Optical properties of GaN grown on Si (111) by gas source molecular beam epitaxy with ammonia

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We report a study of the optical properties of GaN grown on Si(111) by gas source molecular beam epitaxy with ammonia. Temperature dependence of edge luminescence was studied in the range of 77–495 K for samples with low background carrier concentrations, as determined by capacitance voltage profiling and Raman spectroscopy, and the results were fitted using Passler's and Varshni's models. We also demonstrate strong correlation between electron concentration in GaN and relative Raman intensity of A_1 (longitudinal optical) and E_2^2 modes. The binding energy of free excitons is estimated to be 29 ± 2 meV. The contributions of different mechanisms to free exciton line broadening are discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1430535]

INTRODUCTION

Silicon is a very attractive substrate for the growth of gallium nitride due to advantages such as low cost, well-developed postgrowth processes, high thermal conductivity, and large diameter of available wafers.¹ Nitride-based device structures grown on silicon by molecular beam epitaxy (MBE) have been recently demonstrated.^{2–8} Using gas source MBE (GSMBE) with ammonia, nitride layers can be grown at high temperatures,^{9,10} required to achieve device-quality optical and electrical properties.¹¹

GSMBE can be used to grow high quality AlN^{12,13} and GaN^{14–16} on Si(111). High growth temperature for AlN, combined with carefully controlled formation of the Si–N–Al interface layer¹⁶ at the onset of epitaxy, result in very rapid transition to two-dimensional growth mode of AlN and the subsequent GaN. Additional short period blocking superlattices (SLs) of AlGaIn/GaN and GaN spacers reduce dislocation propagation to the upper GaN layer.¹⁷ They also stabilize residual tensile stress level and the resulting layers are free of cracks.¹⁴ All GaN layers studied here were grown at a temperature of 1050 ± 20 K and growth rates of 0.4–1.1 $\mu\text{m/h}$. Formation of a (2×2) surface structure, characteristic of two-dimensional growth, could be seen after deposition of 20–100 nm of GaN. The total thickness of the GaN samples varied from 0.4 to 2.5 μm . Details of the growth can be found elsewhere.^{12,14,16,17}

While the structural perfection of nitride layers grown by GSMBE on Si(111) is by now well established,^{17,18} the optical properties, such as temperature dependence of the band gap and the contribution of different mechanisms to free exciton line broadening are not well known.

In this article we describe optical studies of high quality GaN layers grown on Si(111) by GSMBE with ammonia. For this investigation we select samples with low background carrier concentration. Since the background electron concentration varies from low 10^{16} to high 10^{18} cm^{-3} , depending on growth conditions, careful sample selection is needed to distinguish intrinsic optical properties. When nitride layers are grown on Si substrates, which are conducting, determination of their carrier levels is not simple.¹⁹ We use a combination of capacitance–voltage profiling, with mercury and gold Schottky barriers, and Raman spectroscopy for sample selection. Optical properties of samples with the background electron concentration of $\sim (1-5) \times 10^{16} \text{ cm}^{-3}$ were investigated by photoluminescence (PL) excited by a 2 kW pulse (10 ns, 100 Hz) nitrogen laser operating at a wavelength of 337.1 nm. Sample temperature was varied from 77 to 495 K.

Raman measurements were made at room temperature using 488.0 nm laser excitation. Spectra were collected in a direct backscattering $z(y,y)\bar{z}$ polarization configuration using a Raman microprobe.²⁰ We find that Raman measurements can be used to estimate free carrier concentration. This technique has the advantage of being rapid and contactless. Figure 1 shows a series of Raman spectra taken from GaN/Si samples having different free-carrier concentrations n due to the growth under stoichiometric and nonstoichiometric conditions.²¹ Spectrum 1 is that of a sample grown at stoichiometric conditions and growth rate of 0.57 $\mu\text{m/h}$. This growth rate was found to result in the lowest background level. The narrow E_2^2 phonon, at 565 cm^{-1} , dominated all spectra. A weaker band was observed near 733 cm^{-1} . At low n this peak is related to the A_1 longitudinal optical (LO) phonon. As the free-carrier concentration increases (spectrum 2 and 3), this band shows reduced intensity, and exhibits a broader, asymmetric shoulder at higher energy.

LO phonons in polar semiconductors interact with free-carrier plasmas to produce mixed LO phonon–plasmon bands, usually denoted by L^- and L^+ .²² The L^+ appears at

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FIG. 1. Room temperature Raman spectra of GaN with different background electron concentrations. The spectra are normalized to the same E_2^2 intensity. (1) GaN grown under stoichiometric conditions and optimal growth rate of $\sim 0.57 \mu\text{m/h}$; $n = 1.3 \times 10^{16} \text{ cm}^{-3}$; (2) GaN grown under stoichiometric conditions and high growth rate of $\sim 0.9 \mu\text{m/h}$; $n = 1.5 \times 10^{17} \text{ cm}^{-3}$; and (3) GaN grown under Ga-rich condition and growth rate of $\sim 0.5 \mu\text{m/h}$; $n = 1.0 \times 10^{18} \text{ cm}^{-3}$.

the $A_1(\text{LO})$ phonon frequency at low carrier concentrations, and blueshifts with increasing n . We used the well-known model applied to GaN in Ref. 23 to determine the carrier concentration in our GaN samples based on the L^+ energy and line shape. The filled circles of Fig. 2 compare the values of n determined from analyzing the L^+ band with those obtained from Capacitance-Voltage ($C-V$) measurements. The agreement is excellent. However, the analysis fails at concentrations below $4 \times 10^{16} \text{ cm}^{-3}$ because the L^+ becomes indistinguishable from the $A_1(\text{LO})$ phonon.

The presence of the $A_1(\text{LO})$ phonon band, which should not appear due to the interaction with free-carrier plasmas, can be attributed to the existence of a near-surface depletion region.²⁴ Since the scattering intensity of the residual $A_1(\text{LO})$ is proportional to the width of the depletion region, it decreases with increasing n . Assuming that the E_2^2 phonon intensity is directly proportional to the total epilayer thickness d of the transparent GaN layer, we can use this intensity as an internal standard provided we normalize it by d . When normalized this way, the relative intensity $I_{\text{rel}} = I(A_1)/$

FIG. 2. Correlation between electron concentration, obtained from $C-V$ measurements, and relative Raman intensity (open circles), and from analysis of the phonon-plasmon coupled mode (filled circles). I_{REL} is the relative intensity of the $A_1(\text{LO})$ phonon band to that of the E_2 phonon normalized to the layer thickness. With this calibration curve we estimate carrier concentration using a polynomial fit $\log(n) = 16.0 - 2.6a - 0.735a^2$.

FIG. 3. PL spectra of GaN/Si(111) taken as a function of temperature.

$(I(E_2)/d)$ should be proportional to the width of the depletion region. The open circles of Fig. 2 show the dependence of the relative intensity on n determined by $C-V$. The polynomial fitting of this dependence yields: $\log(n) = 16.0 - 2.6a - 0.735a^2$, where $a = \log(I_{\text{rel}})$. The dependence is not simple at high carrier concentrations, because the Fermi level can be influenced by surface states present, for example, due to oxidation. From our analysis, relative intensity can be used as a rapid means for estimating free-carrier concentrations in epitaxial (less than $8 \mu\text{m}$ thick) n -type GaN without the deposition of contacts. The calibration in Fig. 2 is valid for 488 nm excitation and $z(y,y)\bar{z}$ polarization configuration. The calibration changes with either a different laser wavelength or polarization condition. The Raman measurements were used to identify suitable samples for PL study. Narrow linewidth of the E_2^2 phonon demonstrated high sample quality in all cases, and the E_2^2 energy allowed us to determine the stress. The stress was found to be $\leq 0.3 \text{ GPa}$ and independent of epilayer thickness when an AlN buffer layer, followed by a series of short-period SLs separated by GaN spacers,¹⁴ was used.

The room temperature PL spectrum of the best GaN samples shows a free exciton (FE) peak at 3.408 eV with full width half maximum (FWHM) of less than 40 meV and weak “yellow” luminescence at $\sim 2.2 \text{ eV}$. We did not find strong dependence of either the exciton peak or “yellow” luminescence intensity on the number of blocking SL and GaN spacer layers. PL spectra taken at different temperatures in the range from 77 to 495 K are presented in Fig. 3. At elevated temperatures ($T > 100 \text{ K}$) the PL spectra are dominated by the FE recombination.^{25,26} At temperatures below 100 K bound exciton-related optical transitions contribute to the edge peak spectral contour.²⁵

Integrated PL emission intensity I of the FE band versus temperature is presented in Fig. 4(a). The intensity of FE transition decreases with increased temperature due to thermal activation, and can be described by

$$I(T) = I_0 / [1 + \exp(-E_a/kT)], \quad (1)$$

where we assume the same activation energy for $A(n=1)$ and $B(n=1)$ excitons.²⁷ The fitted value of the activation energy E_a is $29 \pm 2 \text{ meV}$, in agreement with published data for A -exciton binding energy.^{28,29} Some deviation of experimental $I(T)$ dependence from the exponential law at high

FIG. 4. Temperature dependences of intensity of exciton peak, band gap energy, and FWHM of exciton peak: (a) the temperature dependence of the integrated PL intensity of the FE peak: (squares) experiment; (curves) calculations for different activation energies in Eq. (1) (from 19 to 37 meV). The best fit corresponds to $E_a = 29 \pm 2$ meV; (b) the experimental temperature dependence of the band gap energy (shown by circles). Line (1) Passler's model fit for parameters listed in the text; (2) Varshni's model fit; (3) GaN layer (under tension) grown by MOCVD on SiC (data recalculated from Ref. 34); (4) Strain free bulk GaN grown by HVPE (Ref. 35). (c) The temperature dependence of FWHM of the exciton-related PL peak, (squares) experiment, (curve) best fit of Eq. (2).

temperatures ($T > 450$ K) can be explained by nonradiative recombination processes. The value obtained for E_a can be used to estimate the band gap of GaN as the sum of the FE energy plus the value of E_a ($E_g = E_{FE} + E_a$). The main mechanisms of the temperature induced gap shrinkage are: (i) a change of lattice parameters (this also occurs when pressure is applied to a crystal) and (ii) the electron-phonon interaction. According to Ref. 30 the first mechanism contributes about 14% of the total E_g shrinkage in bulk GaN. Thus, the second mechanism is dominant. The temperature dependence of the band gap is presented in Fig. 4(b). The solid line (1) represents the best fit to Passler's model:³¹ $E_g(T) = E_g(0) - (\alpha\Theta/2) \{ [1 + (2T/\Theta)^p]^{1/p} - 1 \}$, where $E_g(0) = 3.495$ eV is the band gap at $T = 0$ K, $\alpha = 0.53$ meV/K is the gap shrinkage coefficient, $\Theta \sim 400$ K is the effective phonon temperature, and $p = 2.6$. Here $p = \nu + 1$ is the power coefficient from the power law electron-phonon spectral function $f(\varepsilon) = (\nu\alpha/k)(\varepsilon/\varepsilon_0)^\nu$ and $\varepsilon \equiv \hbar\omega$ is phonon energy.

At temperatures higher than Θ ($T \gg \Theta$) the electron-phonon interaction mechanism is approximately linear. At low temperatures ($T \ll \Theta$) this mechanism is very weak. According to Ref. 31, the effective phonon temperatures of group IV, III-V, and II-VI materials are nearly proportional to the respective Debye temperatures (Θ_D): $\Theta \sim (2/3)\Theta_D$. The fitted value of $\Theta = 400$ K is in good agreement with this relation and the known $\Theta_D \sim 600$ K.³² Varshni's³³ approxi-

TABLE I. Parameters used to fit Varshni's equation: $E_g(T) = E_g(0) - \gamma T^2/(T + \beta)$.

Sample type	γ (meV/K)	β (K)	Ref.
GaN/Si(111)	0.77	600	This work
GaN/sapphire	0.72	600	38
GaN/sapphire	0.939	772	30
Bulk GaN crystal	0.74	600	34
Bulk GaN crystal	1.08	745	30

mation [Fig. 4(b), curve 2] for the band gap energy shrinkage ($E_g(T) = E_g(0) - \gamma T^2/(T + \beta)$) gives the following parameters: $\gamma = 0.77$ meV/K, $\beta = 600$ K. Here γ represents the $T \rightarrow \infty$ limit of $-dE_g(T)/dT$, and β is comparable to the Debye temperature Θ_D . The fitted parameters are in good agreement with those found previously for GaN layers grown on SiC and sapphire substrates (see Table I).

The temperature dependence of the band gap energy of a GaN layer grown by metalorganic chemical vapor deposition on 6H-SiC substrate³⁴ and of a stress-free bulk GaN crystal grown by HVPE³⁵ are also presented in Fig. 4(b) as lines 3 and 4, respectively. GaN grown on Si lies closer to the stress-free GaN than does the GaN grown on SiC. We attribute this to lower stress. Stress of ~ 0.5 – 1 GPa arises in GaN/SiC primarily due to differences in thermal expansion coefficients of GaN and SiC and high growth temperature. We estimate the tensile stresses in our GaN/Si samples to be in the range 0.08–0.3 GPa, which is in good agreement with our Raman measurements.¹⁴

The temperature dependence of the FWHM of the FE recombination peak is presented in Fig. 4(c). At low temperature the dependence is linear. At higher temperatures (above 200 K) a deviation from the linear dependence is observed. The FE linewidth can be described by³⁶

$$\Gamma_{1/2} = \Gamma_I + \Gamma_{ac} + \Gamma_{opt}, \quad (2)$$

where Γ_I is the inhomogeneous linewidth due to defects and strain, Γ_{ac} is the contribution from acoustic phonon scattering of the excitons ($\Gamma_{ac} = \sigma T$), and Γ_{opt} is due to exciton scattering by LO phonons. The effect of exciton scattering can be described by $\Gamma_{opt} = \nu / [\exp(E_{LO}/kT) - 1]$.³⁷ The best fit of Eq. (2) to our data is shown in the inset of Fig. 4, and the parameters used are listed in Table II. The results of our analysis are in good agreement with those reported in Ref. 36. However, their linewidth Γ_I is smaller, possibly due to lower defect concentration or lower inhomogeneous stress.

In conclusion, the GaN/Si material grown by GSMBE with ammonia¹⁴ exhibits low stress. The temperature dependence of the band gap is close to that of stress free bulk GaN crystals and well described by Passler's and Varshni's models. We studied the contributions of different mechanisms of the FE line broadening. At low temperatures of ~ 100 – 300 K

TABLE II. Parameters used to fit Eq. (2).

Γ_I (meV)	σ (meV/K)	ν (meV)	Reference
11.5	0.035	100	This work
2	0.018	210	36

the dominant line broadening mechanism is the inhomogeneous line broadening due to defects and inhomogeneous stress, while at high temperature above 400 K the dominant line broadening mechanism is the effect of exciton scattering with LO phonons. We show strong correlation between electron concentration in GaN, obtained from $C-V$ measurements and relative Raman intensity of $A_1(\text{LO})$ and E_2^2 modes of GaN.

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