Dynamics of resonantly excited excitons in GaN

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We present resonant fs pump-probe reflectance measurements of excitons in wurtzite GaN epilayers at different lattice temperatures. At 4 K we find that the exciton dynamics is dominated by trapping at defects via acoustic-phonon emission on a time scale of 16 ps. At temperatures above 60 K we observe a much longer relaxation component of 375 ps, which is due to radiative recombination of free excitons. The results are in good agreement with theoretical predictions. [S0163-1829(98)50748-5]

GaN and its alloys are of considerable interest for optoelectronic device applications in the blue and ultraviolet spectral regions,[1] and a detailed understanding of their optical properties is important for designing and optimizing devices such as light-emitting diodes and lasers. As in all direct, wide band gap semiconductors, the band-edge optical response of GaN is dominated by excitonic effects: the exciton binding energy is ~20 meV, and it has already been shown that excitons play an important role in the optical reflection and absorption spectra at low carrier density and low temperature.[2,3] However, the situation at high carrier density and temperature is not so clear. The Coulomb interaction between electrons and holes is expected to become screened with increasing density, and together with phase-space filling, this should lead to a bleaching of the exciton resonance. However, excitonic gain has been reported for GaN at high excitation density.[4] This behavior is complicated by the fact that the emission spectrum of wide band gap materials tends to be dominated by bound exciton recombination, and is therefore highly dependent on sample quality. Consequently, exciton dynamics are determined to a great extent by localization at impurities and defects, and only in high-quality material can intrinsic relaxation and radiative recombination processes be studied.

In this paper we present a time-resolved pump-probe study of high-quality GaN epilayers in reflection geometry. The GaN epilayers are grown by lateral epitaxial overgrowth. In order to probe primarily the radiative exciton population, we resonantly excite excitons with a 250-fs laser pulse, resulting in an exciton population with wave vector $\mathbf{q}\sim 0$. The sharp exciton resonances in the reflectance spectrum bleach as the density of photoexcited excitons increases, and the change in intensity of the reflected light as a function of time is a measure of the $\mathbf{q}\sim 0$ exciton dynamics. At 4 K the dominant excitonic relaxation process is trapping at impurities and defects with a characteristic time τ_{eff}^{1} ~16 ps. At much higher temperatures (>60 K) we observe the emergence of long-lived radiative recombination with $\tau_{\mathrm{eff}}^{2}\sim 375$ ps. The longer lifetime agrees well with the predicted value for the radiative decay of thermalized excitons at the polariton bottleneck.

The GaN sample studied here is a nominally undoped epilayer grown by lateral epitaxial overgrowth, which is a two-step process involving both undoped and Mg-doped GaN deposition.[5] A GaN layer is first grown by metal-organic vapor phase epitaxy under atmospheric pressure on a (0001) Al_2O_3 substrate. A 30-Å dielectric film of silicon nitride is then deposited *in situ* by reaction of silane and ammonia. Standard photolithographic techniques are then used to produce a periodic digital mask that exposes GaN stripes of 5-μm width and 10-μm separation. The stripes are aligned in the $\langle 10\bar{1}0\rangle$ direction. Finally, these patterned layers are overgrown by GaN, the growth being continued until there is a coalescence of the laterally grown areas, producing smooth and optically flat GaN layers. It has been shown that the high defect density usually found in GaN films is significantly reduced using this growth technique.[6]

Figure 1 shows low-temperature photoluminescence (PL) and reflectivity spectra that exhibit characteristic excitonic behavior. The cw PL was excited by a frequency doubled copper vapor laser (255 nm), and the source for the reflectivity measurements was a standard xenon lamp. The reflectivity spectrum exhibits two sharp resonances at 3.492 and at 3.501 eV, which correspond to the $\Gamma_7^{\mathrm{C}}-\Gamma_9^{\mathrm{V}}$ (A) and $\Gamma_7^{\mathrm{C}}-\Gamma_7^{\mathrm{V}}$ (B) excitons, respectively.[7] The calculated reflectivity spectrum (hollow circles) is given by

$$\epsilon(\omega)=\epsilon_\infty+\sum_{j=1}^{2}\frac{4\pi\alpha_j\omega_{0j}^2}{\omega_{0j}^2-\omega^2-i\Gamma_j\omega}, \tag{1}$$

where $\epsilon_\infty=5.35$ is the high-frequency dielectric constant, $\omega_A=3.492$ eV and $\omega_B=3.499$ eV are the resonance energies, $4\pi\alpha_A=5\times10^{-4}$ and $4\pi\alpha_B=4\times10^{-4}$ are the polarizabilities, and $\Gamma_A=\Gamma_B=1.5$ meV are the effective linewidths of the A and B excitons. The latter values are considerably smaller than the linewidths ~6 meV obtained from conventionally grown GaN.[8]

The PL spectrum, on the other hand, is dominated by shallow neutral donor bound excitons (I_1 and I_2), and there is no evidence of recombination from deeper impurity centers.[9] The weak line labeled A at 3.49 eV, is assigned to the $n=1$ free A-exciton state; its very low intensity relative to the bound states indicates that free excitons are localized

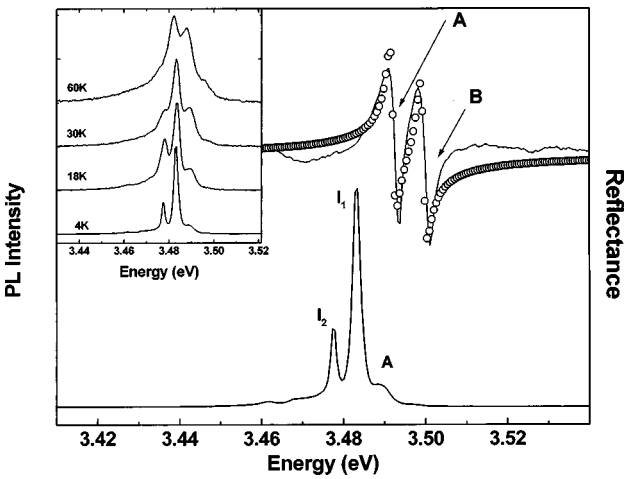

FIG. 1. The cw reflectance and photoluminescence spectra of GaN at 4 K. The exciton resonances are labeled A and B in the reflectance spectrum. Bound exciton peaks in the luminescence are labeled I_1 and I_2. The open circles are a fit to the reflectance data as discussed in the text. The inset shows weak excitation PL spectra at different temperatures. The curves are offset for clarity.

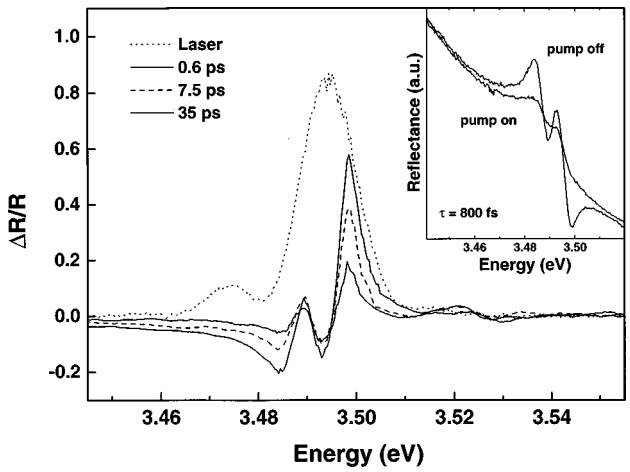

FIG. 2. Differential reflectance spectra measured at various time delays at 4 K. The laser excitation spectrum is shown as a dotted curve. The inset shows the measured reflectance spectra with and without pump at a time delay of 800 fs.

on a time scale that is considerably faster than their recombination time. However, the inset in Fig. 1 shows that the intensity of I_1 and I_2 decreases with increasing temperature, whereas the free exciton intensity increases significantly, which indicates that the bound excitons are thermally ionized and feed the free *A* and *B* exciton population. This thermal quenching of the I_1 and I_2 peaks is even more rapid above 60 K, consistent with excitons being only weakly bound to the neutral donors.

It is apparent from the data presented in Fig. 1 that time-resolved photoluminescence will be of limited use in studying free exciton dynamics. In practice only the bound excitons can be clearly distinguished, and our streak camera measurements reveal that the rise time of the *A* signal is $\leqslant$10 ps, the time resolution of the apparatus.[10] An alternative approach that provides direct information on free exciton behavior is time-resolved reflectance. The excitation source we used was an optical parametric oscillator (OPO) in conjunction with a frequency-doubled amplified Ti:Sapphire laser (operating at 800 nm).[11] A fraction of the frequency-doubled blue light was mixed with the residual red light in an OPO that was tuned to resonance with the GaN band gap at 355 nm (3.495 eV). The pulse duration was 250 fs at a repetition frequency of 800 Hz. The probe beam was a white-light continuum generated in a water cell from the residual frequency-doubled Ti:Sapphire pulses. Group velocity dispersion in the water cell temporally broadened the continuum, resulting in a net time resolution for the experiment of 800 fs. The reflected light was focused into a 0.5-m spectrograph and detected using a liquid nitrogen cooled charge coupled device.

The time-resolved reflectance spectroscopy was performed on the *A*- and *B*-exciton transitions with an average pump power of 0.1 mW. Both pump and probe beams were focused onto the sample with a polarization $E \perp c$. The spot diameter of the focused pump beam on the sample was 130 μm, while that of the probe beam was slightly smaller in order to optimize spatially homogeneity of the photoexcited exciton density. This pump power corresponds to a maximum exciton density of 2.0×10^{19} cm^{-3}, given that 83% of the incident light was transmitted into the sample and assuming that every photon excites an electron-hole pair.

Figure 2 presents differential reflection spectra recorded at several different time delays after the excitation pulse, showing strong bleaching of the excitonic transitions. As can be seen in the inset of Fig. 2, the onset of bleaching occurs within the 800-fs time resolution of our system. The recovery of the excitonic reflectivity takes place on a slower time scale, and even after 35 ps there is a small residual bleaching. A noteworthy feature of the measurements is that the energies of the *A* and *B* excitons are apparently unshifted even in the presence of this relatively strong photoexcitation. This result is consistent with theoretical predictions of excitonic transitions in bulk semiconductors that include only exciton self-screening and no free carrier contribution, an approximation that is likely to apply in the present case of resonant excitation. In this model the band-gap renormalization is exactly canceled by the simultaneous reduction of the exciton binding energy.[12] It is also noteworthy that the *C* exciton, which arises from the spin-split-off valence band, features quite strongly in the differential reflectance at 3.52 eV, although it is not apparent in the cw spectrum (cf. Fig. 1).

Figure 3 shows the amplitude of the differential reflectance signal as a function of time at a temperature of 4 K for both *A* and *B* excitons, which were obtained by fitting the spectra using Lorentzian line-shape functions.[13] The rise time in each case is resolution limited indicating that the excitons are completely bleached after a few hundred fs. The decay of the differential reflectance after the initial transient can be fitted (solid line) using a single exponential with a decay time of $\tau_{\text{eff}}\sim$16 ps for both *A* (hollow circles) and *B* excitons (filled circles). This very small value for the effective lifetime suggests that excitons are trapped very rapidly into lower energy localized states, since the radiative lifetime of excitons is expected to be much longer. The value for the

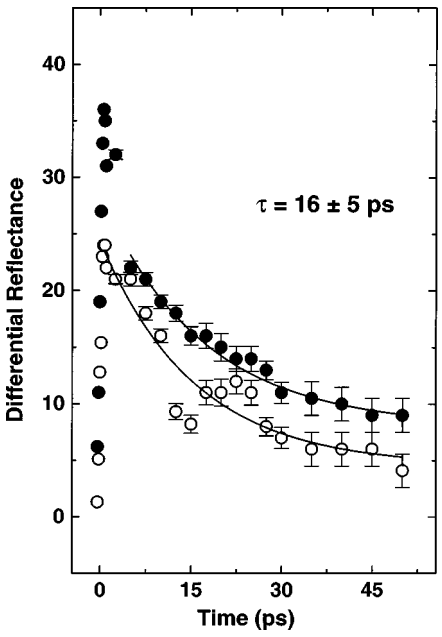

FIG. 3. Time dependence of the differential reflectance signal at 4 K from *A* excitons (hollow circles) and *B* excitons (filled circles). The solid lines show the results of a single exponential fit to the data ($\tau = 16 \pm 5$ ps).

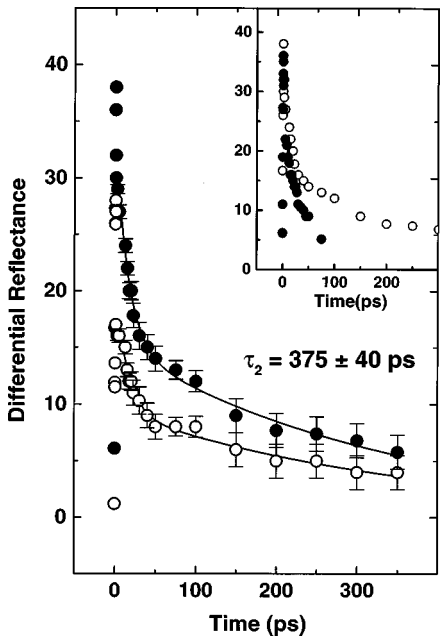

FIG. 4. Time dependence of the differential reflectance signal at 60 K from *A* excitons (hollow circles) and *B* excitons (filled circles). The solid lines show the results of a double exponential fit to the data ($\tau_1 = 16 \pm 5$ ps and $\tau_2 = 375 \pm 40$ ps). The inset shows the *B*-exciton signal at 4 and 60 K, plotted on the same time axis for comparison.

exciton lifetime at low temperatures agrees well with the rise time measured in our time-resolved luminescence measurements of I_1 and I_2,[10] and with previously published PL data.[14,15] This trapping time is considerably longer than the subpicosecond trapping times expected for polar optical phonon emission. As discussed above, shallow donors are the dominant traps of free excitons in our samples. The localization energies of the I_1 and I_2 bound excitons are 6 meV and 11 meV, respectively (cf. Fig. 1), and so for the present experimental conditions of resonant excitation the trapping process will involve only acoustic-phonon emission given that the optical-phonon energy is ~90 meV.

An increase in temperature to 60 K results in the appearance of a long-lived component in the differential reflectance data: as shown in Fig. 4 the decay is now clearly biexponential, with decay times of $\tau_1 \sim 16$ ps and $\tau_2 \sim 375$ ps giving a good fit to the data. Comparison with the cw data presented in the inset to Fig. 1, which show that a significant free exciton population exists at 60 K in thermal equilibrium with the neutral donor bound excitons, suggests that the longer decay component is due to intrinsic radiative recombination.

In bulk semiconductors the radiative decay of free excitons requires scattering to the photonic region of the polariton dispersion branch, and thus the radiative lifetime is practically determined by the time necessary to pass through the excitonic polariton bottleneck region. In the absence of defects this relaxation process involves acoustic-phonon scattering; because of the flat dispersion, the energies involved are small and the relaxation time can be extremely long. A theoretical analysis by Toyozawa[16] yields the following expression for the radiative lifetime:

$$\tau_{\mathrm{rad}} = \frac{1}{2}\left(\frac{5\pi}{3}\right)^{3/5}\left\{\frac{\hbar^2 c^7 M^2 \alpha L^3}{v_0^2 C^4 \omega_A}\right\}^{1/5}\frac{1}{\omega_A}, \qquad (2)$$

where M/v_0 is the mass per unit volume of the unit cell, α is the polarizability, L is the thickness of the excited layer, $\hbar\omega_A$ is the energy of the *A* exciton, and C is the deformation potential. Using values of these parameters for GaN: 3014 kg m^{-3}, 4×10^{-5}, 0.1 μm, 3.492 eV and 4 eV, respectively (obtained from our fit in Fig. 1 and Refs. 17 and 18) we estimate $\tau_{\mathrm{rad}} \sim 300$ ps. This value is in remarkably good agreement with the experimentally observed long-lived component.

In conclusion we have measured the lifetime of resonantly excited excitons by means of time-resolved reflectance spectroscopy. We observe strong time-dependent bleaching of the *A* and *B* excitons. We have measured a lifetime of ~16 ps at low temperatures, which is determined by trapping of excitons by acoustic phonon emission to defects and impurities. At higher temperatures we observe radiative recombination with a lifetime of 375 ps that is in good agreement with theoretical predictions for GaN. It will be important to extend these measurements to higher excitation densities to investigate the process of stimulated emission, and to low-dimensional structures in which direct radiative recombination is permitted due to spatial confinements. Furthermore, comparison of measurements obtained using resonant and non-resonant excitation should permit the influence of phase-space filling and screening on exciton dynamics to be evaluated.

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