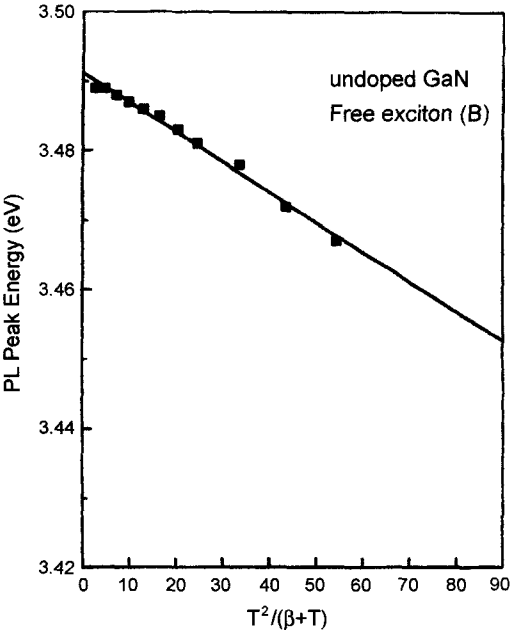


**Fig. 4.** Plot of PL peak energy as a function of $T^2/(\beta+T)$ for free exciton B.

luminescence decreases in intensity and relatively the free exciton luminescence increases. Various peak positions were obtained by Lorentzian fitting of the spectra at each temperature. Figure 2 shows the temperature dependence of the free exciton A and B peak positions. The experimental peak positions of FX(A) are indicated by solid diamonds while the open diamonds indicate those of FX(B). The experimental points were fitted to the well known Varshni's equation [21] for the temperature variation of the bandgap:

$$E(T) = E(0) - \alpha T^2/(\beta + T) \quad (1)$$

In this equation $E(T)$ is the transition energy at any temperature $T$, $E(0)$ is the energy at 0 K, is the linear coefficient and is the nonlinear coefficient. The full curves in the Figure 2 are the least square fits to the Varshni's emperical relationship. Figures 3 and 4 show the plots of PL peak energy vs. $T^2/(\beta + T)$ for free exciton A and B. The plots are straight lines and show the validity of the Varshni's equation and existence of excitons upto room temperature. Table 2 gives the Varshini's coefficients deduced by the fitting procedure for A and B exciton transitions. For comparison purposes we also included the reported values obtained from the other experimental techniques like reflectance and absorption. As can be seen from the Table there is a wide scatter in the val-

**Table 2.** Varshni's fitting parameters for the temperature variation of bandgap of wurtzite GaN

| Experimental techneque | $\alpha/10^{-4}$eV K$^{-1}$ | $\beta$ (K) | Reference |
|---|---|---|---|
| Photoluminescence of FX(A) | 3.75 | 270 | Present work |
| Photoluminescence of FX(B) | 3.75 | 310 | Present work |
| Photoluminescence of donor bound exciton | 7.2 | 600 | [3] |
| Photoluminescence excitation spectra of FX(A) | 5.08 | -996 | [4] |
| Reflectance of FX(A) | 8.32 | 835.6 | [9] |
| Reflectance of FX(B) | 10.9 | 1194 | [9] |
| Absorption | 9.39 | 772 | [15] |

ues of $\alpha$ and $\beta$ reported by various workers.

## IV. Conclusions

Very good quality epilayers of GaN were grown by LP-MOCVD. Well resolved A and B excitons were observed in the photoluminescence. Temperature dependence of these transitions was followed. Varshni's coefficients for the temperature variation of the bandgap were determined.

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