Variation of GaN valence bands with biaxial stress and quantification of residual stress

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Low-temperature reflectance data on epitaxial GaN thin-film samples covering the widest range of tensile and compressive stress (−3.8–3.5 kbar) thus far explicitly show the nonlinear behavior of the B–A and C–A splittings versus the energy of the A exciton. Lineshape ambiguities that hindered previous interpretations have been resolved with reciprocal-space analysis, allowing us to obtain band parameters such as $\Delta_{SO}=17.0\pm1$meV with increased confidence. © *1997 American Institute of Physics.* [S0003-6951(97)02815-5]

With the achievement of the first multilayer nitride laser structure,[1] the task of quantifying residual strain in GaN films becomes more pressing. Although optical methods are convenient for this application, they require the analysis of A, B, and C excitonic lineshapes, a process thus far plagued by ambiguities. Here we address this problem by first studying GaN layers designed to represent the widest range of residual in-plane strain available thus far and by second analyzing lineshapes in reciprocal space, where critical point energies are determined independent of baseline artifacts to ±0.5 meV. With the energies E_A, E_B, and E_C of the A, B, and C excitons known to this precision over a wider range of in-plane strain, parameters such as the spin-orbit splitting $V_{SO}=17.0\pm1$meV are calculated with increased confidence. These data also unambiguously show the nonlinear dependence of the excitonic energy splittings ΔE_{BA} and ΔE_{BC} on the energy E_A of the A exciton, confirming our earlier application[2] of the Hopfield model.[3]

Data were obtained with a single-beam low-temperature reflectometer consisting of a Xe arc lamp and a Cary 14 monochromator whose resolution is better than 1 meV at 3.4 eV. Measurements were done on samples cooled to 10 K with an Air Products cryotip, although other temperatures were also used to confirm assignments. The GaN layers examined were grown by (1) metal organic chemical vapor deposition (MOCVD) on Al_2O_3 substrates with 250 Å GaN buffer layers, (2) hydride vapor phase epitaxy (HVPE) on Al_2O_3 substrates without buffer layers, and (3) MOCVD on 6H−SiC substrates with 1000 Å AlN buffer layers. These shall be referred to as Category 1, 2, and 3 samples, respectively. Details of crystal growth are given elsewhere.[4–6]

A selection of reflectance spectra is shown in Fig. 1 in order of descending excitonic energy separation $\Delta E_{BA}=E_B-E_A$. Exciton energies determined by reciprocal-space analysis[7] are indicated by the points; the historical lineshape of Dingle *et al.*[8] is shown in (d) with the original assignments indicated by the arrows. Our lineshape analysis indicates that ΔE_{BA} and ΔE_{CA} are closer to 5 and 23 meV, respectively, rather than the 6.0 and 20.5 meV reported in Ref. 8.

Figure 1(a) is typical of reflectance spectra of category (1) films. The feature farthest to the left is an interference oscillation; the excitonic features of interest lie to the right. Here ΔE_{BA} and ΔE_{CA} are 9.2 and 27.8 meV, respectively; however, real-space assignments for the same sample yield $\Delta E_{BA}=11$ meV and $\Delta E_{CA}=34$ meV. The other category (1) samples exhibit similar discrepancies as a result of baseline ambiguities. Reciprocal space ΔE_{BA} values are as shown in Table I, but the real-space values for category (1) samples were all ~11 meV. Reliance on real-space analysis in this case would have led us to incorrectly corroborate the work of Orton,[9] who, performing a similar Hopfield model[3] calculation on a few samples grown only on Al_2O_3 concluded that ΔE_{BA} was invariant. Reciprocal-space analysis is sufficiently sensitive to detect the non-negligible variation of ΔE_{BA} for a sample set varying by only 0.5 μm in thickness.

We observe a similar pattern in a sample set within category (3), a 1.32 μm representative of which is shown in Fig. 1(g). These samples are all in the 1.03 to 1.45 μm thickness range, grown on 6H−SiC with 1000 Å AlN buffer layers, and have $\Delta E_{BA}<2$meV with ΔE_{CA} values ranging from 14.2 to 20.4 meV. For this set, the growth temperature of each sample is given in Table I, providing a rationale for the observed variation of ΔE_{CA}. Reciprocal-space analysis confirmed these assignments by showing that in each case $|\Delta E_{BA}|$ could not have exceeded 2 meV; our temperature-dependent reflectance data also support this interpretation. However, as in the case of the category (1) samples, it is premature to conclude that ΔE_{BA} has a single value for ma-

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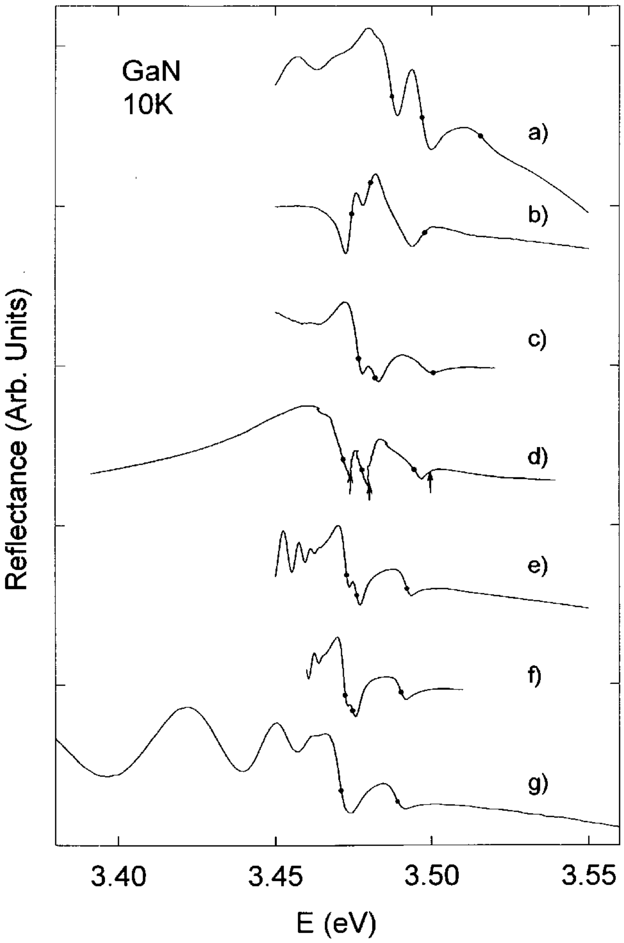

FIG. 1. Representative GaN lineshapes. Reciprocal space assignments of threshold energies are given by points. From top, after Table I: (a) category 1, sample 4; (b) category 2, sample 5; (c) category 3, sample 8; (d) Dingle referenced lineshape (Ref. 2); (e) category 3, sample 7; (f) category 3, sample 6; (g) category 3, sample 12.

terial grown on 6H–SiC. The spectra shown in Figs. 1(e) and 1(f) were obtained from category (3) samples 3.10 and 3.71 μm thick, respectively, and exhibit ΔE_{BA}, ΔE_{CA} values of 3.4, 19.7 and 2.5, 18.1 meV, respectively.

Though category (3) samples tend to show smaller ΔE_{BA} splittings than those grown on $\mathrm{Al_2O_3}$, a general conclusion of this nature would be premature. Figure 1(c) shows a category (3) sample with $\Delta E_{\mathrm{BA}}=6.2$ meV and $\Delta E_{\mathrm{CA}}=23.9$ meV. Such values are typical for GaN grown on $\mathrm{Al_2O_3}$[8,10–15] and are in fact similar to the 250-μm-thick category (2) sample shown in Fig. 1(b) with $\Delta E_{\mathrm{BA}}=6.7$ meV and $\Delta E_{\mathrm{CA}}=23.5$ meV. This result indicates that there is no *a priori* correlation between substrate material and observed excitonic splittings.

To interpret these data, we follow the conventional approach; i.e., we apply the quasicubic model of Hopfield.[3] Neglecting anisotropic relaxation, we can determine the relationship between the in-plane stress $\sigma_{xx}=\sigma_{yy}=\sigma_{11}$ and the in-plane ($\epsilon_{xx}=\epsilon_{yy}=\epsilon_{11}=\epsilon_{22}$) and out-of-plane ($\epsilon_{zz}=\epsilon_{33}$) strains from the known elastic constants of GaN.[16] After Nye,[17] we have $\{C\}^{-1}\equiv\{S\}$and $\epsilon_{ij}=S_{ijkl}\sigma_{kl}$. Assuming that $\sigma_{11}=\sigma_{22}$ and that all remaining $\sigma_{ij}=0$, we find

$$\begin{aligned}\epsilon_{11}&=[C_{11}+C_{12}-2(C_{13}^2/C_{33})]^{-1}\sigma_{11}\\&=(4.18\times10^{-12}\ \mathrm{Pa}^{-1})\sigma_{11},\end{aligned}\tag{1a}$$

$$\epsilon_{33}=(-4.93\times10^{-12}\ \mathrm{Pa}^{-1})\sigma_{11}.\tag{1b}$$

The hydrostatic, and therefore the in-plane strain, can be obtained within an additive constant E_{A0} from the measured gap energy E_{A} and the deformation potential a according to the empirical expression $E_{\mathrm{A}}=E_{\mathrm{A0}}+a\epsilon_{\mathrm{H}}$, where $\epsilon_{\mathrm{H}}=\Delta V/V=\epsilon_{11}+\epsilon_{22}+\epsilon_{33}$, $E_{\mathrm{A0}}=3.477$ eV,[18] and $\alpha\approx-10$ eV. Thus the B–A and C–A splittings can be plotted versus E_{A} as shown in Fig. 2. For the data of Fig. 2, we find that σ_{11} ranges from -3.8 compressive to 3.5 kbar, tensile, suggesting, not surprisingly, that the epitaxial material can withstand roughly equal amounts of tensile and compressive stress. Recalculation of ranges of stress reported by previous workers[10] according to the above, using the reported energy position of the A exciton, shows that the previously reported range of -12.8–-0.8 kbar (compressive) is actually -3.8 (compressive) to 1.2 kbar (tensile).

Given ϵ_{xx}, ΔE_{BA}, and ΔE_{CA} can be written in the quasicubic model as

TABLE I. Summary of GaN samples and corresponding growth parameters.

Sample category		Growth technique	Substrate material	Thickness (μm)		Film growth temp. (°C)	E_{A} (eV)	ΔE_{BA} (meV)	ΔE_{CA} (meV)
1.	I	MOCVD	$\mathrm{Al_2O_3}$	2.7+0.025	GaN buffer	1050	3.4857±0.5	8.6±1	26.5±1
2.	I	MOCVD	$\mathrm{Al_2O_3}$	2.7+	GaN buffer	1050	3.4900	7.1	34.7
3.	I	MOCVD	$\mathrm{Al_2O_3}$	2.6+	GaN buffer	1030	3.4890	8.3	30.9
4.	I	MOCVD	$\mathrm{Al_2O_3}$	2.2+	GaN buffer	1050	3.4876	9.2	27.8
5.	II	HVPE	$\mathrm{Al_2O_3}$	250		1050	3.4743	6.7	23.5
6.	III	MOCVD	6H–SiC	3.7+0.1	AlN buffer	1050	3.4724	2.5	18.1
7.	III	MOCVD	6H–SiC	3.1+	AlN buffer	1050	3.4729	3.4	19.7
8.	III	MOCVD	6H–SiC	2.0+	AlN buffer	1050	3.4767	6.2	23.9
9.	III	MOCVD	6H–SiC	1.5+	AlN buffer	975	3.4726	<2	20.4
10.	III	MOCVD	6H–SiC	1.4+	AlN buffer	1025	3.4651	<2	14.2
11.	III	MOCVD	6H–SiC	1.4+	AlN buffer	975	3.4680	<2	16.3
12.	III	MOCVD	6H–SiC	1.3+	AlN buffer	975	3.4709	<2	18.9
13.	III	MOCVD	6H–SiC	1.3+	AlN buffer	1075	3.4668	<2	14.8
14.	III	MOCVD	6H–SiC	1.0+	AlN buffer	975	3.4668	<2	18.8

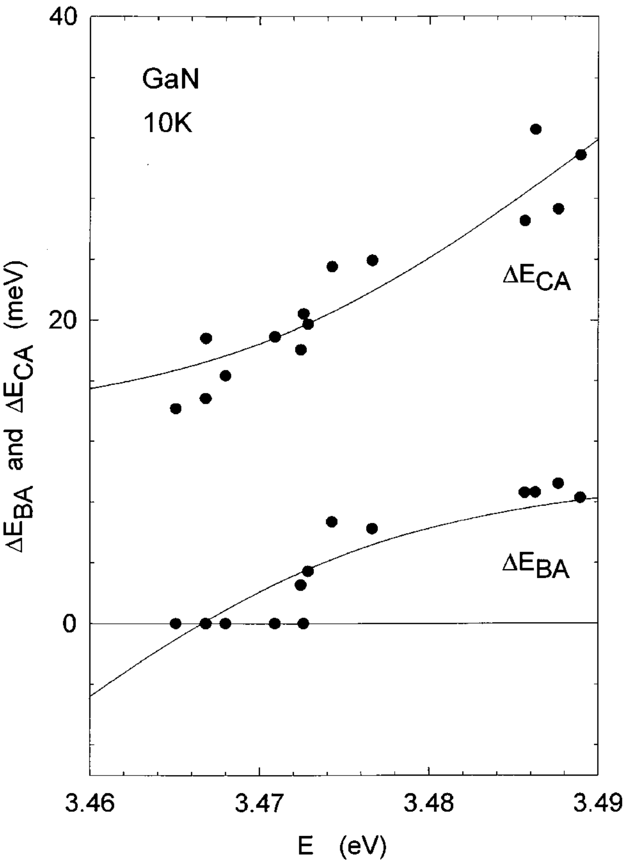

FIG. 2. Excitonic energy splittings ΔE_{BA} and ΔE_{CA} vs energy position of the A exciton; data shown by points. Least squares fit shown by straight lines. Note the nonlinear character of the fit.

$$\Delta E_{\mathrm{BA}},\ \Delta E_{\mathrm{CA}}=(E_{\mathrm{B}}-E_{\mathrm{A}})=2\Delta_2+\frac{1}{2}(\Delta_1-\Delta_2+\Theta_\epsilon) \pm\sqrt{\left(\frac{\Delta_1-\Delta_2+\Theta_\epsilon}{2}\right)^2+2\Delta_3^2} \qquad (2)$$

following the notation of Ref. 19. Here $\Theta_\epsilon = k\epsilon_{xx}$ is the shear term, $\Delta_1=\Delta_{\mathrm{CR}}$ is the crystal-field potential, and $\Delta_2=\Delta_3=1/3\Delta_{\mathrm{SO}}$, where Δ_{SO} is the conventional spin-orbit splitting parameter. Since ΔE_{AB} and ΔE_{AC} are determined experimentally, and since the independent variable Θ_ϵ can be expressed in terms of ϵ_{xx}, then Δ_1 and $\Delta_2=\Delta_3$ are the adjustable parameters for the least-squares fit shown in Fig. 2 by the solid lines. Best fit parameters are $\Delta_{\mathrm{CR}}=9.8\pm 1$ meV and $\Delta_{\mathrm{SO}}=17\pm 1$ meV. Δ_{SO} is significantly larger than earlier values[8,9] and the current theoretical estimates,[20,21] though similar to that of Gil *et al.*,[10] based on a linear approximation to the correct variation of the valence band energies with strain. In fact, our data clearly cannot be represented by a straight line, in contrast to the data and linearization formulas offered in Ref. 10. This has recently also been recognized by Gil *et al.*[22] in a revision of their earlier work on this topic. Although our wider range of data show more scatter than the more narrow range of previous workers,[10,22] we believe (1) that this scatter is due to partial violation of the 1:1 connection assumed between hydrostatic and shear strain, and (2) that it is logical to assume that any partial, anisotropic relaxation would occur differently for each sample represented in a set of dissimilar samples.

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