Higher lying conduction band in GaN and AlN probed by photoluminescence spectroscopy

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(Received 3 March 2006; accepted 11 May 2006; published online 30 June 2006)

Photoluminescence spectroscopy has been employed to study the band edge emissions in GaN and AlN epilayers up to 800 K. Two distinctive activation processes have been observed in both GaN and AlN. The first process occurring below T_t=325 K (T_t=500 K) for GaN (AlN) is due to the activation of free excitons to free carriers, whereas the second occurring above T_t with an activation energy of 0.29 eV (0.3 eV) for GaN (AlN) is believed to be associated with a higher lying conduction band (Γ_3) at about 0.3 eV above the conduction band minimum (Γ_1). An emission line at about 0.29 eV above the dominant transition in GaN was also observed at 700 K, corroborating the assignment of Γ_3. The values of T_t are a direct measure of the onset temperature at which free excitons dissociate into free carriers. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2217160]

III nitrides are recognized as technologically important materials for optoelectronic and electronic devices. In particular, AlN is unique due to its ultrahigh direct band gap as well as the ability of band gap engineering through the use of alloying and heterostructures with GaN and is becoming more important for III-nitride device development. For device realization, understanding the fundamental properties of these materials is crucially important. Probing the optical properties such as the temperature dependence of the band edge transitions reveals important information pertaining to the fundamental band structures, exciton and carrier recombination, and activation processes.

In undoped GaN, the dominant band edge transitions are due to the free exciton or free carrier recombination and the activation process is generally attributed to the dissociation of free excitons into free carriers.[1–9] Free excitons in AlN have a very large binding energy and hence are expected to survive well above room temperatures.[10,11] However, high temperature emission properties of GaN and AlN have not been well studied.

In this letter, we report on the growth and photoluminescence (PL) studies of the band edge transitions in GaN and AlN epilayers up to 800 K. We have observed two different activation processes. The first occurring at lower temperatures is attributed to the well-known process of exciton dissociation into free carriers, whereas the second newly observed process is an evidence for a higher lying energy level (or a satellite valley Γ_3) of about 300 meV above the conduction band minimum (Γ_1). We attribute the second activation process to the electron population into this satellite valley (Γ_3) at higher temperatures. An emission line due to the recombination between free electrons in the Γ_3 satellite band and free holes in the top most *A*-valence band has been directly observed in GaN at high temperatures, which corroborates our assignment. The results reported here are consistent with a previous result obtained by ballistic electron emission microscopy measurement, which revealed a satellite valley (Γ_3) of about 340 meV above the conduction band minimum (Γ_1) in GaN.[12] The onset temperature at which free excitons dissociate into free carriers has been determined for both GaN and AlN.

The 1 μm thick GaN and AlN epilayers were grown by metal organic chemical vapor deposition (MOCVD) on sapphire (0001) substrates. Trimethylgallium (TMGa) and trimethylaluminium (TMAl) were used as Ga and Al sources, respectively. Atomic force microscopy (AFM) reveals a crack-free smooth surface with a 1 nm roughness across a $2\times 2\ \mu m^2$ scanning area. The samples were mounted stress-free on a high temperature stage with a cold finger in a closed-cycle helium refrigerator, and the temperature was controlled between 10 and 800 K. Deep ultraviolet (UV) PL spectroscopy was employed to investigate the emission properties of these samples. The PL system consists of a frequency quadrupled 100 fs Ti:sapphire laser with a repetition rate of 76 MHz and an average power of 3 mW at an excitation photon energy of 6.28 eV and a monochromator (1.3 m).[13]

The temperature evolutions of the dominant band edge emission lines in GaN and AlN epilayers have been measured in the temperature range from 10 to 800 K and are presented in Fig. 1. For GaN, the PL signals above 700 K were below the detection limit of our system, whereas the PL emission in AlN exhibits much weaker thermal quenching effect than in GaN due to the larger band gap. In general, the spectral peak positions redshift with increasing temperature following the band gap variations with temperature.

The Arrhenius plot of the integrated PL emission intensity (I_{emi}) of the band edge transition between 150 and 700 K for GaN epilayer is shown in Fig. 2(a). The solid curves are the least squares fit of the experimental results with the following equation:

$$\ln(I_{emi}) = \ln(I_0) - \left(\frac{E_{act}}{k}\right)\frac{1}{T}, \tag{1}$$

where E_{act} is the activation energy and k is the Boltzmann constant. It is clear that there are two distinctive activation processes in GaN. The first occurring between temperatures 150 and 325 K has been well studied and is due to the dissociation of free excitons into free carriers. The measured activation energy of 26 meV is very close to the exciton

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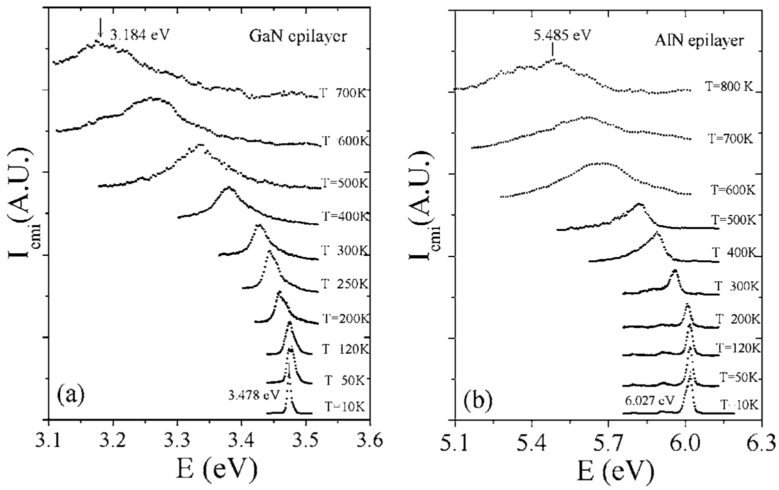

FIG. 1. (a) PL spectra of GaN epilayer measured from 10 to 700 K. (b) PL spectra of AlN epilayer measured from 10 to 800 K.

binding energy in GaN.[2–9] The second activation process occurring at elevated temperatures ($T_t > 325$ K) has not been previously observed. Above T_t(=325 K), I_{emi} decreases more rapidly with temperature and the fitted value of the second activation energy is 0.29 ± 0.01 eV. The temperature T_t, which separates the two distinctive activation processes, is also the measure of the onset temperature at which free excitons dissociate into free carriers.

A similar feature was observed for AlN epilayers. Figure 2(b) shows the Arrhenius plot of the integrated PL emission intensity I_{emi} of the band edge transition in AlN epilayer measured between 150 and 800 K. The band edge emission in AlN also exhibits two different activation processes, which, however, is separated by a temperature of $T_t = 500$ K that is much higher than that in GaN (325 K). The first activation energy of 79 meV is very close to the free exciton binding energy in AlN,[10,11] once again, suggesting that the process below T_t is due to the dissociation of free excitons into free carriers. The measured second activation energy is about 0.30 ± 0.01 eV. It is interesting to note that the onset temperature T_t is much higher in AlN than in GaN and the free excitons survive up to 500 K in AlN, which is a direct consequence of a larger binding energy of free excitons in AlN. This demonstrates the advantage of AlN for high temperature and high power device applications.

Previous ballistic electron emission microscopy measurements revealed the existence of Γ_3 satellite valley at about 0.34 eV above Γ_1.[12] Previous high-resolution reflectivity experiment performed on GaN also showed evidence for a higher lying conduction band Γ_3 at 300–400 meV above Γ_1.[14] Although, these previous experimental results are inconsistent with the generally assumed energy band structure, which predicated that the nearest satellite valley is at about 2 eV above Γ_1,[15,16] our PL results presented here support a close higher lying energy level of about 0.29 eV (0.30 eV) above the conduction band minimum Γ_1 in wurtzite GaN (AlN). The newly observed second activation process in GaN and AlN can be naturally attributed to the activation of free electrons from in the conduction band minimum (Γ_1) to the satellite valley (Γ_3) at elevated temperatures.

Recent time-resolved electroabsorption measurements[17] have revealed an electron peak velocity lower and shifted to higher field than its theoretical counterpart obtained by assuming Γ_3 is about 2 eV above Γ_1,[18] which also hinted on the existence of a more closely located satellite valley above Γ_1 band that limits the electron drift velocity. A recent theoretical model has suggested a more closely located satellite valley at about 400 meV above Γ_1.[19]

To directly probe this higher lying satellite valley, we have performed more careful measurements on PL emission spectra of GaN and AlN at high temperatures and the result obtained at 700 K for GaN is shown in Fig. 3. An emission peak at 3.474 eV is clearly resolved, which is about 0.29 eV above the dominant band edge transition (at 3.184 eV). We believe that this is a direct observation of the recombination between the free electrons in the higher lying conduction band Γ_3 and the free holes in the *A*-valence band. The energy separation (0.29 eV) obtained from the PL spectrum shown

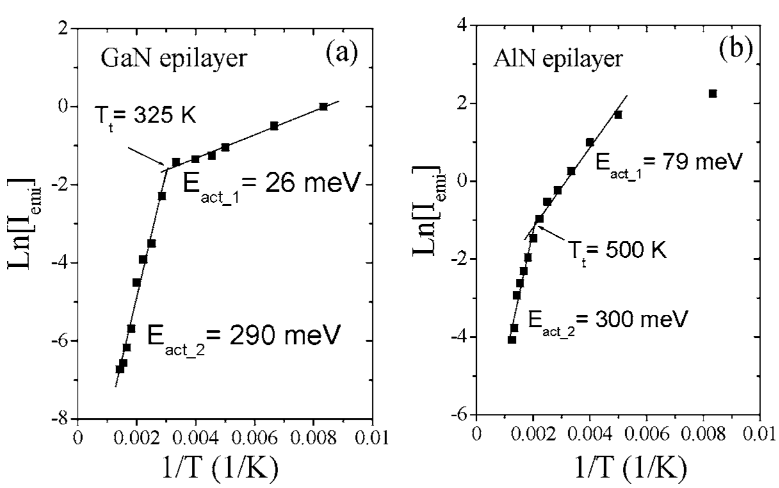

FIG. 2. (a) Arrhenius plot of the integrated PL emission intensity (I_{emi}) of the dominant band edge transition in (a) GaN and (b) AlN. The solid lines are the least squares fit of the data with Eq. (1) for two different temperature ranges. Measured values of activation energies ($E_{act,1}$ and $E_{act,2}$) are also indicated.

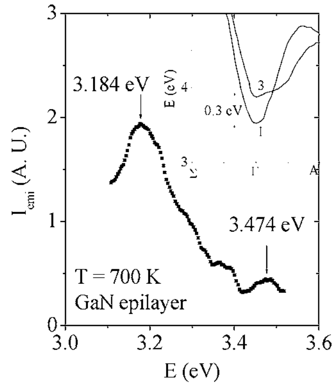

FIG. 3. PL spectrum of GaN epilayer at 700 K. A new emission peak at 3.474, which is 0.29 eV above the dominant band edge transition at 3.184 eV, is evident. The inset shows the conduction band of GaN near the Γ point (after Ref. 14).

in Fig. 3 agrees with the second activation energy measured from the temperature dependence of I_{emi} for $T > T_t$ shown in Fig. 2(a). An emission line of the same nature in AlN was not observable up to 800 K. It is possible that even higher measurement temperatures may be needed in order to directly observe this emission line in AlN.

Since wurtzite structure has four atoms per cell, there are twice as many bands per k point in the Brillouin zone (BZ) compared to that of zinc blende (Z.B.) structure. Consequently Γ_{3c} band in the wurtzite structure is the projection of L_c band in the Z.B. structure and has less symmetry compared to Γ_{1c} band.[20] Because of the folded band, the radiative recombination efficiency associated with electrons in the Γ_3 band is expected to be low. Based on the experimental observations, the conduction band of wurtzite GaN near the Γ point with the proposed Γ_3 satellite band can be constructed and is schematically shown in the inset of Fig. 3.[14]

In summary, we have studied the band edge transitions in GaN and AlN epilayers by PL spectroscopy at elevated temperatures. Two different activation processes have been observed. The first activation process was due to the dissociation of free excitons into free carriers and the second activation process was attributed to the electron population in a higher lying conduction band Γ_3 at about 290 meV (300 meV) above the conduction band minimum Γ_1 of GaN (AlN). At 700 K, a PL emission peak at 0.29 eV above the dominant band edge transition, which is associated with the Γ_3 satellite valley, was directly observed in GaN. The optically measured value of the Γ_3 satellite valley position in GaN is in good agreement with previously reported value obtained by ballistic electron emission microscopy (BEEM) measurements. The onset temperature at which free excitons dissociate into free carriers has been determined for both GaN and AlN.

The authors gratefully acknowledge useful discussions with Dr. S. H. Wei. This research is supported by grants from NSF and ARO.

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