Optical properties of AlN and GaN in elevated temperatures

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(Received 2 June 2004; accepted 17 August 2004)

Deep ultraviolet photoluminescence spectroscopy has been employed to study the optical transitions in AlN and GaN epilayers at temperatures from 10 to 800 K, from which the parameters that describe the temperature variation of the energy band gap (α and β or a_B and θ) and linewidth broadening have been obtained. These parameters are compared with the previously reported values in AlN and GaN obtained by different methods in narrower temperature ranges. Our experimental results demonstrate that the broader temperature range of measurements is necessary to obtain accurate values of these parameters, particularly for AlN. These results, together with other well-known physical properties of AlN, may expand future prospects for the application of III-nitride materials. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1806545]

Tremendous progress has been made for III-nitrides research and development in terms of both fundamental understanding as well as devices applications. AlN is a particularly unique and promising material due to the fact that no other semiconductors possess such a large direct band gap as well as the ability of band-gap engineering through the use of heterostructures. Recently, our group has grown AlN epilayers on sapphire substrates with high optical qualities by metalorganic chemical vapor deposition (MOCVD).[1] Very efficient band-edge photoluminescence (PL) emission lines have been observed at low temperature with above band-gap deep ultraviolet (UV) laser excitation. We have shown that the thermal quenching of the PL emission intensity is much smaller in AlN than in GaN and the optical quality of AlN is comparable with that of GaN.[1]

The temperature dependence of the band-gap energy and linewidth broadening of the interband transitions can provide important information about electron–phonon interactions, excitonic effects, and etc. The Varshni coefficients (α and β) of semiconductors have been extensively studied to explore the temperature dependence of the band-gap energy in other nitride semiconductors. However, it becomes problematic to determine β accurately if β becomes large, such as in the case of AlN. The temperature dependence of the band-edge transition in GaN has been studied up to about 600 K by using absorption, electroreflectance, and ellipsometry measurements,[2–6] but only to 300 K by PL measurements.[7,8] The measured parameters of α and β are scattered and sometimes controversial in GaN. Measurements in a broader temperature range are needed to obtain these parameters more accurately. Guo *et al.*[9,10] reported the Varshni coefficients of the AlN energy band-gap parameters by absorption measurements up to 300 K with large uncertainty. Since larger β is expected for AlN than GaN due to larger band gap, an even higher temperature range than that of GaN is required to determine these parameters with a certain degree of accuracy in AlN.

In this letter, we present the temperature dependence of fundamental optical transitions in AlN and GaN epilayers with high optical qualities covering a temperature range from 10 to 800 K, from which the parameters that describe the temperature variation of the band gap and linewidth broadening have been obtained. The results are compared with the previously reported values in both AlN and GaN that were deduced from measurements in narrower temperature ranges.

The 1 μm thick AlN and GaN epilayers were grown by MOCVD on sapphire (0001) substrates. Atomic force microscopy (AFM) studies upon the AlN epilayers revealed smooth surfaces (with a typically 1 nm roughness across a 2 μm $\times$ 2 μm scanning area) free of cracks. The samples were mounted on a high temperature stage with a cold finger in a closed-cycle helium refrigerator and temperature was controlled between 10 and 800 K. The deep UV laser spectroscopy system used here consists of a frequency quadrupled 100 femtosecond Ti:Sapphire laser with an excitation photon energy at around 6.28 eV (with a 76 MHz repetition rate and a 3 mW average power), a monochromator (1.3 m), and a streak camera with a detection capability ranging from 185–800 nm and a time resolution of 2 ps.[11]

Figure 1(a) shows the temperature evolution of the PL spectra from 10 to 800 K for the AlN epilayer. In general, PL emission intensity decreases with increasing temperature up to 800 K The free exciton (FX) transition at 6.027 eV is a dominant transition in AlN at 10 K, and the neutral donor bound exciton transition (or I_2 transition) is observed at the

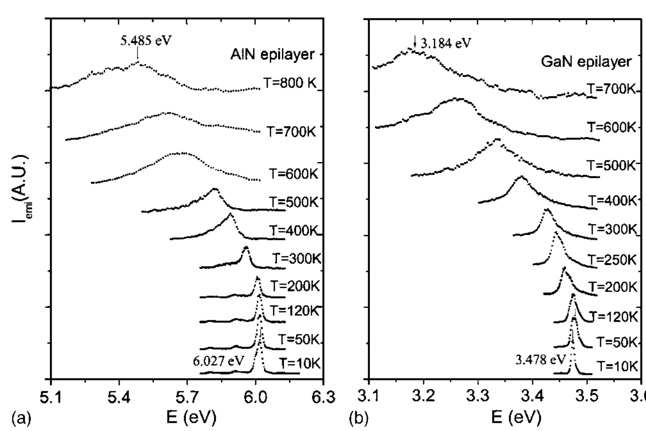

FIG. 1. (a) PL spectra of the exciton transition in an AlN epilayer measured at different temperatures from 10 to 800 K. (b) PL spectra of the exciton transition in a GaN epilayer measured at different temperatures from 10 to 700 K. The dissociation of the bound excitons into the free excitons with increasing temperature is clearly seen between 10 and 100 K. The spectra are vertically shifted for a better illustration in (a) and (b).

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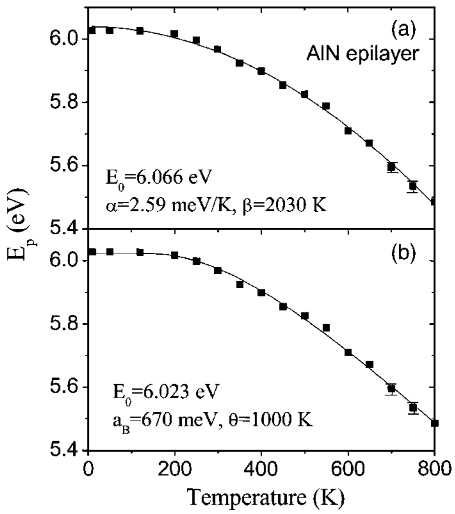

FIG. 2. Temperature dependence of the exciton emission peak position in the AlN epilayers. The solid lines are the least-squares fit of data with (a) Eq. (1) and (b) Eq. (2). The error bars are indicated for two representative measurement temperatures.

TABLE I. The parameters of α, β, a_B, θ of AlN and GaN epilayers. The shaded region indicates the reported values from high-temperature measurements (T up to 600 K) in GaN.

	α (meV/K)	β (K)	a_B (meV)	θ (K)	Temperature range (K)	Reference
AlN	1.80	1462	471	725	4–300	9,10
	2.59 (±0.30)	2030 (±100)	670 (±40)	1000 (±50)	10–800	This work
GaN	0.57	738	38	289	13–300	3
	0.50	400			10–300	8
	0.72	600			4–400	7
	1.18	1414			10–475	4
	1.28	1190	110	405	15–475	6
	1.08	745			10–624	2
	0.94	772			10–624	2
	0.86	700	126	607	110–630	5
	0.89	819	91	433		Average
	0.84 (±0.04)	789 (±30)	158 (±4)	564 (±20)	10–700	This work

lower-energy side around 6.011 eV. Energy peak position of the FX transition varies slightly for samples grown under different conditions (from 6.027 to 6.060 eV). This is most likely due to different magnitudes of strain involved, similar to the case in GaN. For instance, our recently grown samples show peak positions at 6.060 eV for the FX transition. The spectral peak positions of the FX transition red-shift from 6.027 eV at 10 K to 5.485 eV at 800 K, which is quite typical in semiconductors due to the band-gap variation with temperature.

For comparison, the temperature evolution of the GaN PL spectra was also measured and plotted from 10 to 700 K in Fig. 1(b). The temperature behavior of the GaN PL spectra is very similar to that of AlN. PL emission intensity decreases with increasing temperature up to 700 K. The PL signal of the GaN epilayer above 700 K was too weak and below the detection limit of our PL system. This comparison clearly demonstrates the advantage of AlN over GaN for many applications in elevated temperatures.

The PL spectral peak position of AlN as a function of temperature is plotted in Fig. 2. In obtaining the results shown in Fig. 2, we have fitted the PL spectra near the emission peaks by the Guassian functions to accurately determine the peak positions. As shown in Fig. 2(a), the temperature dependence of the transition energies can be well described by the Varshni empirical equation

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

where $E(0)$ is the transition energy at 0 K, α and β are the Varshni coefficients.[12] The value of α represents the slope of E_g versus temperature at high temperatures, while the band gap follows $-\alpha T^2/\beta$ at low temperatures. The fitted values of α and β are 2.59 meV/K and 2030 K in AlN, respectively. The slope of E_g versus temperature at high temperatures measured directly from the data between 500 and 800 K is about 2.40 meV/K, which is close to the fitted value of $\alpha = 2.59$ meV/K obtained from Eq. (1). Guo *et al.*[9,10] reported the Varshni coefficients of $\alpha = 1.80$ meV/K and $\beta = 1462$ K for AlN epilayer by absorption measurements up to 300 K, which are about 40% smaller than our values obtained here. To identify the discrepancy, we have also fitted our data with Eq. (1) in a relatively low-temperature range between 10 and 300 K. Apparently, we were unable to obtain any reasonable fitting due to large mean deviations over 80%, which indicates that a broader temperature range is needed to determine these parameters accurately in AlN. The mean deviations of fitted values of α and β using the data between 10 and 800 K are less than 10%. The obtained values of $E(0)$, α, and β are listed in Table I.

As illustrated in Fig. 2(b), the temperature dependence of the interband transition energies can also be described by the Bose–Einstein expression

$$E(T) = E(0) - 2a_B/[\exp(\theta/T) - 1], \quad (2)$$

where a_B is the strength of the average exciton–phonon interaction and θ is the average phonon frequency (in the unit of temperature).[13,14] The fitted values for AlN are $a_B = 670$ meV and $\theta = 1000$ K, which are again about 40% larger than the values of $a_B = 471$ meV and $\theta = 725$ K obtained by Guo *et al.*[9,10] This discrepancy is also due to a temperature range about three times narrower in the previous measurements as compared to ours. The reported mean frequency of phonon is 940 K in AlN,[15] which agrees very well with the value we obtained, $\theta = 1000$ K.

The PL spectral peak position of GaN as a function of temperature is plotted in Fig. 3 and was also fitted with Eqs. (1) and (2). The fitted values are $\alpha = 0.84$ meV/K and $\beta = 789$ K, which are about three times smaller than those of AlN ($\alpha = 2.59$ meV/K and $\beta = 2030$ K). The fitted values of $a_B = 158$ meV and $\theta = 564$ K are also obtained for GaN. Since the strength of the average exciton–phonon interaction (a_B) in AlN (670 meV) is four times stronger than that in GaN (158 meV), the longitudinal optical (LO) phonon replicas of the exciton transition are expected to be more enhanced in AlN than in GaN, as demonstrated in the 10 K PL spectra of Figs. 1(a) and 1(b). The reported mean frequency of phonon is 790 K in GaN,[15] which is a little larger than the value of $\theta = 567$ K obtained here.

In Table I, we summarized the results of α, β, a_B, and θ of AlN and GaN obtained here together with previously reported values obtained from different techniques and temperature ranges.[2–10] By averaging previous reported values, the averaged values of $\langle\alpha\rangle = 0.89$ meV/K and $\langle\beta\rangle = 819$ K,

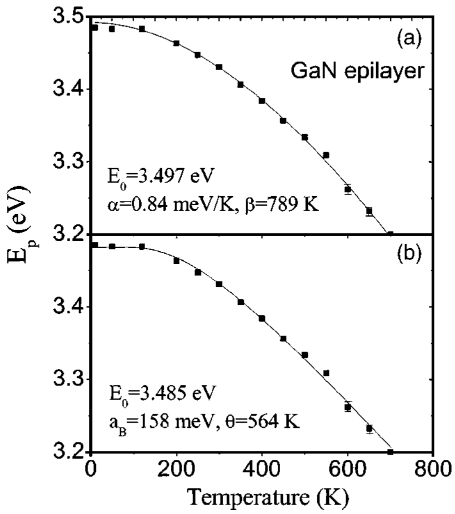

FIG. 3. Temperature dependence of the exciton emission peak position in the GaN epilayer. The solid lines are the least-squares fit of data with (a) Eq. (1) and (b) Eq. (2). The error bars are indicated for two representative measurement temperatures.

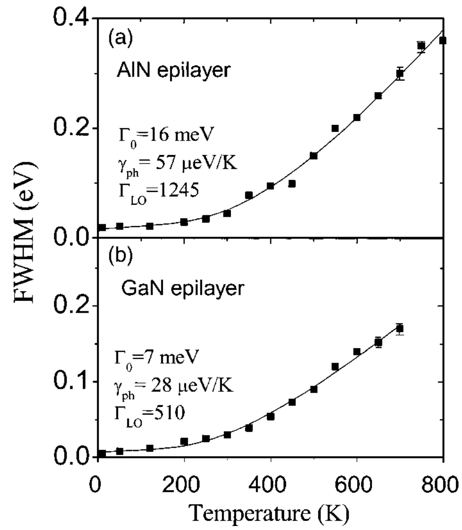

FIG. 4. PL emission linewidth as a function of temperature for AlN and GaN epilayers. The solid lines are the least-squares fit of data with Eq. (3) for (a) AlN and (b) GaN. The error bars are indicated for two representative measurement temperatures.

$\langle a_B \rangle = 91$ meV, and $\langle \theta \rangle = 433$ K are obtained for GaN. Our results of $\alpha = 0.84$ meV/K and $\beta = 789$ K in GaN are very close to the averaged values of $\langle \alpha \rangle = 0.89$ meV/K and $\langle \beta \rangle = 819$ K. The shaded region indicates the previously reported values obtained from high-temperature measurements (T up to 600 K) in GaN. Our results of α, β, a_B, and θ are closer to the values obtained from a broader temperature range measurements ($T > 600$ K) than those from narrower temperature ranges ($T < 475$ K). It is obvious that a broader temperature range of measurements provides more accurate values of these parameters, even for GaN. It was believed that these parameters could depend on the measurement and growth techniques. Our results clearly point out that the temperature range of measurements is the most critical factor in determining these parameters accurately. The mean deviations of our obtained parameters are about 3% for GaN and vary from 5% to 10% for AlN, which provides a very narrow range of these parameters. Overall, the Bose-Einstein expression of Eq. (2) fits better to the data for both AlN and GaN epilayers than the Varshni expression of Eq. (1). There is little report on standard deviations of the previously reported values.

Figure 4 shows the full width at half maximum (FWHM) of PL emission lines as a function of temperature for AlN and GaN epilayers. The FWHM can be described by

$$\mathrm{FWHM}(T) = \Gamma_0 + \gamma_{\mathrm{ph}} T + \Gamma_{\mathrm{LO}} / [\exp(h\nu_{\mathrm{LO}}/kT) - 1] \qquad (3)$$

where Γ_0 is the intrinsic linewidth at 0 K arising due to electron–electron interaction, impurity, and dislocation, γ_{ph} is electron–acoustic phonon coupling constant, and Γ_{LO} is the strength of electron–LO phonon interaction.[14] The LO phonon energies ($h\nu_{\mathrm{LO}}$) were taken as 110 and 90 meV for AIN and GaN, respectively.[15] The fitted values for AlN are $\Gamma_0 = 16$ meV, $\gamma_{\mathrm{ph}} = 57$ μeV/K, and $\Gamma_{\mathrm{LO}} = 1245$ meV, while those for GaN are $\Gamma_0 = 7$ meV, $\gamma_{\mathrm{ph}} = 28$ μeV/K, and $\Gamma_{\mathrm{LO}} = 510$ meV. The FWHM of AlN increases from 16 meV at 10 K to 380 meV at 800 K, while that of GaN increases from 7 meV at 10 K to 170 meV at 700 K. At low temperatures, the linewidth increases with temperature due to the electron–acoustic phonon interaction. The electron–LO phonon interaction becomes important above 200 K and eventually dominant at high temperatures for both AlN and GaN. Besides the intrinsic linewidth at 0 K(Γ_0), the obtained values of γ_{ph} and Γ_{LO} in AlN are almost two times larger than those of GaN, implying stronger exciton–phonon interaction in AlN than GaN.

In summary, we have investigated the temperature dependence of the bandgap and linewidth in AlN and GaN epilayers by using deep UV PL measurements from 10 to 800 K. Our obtained values of α β, a_B, and θ in AlN are about 40% larger than the values reported previously. Our experimental results demonstrate that a broader temperature range of measurements is necessary to obtain accurate values of these parameters, particularly for AlN. The obtained values of γ_{ph} and Γ_{LO} in AlN are found to be two times larger than those of GaN, implying stronger exciton–phonon interaction in AlN than GaN.

This research is supported by grants from the NSF, DOE, and ARO.

[1] J. Li, K. B. Nam, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **81**, 3365 (2002).
[2] H. Teisseyre, P. Perlin, T. Suski, I. Grezegory, S. Porowski, J. Jun, A. Pietraszko, and T. D. Moustakas, J. Appl. Phys. **76**, 2429 (1994).
[3] M. O. Manasreh, Phys. Rev. B **53**, 16425 (1996).
[4] A. J. Fisher, W. Shan, J. J. Song, Y. C. Chang, R. Horning, and B. Goldenberg, Appl. Phys. Lett. **71**, 1981 (1997).
[5] J. Petalas, S. Logothetidis, and S. Boultadakis, M. Alouani, and J. M. Wills, Phys. Rev. B **52**, 8082 (1995).
[6] C. F. Li, Y. S. Huang, L. Malikova, and F. H. Pollak, Phys. Rev. B **55**, 9251 (1997).
[7] M. Ilegems, R. Dingle, and R. A. Logan, J. Appl. Phys. **43**, 3797 (1972).
[8] A. K. Viswanath, J. I. Lee, S. Yu, D. Kim, Y. Choi, and C. H. Hong, J. Appl. Phys. **84**, 3848 (1998).
[9] Q. Guo and A. Yoshida, Jpn. J. Appl. Phys., Part 1 **33**, 2453 (1994).
[10] Q. Guo, M. Nishio, H. Ogawa, and A. Yoshida, Phys. Rev. B **64**, 113105 (2001).
[11] http:/www.phys.ksu.edu/area/GaNgroup
[12] Y. P. Varshni, Physica (Utrecht) **34**, 149 (1967).
[13] R. R. Reeber and K. Wang, MRS Internet J. Nitride Semicond. Res. **6**, 3 (2001).
[14] P. Lantenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **35**, 9174 (1987).
[15] *Gallium Nitride and Related Semiconductors*, edited by J. H. Edgar, S. Strite, I. Akasaki, H. Amano, and C. Wetzel (Inspec, London, 1999).