Photoluminescence and reflectance spectroscopy of excitonic transitions in high-quality homoepitaxial GaN films

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We report on highly resolved photoluminescence (PL) and reflectance (RF) spectra of a homoepitaxial GaN layer grown by metal-organic vapor phase epitaxy. This sample exhibits narrow linewidths of several PL emission peaks, down to ≈100 μeV full width at half maximum for some bound exciton transitions. As a consequence, we have detected new PL features as, e.g., a fivefold fine structure of the donor-bound exciton line at ≈3.471 eV, and other known PL transitions could be determined with high precision. In RF measurements, the extraordinary quality of the epitaxial layer allowed observation of weakly damped excitonic ground-state transitions and of narrow excited exciton transitions with high signal-to-noise ratio.
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I. INTRODUCTION

GaN is presently one of the most intensely studied materials owing to important applications in transport and optical devices. However, evaluation of basic optical parameters, such as the energy of the lowest free exciton transition, the excitonic Rydberg energy, or the binding energy of the residual donor found in nominally undoped GaN layers, is often difficult due to strained growth on lattice mismatched substrates, e.g., sapphire, or broad and little detailed spectra. These parameters can be best determined from a sample with low background charge, carrier concentration grown in a homoepitaxial growth process on a GaN substrate as in the present report. Here, we apply low-temperature photoluminescence (PL) and reflectance (RF) techniques to detect spectra with unusual rich and sharp structures. The experimental data are evaluated using a model of damped oscillators in a polarizable medium.

II. EXPERIMENT

The sample used in the present work is a high quality 1.5-μm thick metal-organic vapor phase epitaxy (MOVPE) grown GaN layer on a single-crystal GaN substrate. The detailed production process of the substrate is reported elsewhere.[1] Prior to the growth of the homoepitaxial layer,

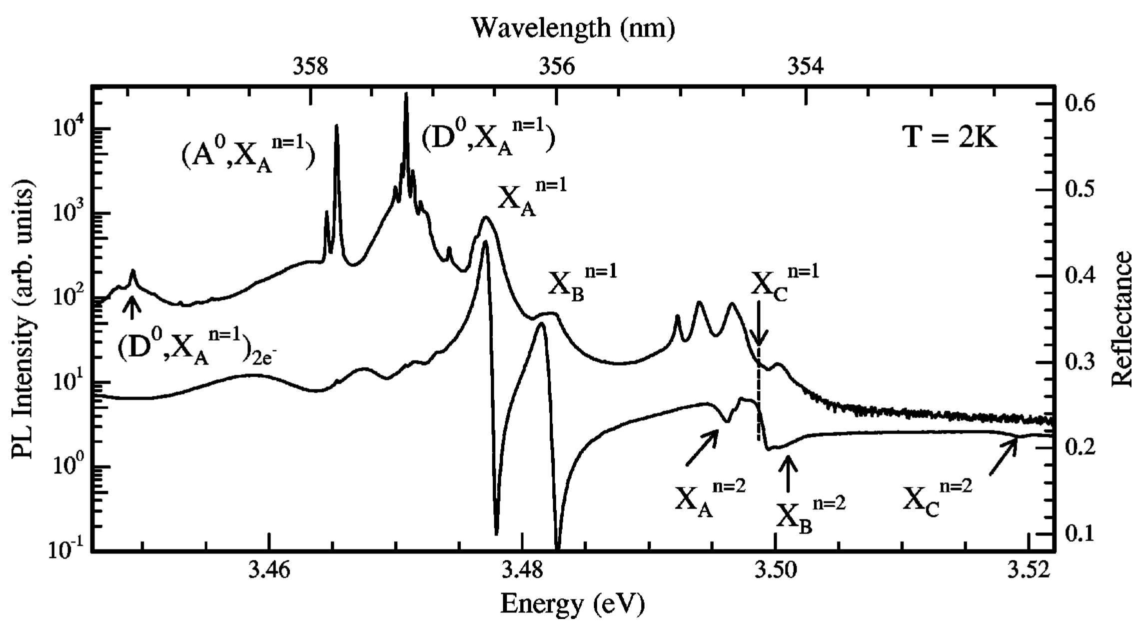

FIG. 1. Low-temperature PL and RF spectra of the homoepitaxial GaN layer in the band-edge region. The resolution is 0.12 meV.

TABLE I. Comparison of bound and free exciton peak positions reported by other groups and present values recorded at low temperatures ($T<10$ K). The energies for the free excitons were taken from damped oscillator fits to the RF spectra. Accuracy is ± 0.2 meV.

Substrate material	Layer thickness	A^0, $X_A^{n=1}$ (eV)	D^0, $X_A^{n=1}$ (eV)	$X_A^{n=1}$ (eV)	$X_A^{n=2}$ (eV)	$X_B^{n=1}$ (eV)	$X_B^{n=2}$ (eV)	$X_C^{n=1}$ (eV)	$X_C^{n=2}$ (eV)
Sapphire (Ref. 10)	100–250 μm	3.455	3.466–3.468	3.474		3.480		3.501	
Sapphire (Ref. 4)	>100 μm		3.469	3.4751		3.4815		3.493	
GaN (Ref. 7)	0.4 μm	3.4663	3.4709/3.4718	3.4785		3.4832		3.499	
GaN (Ref. 6)	1 μm			3.4776		3.4827		3.5015	
Sapphire (Ref. 5)	400 μm		3.4727/3.4762	3.4799		3.4860		3.5025	
GaN (this work)	1.5 μm	3.4655	3.4709	3.4771	3.4957	3.4817	3.5002	3.4986	3.5187

chemically-assisted ion-beam etching (CAIBE) was used to remove subsurface damage from the polished bulk substrate in order to improve the layer quality.[2] The CAIBE-treated part of the sample indeed showed drastically increased signals and reduced linewidths in the PL and RF spectra. The optical measurements were performed in a temperature range from 2 K to 300 K with the sample mounted on a copper holder cooled by a helium gas stream.

For the RF measurements, light from a 75 W Xe lamp impinged almost normally onto the sample with the $\boldsymbol{E}$ field perpendicular to the C_6 growth axis, i.e., we observe allowed electric dipole σ transitions. The reflected light was dispersed by a 1-m monochromator with a 2400 rules/mm grating and detected with a LN_2-cooled charge coupled device (CCD) camera. The measured RF spectra were corrected for the spectral characteristics of the lamp and the complete spectrometer.

For the PL measurements, a He-Cd laser ($\lambda_{exc} = 325$ nm) was used as the excitation source. The laser spot on the sample was about 1 mm^2 with a maximum power of 20 mW. The setup for the detection of the emitted light was basically the same as for the RF measurements. Spectral resolution with this assembly was better than 0.12 meV in the region from 3.15 eV to 3.55 eV. For the high-resolution PL measurements, a photomultiplier system with lock-in technique was used instead of the CCD camera, allowing for a resolution better than 0.03 meV. All spectra were calibrated with the emission lines of a mercury lamp, the lines of which were also used to check the resolution. The energy-dependent refractive index of air was taken into account to evaluate the correct wavelength-to-photon energy conversion, and measured intensities $I(\lambda)d\lambda$ were transformed into $I(E)dE$ using $dE = -(nc/\lambda^2)d\lambda$.

III. RESULTS AND DISCUSSION

Figure 1 presents a survey of PL and RF spectra in the band-edge region, both recorded with high resolution at 2 K. The RF spectrum shows well-resolved, very sharp resonances for the free excitons $X_A^{n=1}$, $X_B^{n=1}$, and $X_C^{n=1}$ associated with the threefold split valence band and the first excited states of all three excitons. The lower dips of the resonances are very sharp indicating an exceptionally low damping and thus a long lifetime of the excitons. An exact fit to the experimental curve is only possible within an exciton-polariton model including spatial dispersion,[3] yet many optical parameters can already be extracted with good accuracy ($\Delta E < 0.1$ meV) from fits using simply damped oscillators for the excitons. Values from an analysis are summarized in Table I. They deviate by 3–4 meV from those quoted for thick, relaxed samples grown on sapphire[4,5] but come close to those reported earlier for GaN grown on GaN substrates.[6,7] X-ray data on samples equivalent to the present one show that the lattice mismatch $(a_{\text{substrate}} - a_{\text{layer}})/a_{\text{substrate}}$ of our MOVPE layer is $\approx 3\times10^{-4}$. Since the layer has very low-carrier and impurity concentration, it should match closer the ideal situation of a strain-free, bulklike crystal. The suggested accuracy of our data implies that in the reference diagram (Fig. 3) of Gil *et al.*,[8] which is frequently used to determine strain conditions of GaN epilayers, the strain axis should be shifted by ≈ 4 kbar. The weak oscillations seen in RF between 3.44 eV and 3.48 eV are due to Fabry-Pérot resonances in the MOVPE layer between the surface and the high-n substrate. Their shorter period towards the exciton

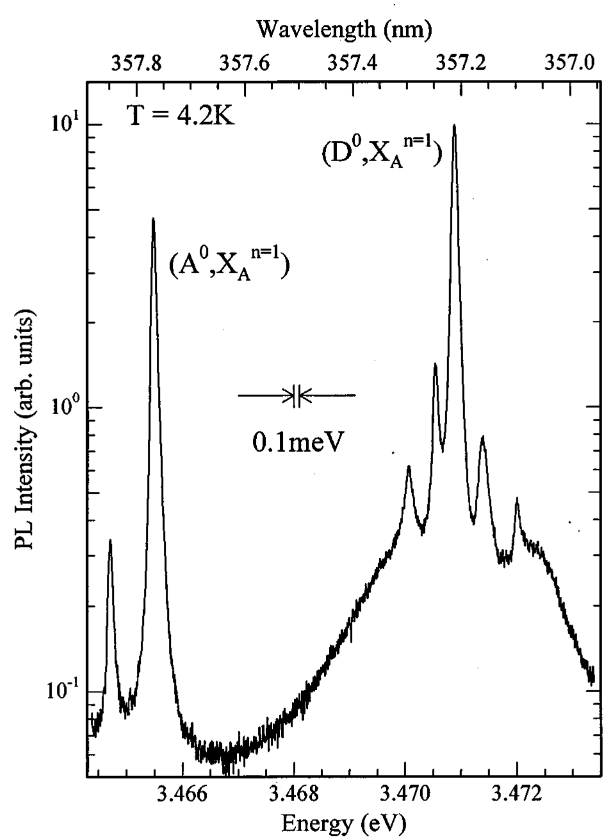

FIG. 2. Highly resolved donor- (D^0, $X_A^{n=1}$) and acceptor- (A^0, $X_A^{n=1}$) bound exciton spectra (resolution <0.03 meV). Resolved multiple fine structure is observed on both transitions.

resonance at ≈ 3.478 eV is given by the strong increase of the refractive index closely below the resonance.

All the features seen in RF are reproduced in the PL spectra, mostly with additional splittings as, e.g., readily observed for the $X_A^{n=1}$ and $X_B^{n=1}$ excitons. Work is in progress to investigate such splittings in detail. At 2 K the $X_C^{n=1}$ exciton line is hidden below the structure between the $X_A^{n=2}$ and $X_B^{n=2}$ peaks from the excited excitons but becomes dominant at higher temperatures. The assignment that we make is different from the one advanced by Volm *et al.*,[5] who ascribed the peak at 3.5025 eV (our $X_B^{n=2}$) to $X_C^{n=1}$. With our values, the simple quasicubic model of Hopfield[9] yields a spin-orbit parameter $\Delta_{SO} = 17.7$ meV and a crystal-field splitting $\Delta_{cr} = 8.4$ meV, in agreement with values reported recently.[6] If hydrogen models are adopted for the excitons with energy spacings between the $n=1$ and $n=2$ states of $\frac{3}{4}$ of Ry* (the Rydberg energy) similar binding energies for all three cases result: $Ry_A^* = 24.8$ meV, $Ry_B^* = 24.7$, and meV $Ry_C^* = 26.8$ meV (all ± 0.1 MeV). Corrections to the ground-state energy have presumably been taken into account, since at least the Ry_C^* value, indicating a higher effective hole mass for the *C* valence band, disagrees with theoretical calculations.

Particularly sharp in our sample are the PL lines from the donor-bound exciton (D^0, $X_A^{n=1}$) at 3.4709 eV, and the acceptor-bound exciton (A^0, $X_A^{n=1}$) at 3.4655 eV. They are much narrower in the present homoepitaxial layer than reported previously. Both lines are recorded with (100 ± 10) μeV [full width at half maximum (FWHM)] (Fig. 2). Details of the fine structures will be reported elsewhere. The exciton localization energies are 6.2 meV for D_0, $X_A^{n=1}$ and 11.6 meV for A^0, $X_A^{n=1}$. The two-electron transition (D^0, $X_A^{n=1})_{2e^-}$ emerges when in the exciton recombination process the donor is left in the excited $2s$-like state. The spacing of this line from the D^0, $X_A^{n=1}$ transition yields a $1s \rightarrow 2s$ donor excitation energy of 21.6 meV, which—neglecting central-cell corrections—corresponds to an effective-mass donor binding energy of $E_d = 28.8$ meV. Such a donor binding energy is commonly ascribed to silicon atoms on gallium sites.

IV. SUMMARY

Extraordinarily clear, intense and narrow spectral features are observed in emission and reflection measurements from a homoepitaxial GaN layer, grown on a pretreated GaN substrate. Especially the half-widths of the donor- and acceptor-bound excitons of only 100 μeV are drastically narrower than reported previously, allowing a very precise evaluation of electronic parameters characteristic for pure GaN. Full theoretical analysis involving an exciton-polariton model with spatial dispersion and analysis of the fine structure of the donor and acceptor exciton lines will be advanced in a forthcoming paper.

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