

Impact of exciton diffusion on the optical properties of thin GaN layers

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We study the optical properties of thin (0.4–0.7 μm) GaN layers directly grown on 6H-SiC(0001). These structures are found to always exhibit a broad luminescence band in the blue spectral range, which is identified as exclusively being due to (D^0, A^0) transitions in 6H-SiC. It is shown that the SiC substrate is excited indirectly via diffusion of carriers photogenerated in the GaN layer. The drastic differences found between samples of different electron concentration suggest correspondingly large differences in the diffusivity, which cannot be explained simply by different ambipolar carrier mobilities. Instead, different diffusion mechanisms are required, namely, ambipolar and excitonic diffusion at carrier concentrations above and below the Mott density, respectively. [S0163-1829(98)51344-6]

Photoluminescence spectroscopy is amongst the most frequently used tools for evaluating the quality of an epitaxial layer.¹ Thin epilayers are known to often exhibit a low internal quantum efficiency due to nonradiative recombination both at the epilayer surface and at the epilayer/substrate interface.² This phenomenon has usually been analyzed by measuring the steady-state and transient emission of samples of different thickness, assuming that $D/d \gg S$, where D is the diffusion coefficient, d the layers' thickness, and S the interface recombination velocity. Under these conditions, interface recombination represents the rate-limiting step.²

In this paper, we investigate the optical properties of thin (0.4–0.7 μm) GaN layers directly grown on 6H-SiC(0001). This substrate has recently attracted much interest, since besides the compatible cleavage planes between GaN and 6H-SiC, both the lattice and thermal mismatch are small when compared to the GaN/Al₂O₃ system. Furthermore, the growth of GaN directly on 6H-SiC offers the potential of fabricating vertically conductive devices, which would significantly simplify device processing.³ However, insulating AlN buffer layers are commonly used,⁴ since GaN layers directly grown on SiC are discredited by the presence of a broad photoluminescence band, which has been taken as evidence for the poor crystal quality of the GaN layer. In this paper we show that this conclusion is, in general, incorrect since even the contrary may be true.

The series of samples under investigation is directly grown on *n*-type Si-terminated 6H-SiC(0001) substrates by plasma-assisted molecular-beam epitaxy (MBE). We focus in this paper on two samples, namely, Nos. 1 and 2, for which N rich and Ga rich conditions were employed for growth and which have thicknesses of 0.52 and 0.43 μm , respectively. These samples have comparable structural properties [e.g., a width of the (0002) reflection in ω scans of about 15°] and a virtually identical morphology (e.g., a rms roughness as measured by atomic-force microscopy of 1

nm). Their background electron concentration as measured by CV profiling, however, is different, namely, about 10¹⁸ cm⁻³ for sample No. 1 and 10¹⁶ cm⁻³ for samples No. 2. The optical properties of the GaN films are studied by cw photoluminescence (PL), cathodoluminescence (CL), reflectance, and time-resolved PL spectroscopy. cw PL measurements are performed using the 325-nm line of a He-Cd laser as excitation source and a cooled GaAs photomultiplier as detector. The excitation intensity is about 1 W/cm². CL experiments are carried out in a scanning electron microscope (SEM) equipped with an Oxford Mono-CL2 and He cooling stage. Reflectance spectra are recorded with $E \perp c$ and $k \parallel c$. A halogen lamp is employed as the light source and the reflected light is detected by a photomultiplier connected with a lock-in amplifier. Time-resolved PL measurements are performed using a frequency-tripled femtosecond Ti:sapphire laser and a syncroscan streak-camera system. The excitation energy and fluence are set to 4.96 eV and 1 nJ/cm², respectively. The overall temporal resolution of this setup is 2 ps.

Figure 1 displays the 5 K PL spectra of two samples, as well as the PL spectrum of a piece of bare 6H-SiC. For sample No. 1, the PL line near the GaN band edge is dominant but broad (100 meV). In contrast, the sample No. 2, the PL peak near the GaN band edge is sharp but weak. The common feature in both spectra is the deep PL band centered at about 2.6 eV, which is dominant for sample No. 2. This band, however, is similar in shape and position to the emission of bare 6H-SiC, raising the question whether it truly stems from the GaN layer.

The actual origin of this deep PL band from the GaN/SiC heterostructure is clarified by high-resolution CL measurements from the epilayer and the substrate side as shown in Fig. 2. The coincidence of the resonancelike feature at 2.992 eV, which is the exact position of the zero-phonon exciton bound to a neutral nitrogen donor in 6H-SiC,⁵ demonstrates

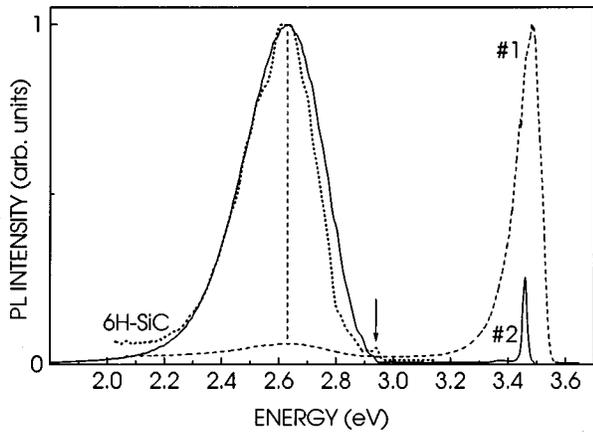


FIG. 1. PL spectra at 5 K of sample Nos. 1 (dashed line) and 2 (solid line), as well as the PL spectrum of bare 6H-SiC (dotted line). The arrow points to a peak at about 3 eV present in all spectra.

that the deep PL band is, in fact, due to the substrate, specifically, due to the (D^0, A^0) emission of 6H-SiC (note that the position and shape of this band may vary depending on dopant concentration). This finding is additionally confirmed by depth-resolved measurements using excitation energies between 4 and 20 keV (not shown here). The presence of this band should thus not be confused with the deep-level luminescence observed from GaN layers of poor quality.

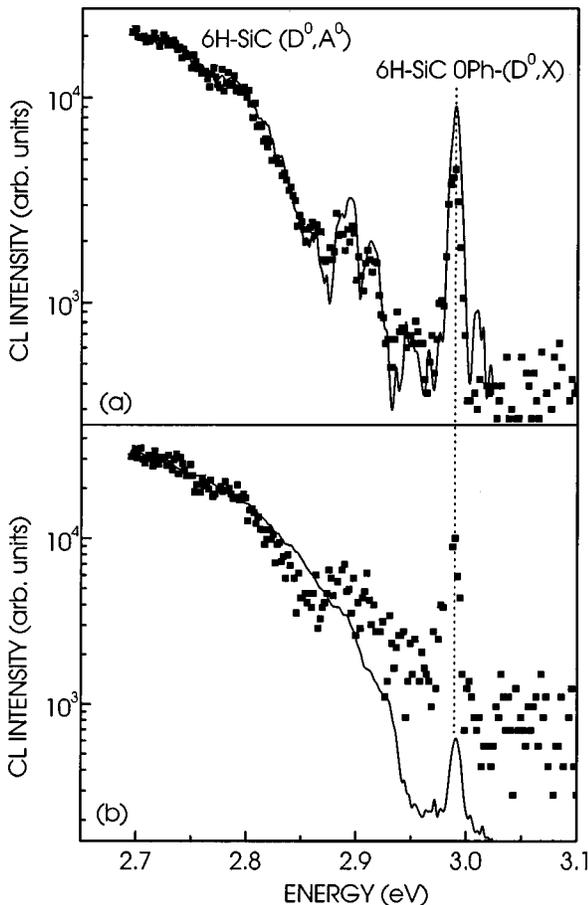


FIG. 2. Logarithmic display of high-resolution CL spectra at 5 K of sample Nos. 1(a) and 2(b) from the front (line) and the backside (squares).

This identification raises the questions of (i) how the SiC substrate is actually excited, and (ii) why sample Nos. 1 and 2 are so different in terms of the intensity ratio between GaN- and SiC-related PL. In fact, direct excitation can be safely ruled out, since the absorption coefficient α of GaN at the excitation wavelength is well above 10^5 cm^{-1} , and also should be the same for both samples (both layers are connected and massive as shown by a variety of microscopic techniques probing the sample from the sub-mm to the nm scale). The same argument applies to indirect excitation via the internal GaN emission. Drift of holes to the n -type SiC substrate can be excluded too, since the CV measurements show the surface band bending in (the almost entirely depleted) sample No. 2 to oppose hole drift. The explanation remaining is thus diffusion. Intuitively, a low carrier concentration means a high carrier mobility and, hence, diffusivity, but this relation only holds for uncompensated material. Furthermore, the dependence of mobility on carrier concentration is, in general, too weak to explain the orders of magnitude difference between sample Nos. 1 and 2. (Note that, due to the conducting substrates, Hall measurements are not possible for our samples.)

To go further, we measure the reflectance of both samples and compare it to the respective PL spectra as shown in Fig. 3. The reflectance of sample No. 2 exhibits strong resonances from A/B and C excitons (the samples are tensilely strained such that A and B excitons are at or close to their anticrossing and cannot be spectrally resolved).⁶ The maximum of the PL band is redshifted with respect to the A/B resonance, suggesting that the PL peak stems from donor-bound exciton (D^0, X) emission. For temperatures above 50 K, the free (A/B) exciton gradually takes over and finally dominates emission at 300 K (not shown here). In comparison to sample No. 2, both PL and reflectance of sample No. 1 are strongly blueshifted and broadened. Only a weak, if any, exciton resonance is detected which coincides with the PL maximum. In fact, this sample's background carrier concentration is at or above the Mott density for GaN,⁷ and discrete excitonic states are not expected in this regime.

Next, we examine the temperature dependence of the GaN- and SiC-related emission. Figure 4(a) shows that the total radiative efficiency η_t (i.e., the sum of the PL intensities I_{SiC} and I_{GaN} normalized to unity) from sample No. 1 drops by two orders of magnitude when the temperature is raised from 5 to 300 K. Simultaneously, the ratio $f_d = I_{\text{SiC}}/I_{\text{GaN}}$ increases with temperature until 200 K, as shown in Fig. 4(b), and decreases slightly thereafter. In complete contrast to this behavior, the total radiative efficiency from sample No. 2 [Fig. 4(a)] decreases by only a factor of 2, whereas f_d increases linearly with temperature up to 300 K. Supposing that the internal quantum efficiencies of the SiC substrates (which were cut from the same wafer) are comparable, these results suggest that the diffusion of the recombining species is very much faster for sample No. 2 when compared to sample No. 1, such that nonradiative channels in the bulk of the epilayer are bypassed. If this hypothesis is true, the PL decay time of sample No. 2 should be dominated by a transit time with the condition $D/d \ll S$. Note that this situation is just the opposite to what is commonly assumed,

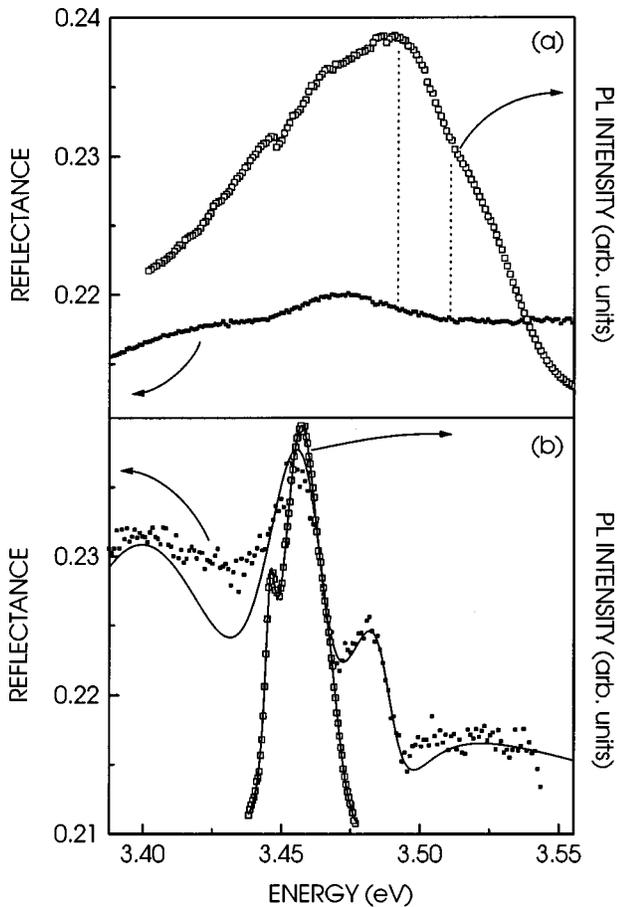


FIG. 3. Reflectance (solid squares) and PL (open squares) spectra at 5 K of sample Nos. 1(a) and 2(b). The lines represent fits using a phenomenological Gaussian/Lorentzian line shape for the PL, and a two-layer transfer-matrix simulation based on an excitonic model dielectric function for the reflectance spectrum, respectively. The sharp peak at 3.447 eV in both PL spectra is due to the outgoing resonance with the free-exciton state for fourth-order Raman scattering.

namely, that interface recombination is the rate limiting step ($D/d \gg S$). The diffusion-limited transit time may be defined in general as

$$\tau_d = \tau_r \eta_{\text{SiC}} / f_d, \quad (1)$$

where τ_r is the radiative lifetime for GaN, and η_{SiC} is the internal quantum efficiency for SiC which here is simply taken to be the value for I_{SiC} measured from the samples' backside, normalized to unity. Note that nonradiative losses in the GaN layer equally constitute a loss for the SiC substrate, and thus cancel each other in Eq. (1).

To determine τ_d using Eq. (1), we perform time-resolved PL measurements and evaluate τ_r in the standard way,⁸ i.e., by taking $\tau_{\text{GaN}}(T) = [1/\tau_r(T) + 1/\tau_{\text{eff}}(T)]^{-1}$, where τ_{eff} includes all possible nonradiative contributions, and $I_{\text{GaN}}(T) = \eta_{\text{GaN}}(T) I_{\text{PL}}(0)$, with $\eta_{\text{GaN}}(T) = \tau_{\text{GaN}} / \tau_r$. This procedure requires assigning a value for τ_r at the lowest temperature (or, equivalently, a value for η_{GaN}). Since the emission of GaN at low temperatures is dominated by bound excitons, we somewhat arbitrarily set the radiative lifetime at 4 K to 250 ps, which is in the range of values being calculated in

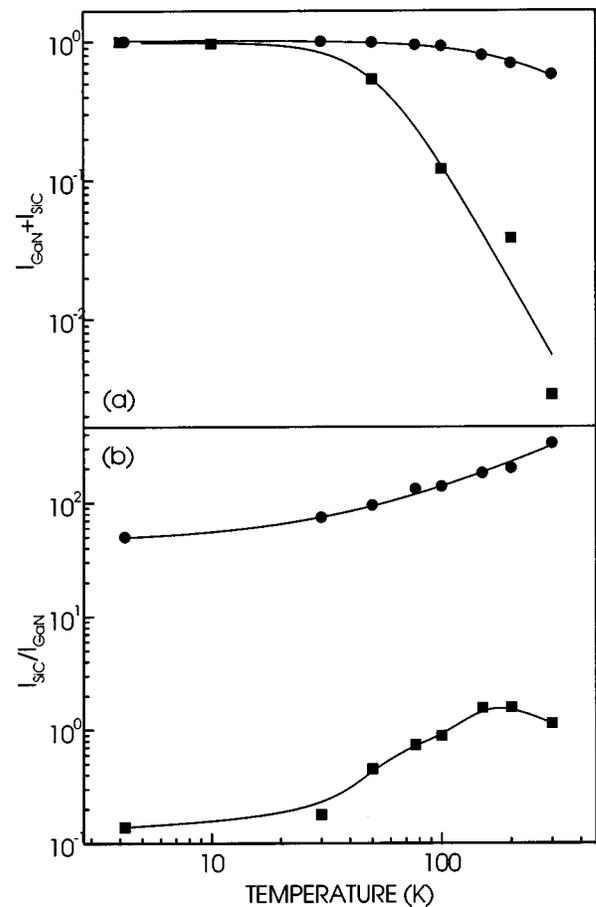


FIG. 4. Temperature dependence of (a) the total radiative efficiency and (b) the intensity ratio between the emission from SiC and GaN for sample Nos. 1 (solid squares) and 2 (solid circles). The lines are a guide to the eye.

the frame Rashba's treatment.⁹ Note that similar values apply for band-to-band transitions in degenerate layers (for band-to-band transitions in nondenerate layers, τ_r is strictly inversely proportional to the carrier concentration n).¹⁰

Proceeding in this way, we compare the values for τ_d with the experimental PL decay times in Fig. 5. Sample No. 1 exhibits the "normal" behavior for an epitaxial layer which, at low temperatures is dominated by radiative recombination, and becomes dominated by bulk nonradiative recombination with increasing temperature. Evidently, diffusion does only slightly influence the recombination dynamics for this sample. Sample No. 2, however, clearly displays an "anomalous" behavior in that its decay time, which obviously is determined by a nonradiative channel, is essentially constant. The agreement of τ_d with the PL decay time suggests that the recombination dynamics for this sample is determined exclusively by diffusion to the SiC substrate.

To check the consistency of these results, we finally perform a theoretical analysis of the coupled diffusion-recombination process. Assuming that recombination is monomolecular and can be described by a lifetime $\tau = (1/\tau_r + 1/\tau_{\text{nr}})^{-1}$, where τ_{nr} is the (bulk) nonradiative lifetime, the spatiotemporal evolution of the carrier/exciton density $n(z, t)$ upon a small-signal excitation $G(t, z) = G_0(t) e^{-\alpha z}$ is governed by the diffusion-recombination equation

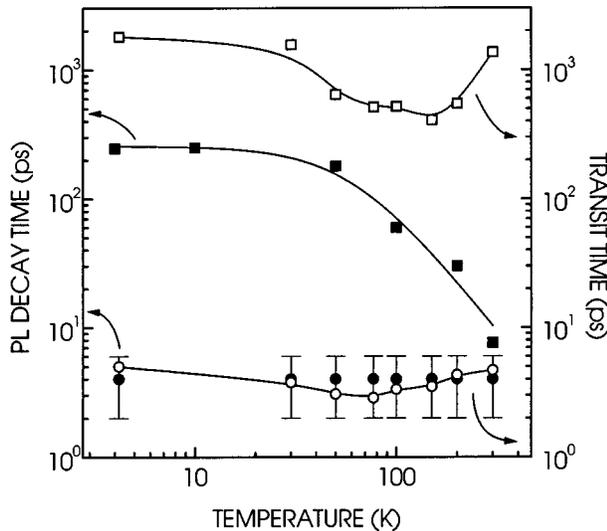


FIG. 5. Experimentally observed PL decay times (solid) and calculated transit times (open) vs temperature for sample Nos. 1 (squares) and 2 (circles). The lines are a guide to the eye.

$$G + D \frac{\partial n^2}{\partial z^2} - n/\tau = \frac{\partial n}{\partial t}, \quad (2)$$

with the boundary conditions $\frac{\partial n}{\partial z}|_{z=0} = 0$ at the surface and $D \frac{\partial n}{\partial z}|_{z=d} = S n(d)$ at the GaN/SiC interface. The respective PL intensities are then given as $I_{\text{GaN}} = \int dz n/\tau_r$ and $I_{\text{SiC}} = -D \frac{\partial n}{\partial z}|_{z=d}$. Equation (2) can be solved in closed form, but a good and physically reasonable approximation to the exact solution is gained in the limit of $S \rightarrow \infty$ and $\alpha d \gg 1$. The transit time is then acquired from the *stationary* solution of Eq. (2), yielding $\tau_d = \tau [\cosh(d/L) - 1]$, where L is the diffusion length. On the other hand, the PL decay time is acquired from the *transient* solution of Eq. (2) as $\tau_{\text{PL}} = \tau [1$

$+ (\pi L/2d)^2]^{-1}$.¹¹ Simple algebra shows that $\tau_d/\tau + 1 = (1 + 1/f_d)/\eta_t$, allowing us to derive L and thus τ_{PL} . The values obtained for τ_{PL} are, in fact, almost identical to those experimentally observed, demonstrating the consistency of our analysis.

These results support the following conclusion. For GaN with background carrier concentrations above the Mott density, excitons are effectively screened and diffusion has an ambipolar nature. In contrast, for GaN below the Mott density, exciton formation is rapid and diffusion is excitonic in the sense that the scattered species is an essentially neutral entity.¹² The experimental data reported in Fig. 5, together with the simple expression for τ_d derived above, imply large exciton diffusivities particularly at low temperatures: the diffusion lengths obtained for sample No. 2 decrease from 2 μm between 4 and 50 K to 0.4 μm at 300 K. A comparison with theory is at present impossible, since exciton diffusivities have not been calculated for the whole temperature range between 4 and 300 K. There have, however, been reports on unusually large diffusivities for both bulk (Al, Ga)As and InP determined by time-of-flight measurements, though these findings were left largely unmentioned.¹³ For GaN, this phenomenon is expected to be much more pronounced and to persist to higher temperatures, opening the way to systematically study exciton diffusivities over a wide temperature range either as outlined above or by direct time-of-flight measurements.

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