APPLIED PHYSICS LETTERS **94**, 203102 (2009)

Influence of surface-related states on the carrier dynamics in (Ga,In)N/GaN single quantum wells

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(Received 31 March 2009; accepted 28 April 2009; published online 18 May 2009)

We report on the influence of surface-related states on the relaxation of carriers within single (Ga,In)N/GaN quantum wells. Two identical samples that differ only in the thickness of the top GaN cap layer were studied. Photoluminescence and pump-probe measurements reveal significant variations in the quantum well integrated emission and the carrier relaxation decay times in the two samples, when probing both the ground and excited states of the wells. The variations are attributed to the presence of an efficient nonradiative relaxation channel associated with the proximity of the quantum well excitations to the surface-related states in the thin-cap sample. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3139079]

(Ga,In)N-based structures have attracted a lot of attention due to their applications as efficient light emitting devices in the green, blue, and ultraviolet part of the spectrum.[1] The emission efficiency and spectral coverage of (Ga,In)N-based materials can be further enhanced when combined with other luminescent materials, such as colloidal nanoparticles or semiconducting polymers. In recent reports, (Ga,In)N single quantum well (SQW) structures have been combined with the aforementioned materials in planar hybrid geometries in which efficient transfer of energy occurs from the SQWs (donor of energy) to overlayers of nanoparticles/polymers (acceptor of energy) via nonradiative Förster-type interactions.[2–7] Such interactions occur over nanoscale ranges so the hybrid geometry requires a close proximity of the materials constituents. This dictates the use of (Ga,In)N/GaN quantum well structures with GaN top caps <10 nm in thickness.

It is evident that any investigation of the Förster interaction processes based on such SQWs requires accurate control of the thickness and morphology of the cap layer. In recent reports we have used grazing-incidence Rutherford backscattering spectroscopy and atomic force microscopy[6,8] to directly measure the thickness and morphology of the GaN cap layer, respectively. To complete our understanding of the influence of the cap layer in the carrier dynamics in the well, we report here a pump-probe study on ultrathin cap (Ga,In)N SQWs, performed with femtosecond time resolution.[9] We find that the carrier relaxation rates are significantly enhanced as the cap thickness reduces and we attribute this enhancement to efficient carrier relaxation at the GaN surface-related states.[10–13]

In this study two (Ga,In)N/GaN SQW structures, labeled A and B, are studied. They were grown using metalorganic vapor phase epitaxy on single-side polished (0001)-oriented sapphire substrates followed by a thick GaN buffer layer and a single GaN/(Ga,In)N QW heterostructure in consecutive growth runs. The InN fraction and thickness of the well material was adjusted to achieve room-temperature emission at $\sim$415 nm. Details of the QW growth can be found elsewhere,[14] and the QW thickness can be assumed to be $\sim$2.0 nm, as measured for analogous samples emitting at 390 nm.[8] Samples A and B differ only in the average thicknesses of the GaN cap layer above the QW, with nominal values of 15 and 2.5 nm, respectively.

The samples were initially characterized using room-temperature power-dependent (excitation densities in the 100 μJ/cm^2–50 mJ/cm^2 range) photoluminescence (PL) with excitation above the GaN band-edge at 355 nm. Care was taken to assure that the PL measurements in the two samples were carried out in a side-by-side geometry under at identical experimental conditions. Characteristic comparative PL spectra at excitation density of 1 mJ/cm^2 are displayed on the inset of Fig. 1(a). Assuming an absorption coefficient of 9.5×10^{-4} cm^{-1} for the GaN at 355 nm,[15] this excitation corresponds to an estimated photoexcited carrier density of approximately 1.8×10^{20} cm^{-3} carriers. A large fraction of these carriers is collected by the QW and recombines radiatively on it. This is evident in the PL spectra of both samples that are dominated by a broad feature centered at 405–410 nm, attributed to radiative recombination in the well. We note that at such relatively high carrier densities, spontaneous emission from the QW is broadened by carrier-carrier interactions and QW state filling effects while stimulated emission also occurs.[16] Despite the rather complex character of the QW radiative recombination in the high densities used, the comparative PL study shows: (a) Strong QW emission from both samples for all densities used and (b) higher QW integrated emission from sample A (1.4–1.6 times) compared to that of sample B for all densities. The strong emission from the surface wells observed for all densities is consistent with previous reports on the literature on low GaN surface recombination velocity.[12,13] On the other hand the consistently weaker emission from the thin-cap sample B com-

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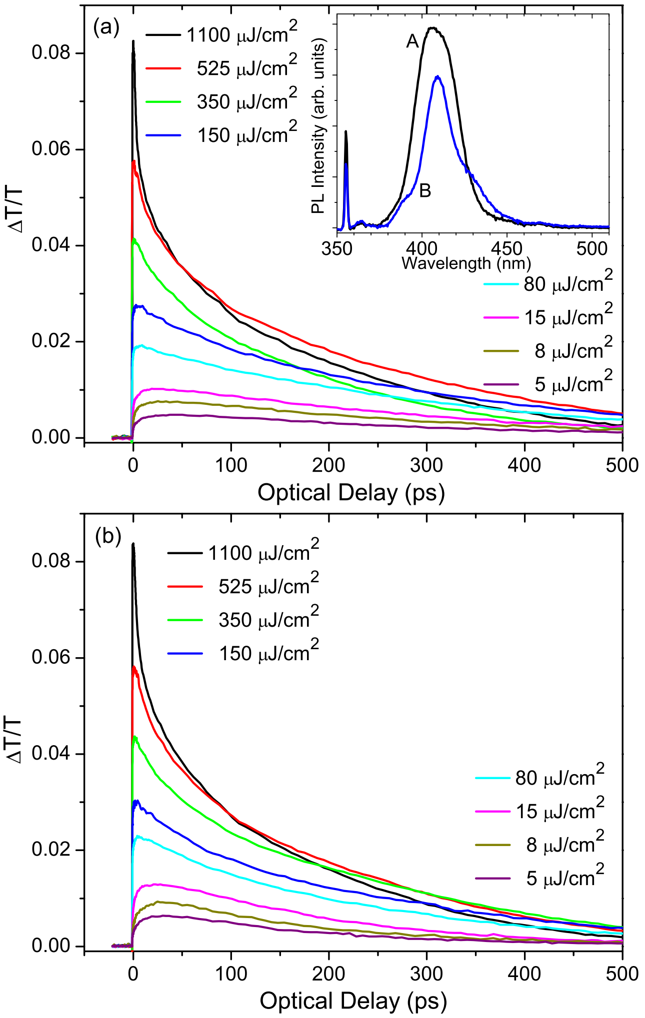

FIG. 1. (Color online) Transient transmission measurements carried out on the two different cap SQWs (a) sample A and (b) sample B. The excitation was set at 325 nm and the probing wavelength was selected to probe the population of the energy states within the QW at 410 nm. The inset displays room-temperature comparative PL for the two samples. (The transmission signal scales with the incident fluence.)

pared to A is indicative of the presence in B of an enhanced nonradiative relaxation channel associated with the proximity of the QW excitations to the surface.

To further investigate the effect of the surface on the carrier dynamics within the QW we have used femtosecond pulse excitation. The dynamic behavior of carriers in the InGaN/GaN SQWs is investigated through the temporal behavior of ultrafast time-resolved transmission.[9,17,18] The experiments were carried using a Ti:sapphire ultrafast amplifier system generating 45 fs pulses at 800 nm and running at a repletion rate of 5 kHz. An optical parametric amplifier provided wavelength tunability in the UV range of the spectrum. A super continuum light in the UV spectral range was used as the probe beam in a typical pump-probe configuration, where the pump beam was generated from the OPA.

Time-resolved transmission intensity measurements are shown in Fig. 1 for the two samples. The OPA wavelength was set at 325 nm providing efficient photoexcitation of carriers above the GaN band-edge. The probing wavelength was selected to lie between 370–440 nm such that carrier population of the energy states within the QW can be monitored. Typical measurements are shown in Fig. 1 where the probing

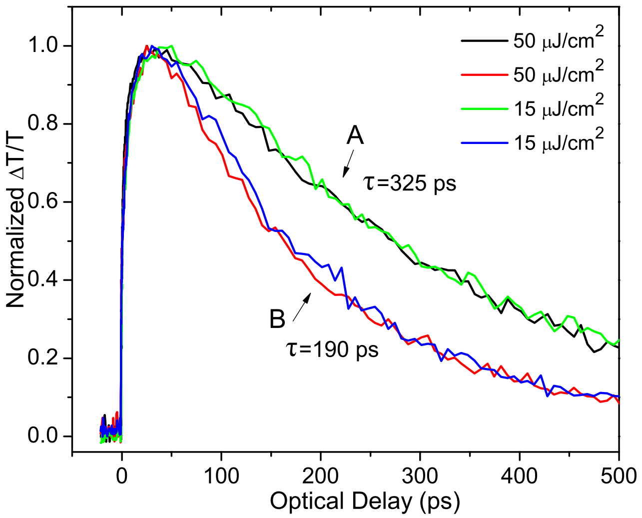

FIG. 2. (Color online) Normalized transient transmission measurements at the lowest fluence for the two different samples plotted for comparison purposes. Clearly evident is the different single-exponential decay for the two samples.

wavelength was set at 410 nm corresponding to the energetic position of the PL ground state emission. The measurements show an initial increase in the transmission following the excitation by an ultrafast pulse, reaching a maximum signal after a few picoseconds and then followed by a much slower decay. This behavior however, becomes more complex with increasing pump intensity. There appears to be a sharp transient developing close to the zero delay between the pump and probe pulses with increasing fluence. This transient becomes a dominant feature at the highest fluence utilized in this work. This feature is attributed to stimulated emission within the QW. To simplify the analysis of the measurements we have examined the data at the lowest fluences where stimulated emission is negligible. It appears that for energy densities lower than 50 $\mu\mathrm{J/cm}^2$ the recovery of the transmission signal is a single exponential, whereas at fluence higher than 80 $\mu\mathrm{J/cm}^2$ the recovery appears to become multiexponential with the fast component associated with the stimulated emission.

Normalized differential transmission spectra for the two samples in the low excitation regime are displayed in Fig. 2. The decays can be adequately fitted with single-exponential curves and show a distinct difference in the decay time of the two samples. Fitting of the data results in time constants of $t_{1\mathrm{A}} \sim 325$ ps, and $t_{1\mathrm{B}} \sim 190$ ps for samples A and B, respectively. The same relaxation rates are observed for lower fluences down to the lowest fluence of 2 $\mu\mathrm{J/cm}^2$ corresponding to an estimated photogenerated carrier density of 4×10^{18} cm^{-3}. Given the identical excitation conditions that the samples were subjected to, we attribute the variation in the observed relaxation rates to the enhancement in the nonradiative surface recombination rate in the thin-cap sample due to the closer proximity of the QW carriers to the surface. This is further supported by the reduced radiative recombination rate of sample B observed in the PL. A rough estimation of the efficiency of this relaxation channel Φ_1 can be derived if we assume that surface relaxation in sample A is negligible compared to B and if we assume the efficiency of all other radiative and nonradiative recombination channels in the two samples approximately equal. Φ_S is then given by

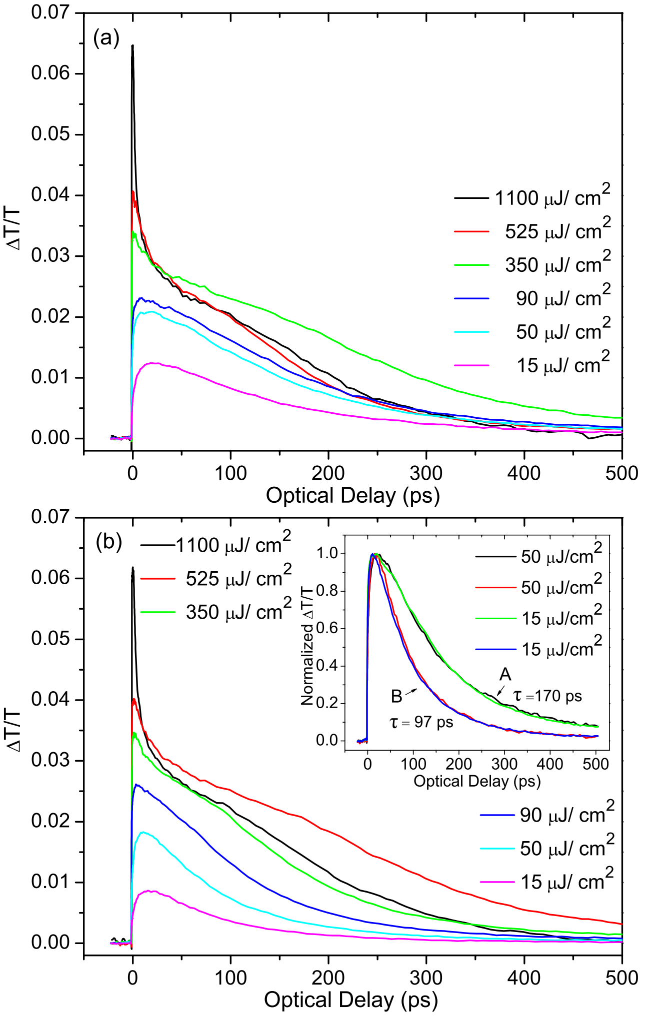

FIG. 3. (Color online) Transient transmission measurements carried out on the two different cap SQWs (a) sample A and (b) sample B. The excitation was set at 325 nm and the probing wavelength was selected to probe the population of the excited energy state within the QW at 385 nm. The inset in (b) shows the normalized differential transmission for the lowest fluence of sample A and B for comparison purposes.

$$\Phi_1 = \frac{t_{1B}^{-1} - t_{1A}^{-1}}{t_{1B}^{-1} + t_{1A}^{-1}} \approx 26\%, \qquad (1)$$

where $t_{1A}{}^{-1}$ and $t_{1B}{}^{-1}$ are the recombination rates of the two samples when probing the ground state of the QW.

To further investigate the effects of surface-related states on the carriers within the QW we have examined the carrier relaxation near the excited state of the QW. Figure 3 shows time-resolved transmission measurements for the two samples when the probe pulse wavelength is set to 385 nm. At this wavelength the excited state of the QW is probed; this is supported by the fact that the PL spectra at high excitation densities contain a distinct shoulder at 385–390 nm, attributed to emission from the excited states of the well. In the transient measurements we observe a similar behavior as that observed when the ground state of the QW was probed (Fig. 1). Stimulated emission appears to become noticeable for fluence larger than 80 μJ/cm^2 but it seems to be more pronounced in respect to the ground state as seen in Fig. 3. At fluences lower than 50 μJ/cm^2 the carrier relaxation rates in both samples appear to be faster from those measured for the ground state. Adequate fitting of the decays is again provided by single-exponential curves with time constants of $t_{2A} \sim 170$ ps and $t_{2B} \sim 97$ ps for samples A and B, respectively. The difference observed between the ground state and excited state relaxation rate is probably due to the to the higher carrier escape rate from the wells, due to the closer energetic proximity of the excited state to the GaN barrier band-edge. The slightly higher efficiency of decay in the excited state Φ_2 of $\sim$31% obtained with the simplistic formulation of Eq. (1) may point toward a stronger coupling of the surface states to the excited QW states.

In conclusion we have investigated the effects of the surface on the relaxation dynamics of two (Ga,In)N/GaN SQW structures that differ only on the average thicknesses of the GaN cap layer above the QW. A combination of steady-state PL and differential transmission measurements were used to probe the relaxation of photoexcitated carriers in the SQWs. The transient measurements show single-exponential decays at low fluencies, while multiexponential decays due to stimulated emission are observed at higher excitation densities. For all densities studied, we observed weaker QW integrated emission and enhanced QW carrier relaxation rates in the thinner-cap sample when probing both the ground and excited states of the well. The behavior is attributed to the enhanced nonradiative recombination in surface-related states due to the close surface proximity of the QW excitations. Investigation of the surface recombination of carriers in GaN is crucial in order to determine the limitations of nitride-based devices with active regions in nanoscale proximity to the surface.

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