Alloy states in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys ($x < 1\%$)

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(Received 3 December 2002; accepted 23 January 2003)

A set of $\text{GaAs}_{1-x}\text{N}_x$ samples with small nitrogen composition ($x < 1\%$) were investigated by continuous-wave photoluminescence (PL), pulse-wave excitation PL, and time-resolved PL. In the PL spectra, an extra transition located at the higher-energy side of the commonly reported N-related emissions was observed. By measuring the PL dependence on temperature and excitation power, the PL peak was identified as a transition of alloy band edge-related recombination in GaAsN. The PL dynamics further confirms its intrinsic nature as being associated with the band edge rather than N-related bound states. © 2003 American Institute of Physics. [DOI: 10.1063/1.1560872]

Heavily nitrogen (N)-doped GaAs, often referred to as a dilute $\text{GaAs}_{1-x}\text{N}_x$ alloy, has been intensively studied in the past decade. The incorporation of small amounts of N leads to giant band structure changes in the host semiconductor GaAs.^{1,2} However, the mechanisms underlying the N-induced band gap reduction remain contentious.^{3–5} The results of luminescence and absorption by Makimoto *et al.*⁶ suggested that the band gap reduction in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloy ($x < 0.3\%$) starts at a nitrogen-concentration as low as 10^{18} cm^{-3} . Grüning *et al.*⁷ investigated the unusual band formation at the Γ point and found that the GaAs-like band edge excitonic state shifts to lower energy with increasing N concentration ($x < 0.2\%$) in GaAsN epilayers. When the N concentration was further increased N-cluster states merged into one broadband, which then dominated the photoluminescence (PL) spectra, and the actual PL corresponding to the excitonic band gap gradually became invisible. However, Zhang *et al.* proposed that the impurity band formation from N-induced bound states in GaAs:N played a key role in the band gap reduction,⁸ and pointed out that the observed-scaling rule of band gap reduction was supportive of their argument.⁹ A recent study of Zhang *et al.* has indicated that the effect of the impurity band formation on the band edge electronic structure critically depends on the band structure of the host material.¹⁰ Very recently, Wang *et al.*¹¹ explored a PL emission in GaAsN under high magnetic fields and assigned it as an on-set of delocalized states, resulting from the interaction of localized impurity state and the approaching delocalized host state. In theoretical effort, Kent *et al.*¹² explained the evolution of the electronic structure of $\text{GaAs}_{1-x}\text{N}_x$ from the dilute nitrogen impurity regime to the nascent nitride alloy using empirical pseudopotential

method. Up to now, it is unclear as to how and at what composition the GaAsN band edge states remain distinguished from impurity states.

In this work we have investigated a series of heavily doped $\text{GaAs}_{1-x}\text{N}_x$ samples with small N composition ($x < 1\%$) using cw photoluminescence PL, pulse-wave (pw) excitation PL, and time-resolved PL (TRPL). In the PL spectra we have observed an extra transition located on the higher energy side of the previously reported N-related emissions. The relative intensity of this emission is found to increase with increase of either temperature or excitation power. By measuring the PL dependence on temperature and excitation power, we have identified the PL peak as a transition of alloy band edge-related recombination in GaAsN. The PL dynamics further confirms its intrinsic nature, well distinguished from transitions associated with N-related bound states.

The $\text{GaAs}_{1-x}\text{N}_x$ samples investigated here were grown by gas-source molecular beam epitaxy on semi-insulating (001) GaAs substrates at 420°C and a growth rate of $0.8 \mu\text{m/h}$ using a rf nitrogen radical beam source with a mixture of N_2 and Ar in a ratio of 1:9. The epilayer thickness of the samples is nominally 400 nm. Four samples [No. 2658 ($x \sim 0.10\%$), No. 2846 ($x \sim 0.22\%$), No. 2847 ($x \sim 0.36\%$), and No. 2848 ($x \sim 0.62\%$)] were used in this study. The detailed growth process has been described elsewhere.^{8,10} The N concentration was determined by high-resolution x-ray rocking curve measurements and theoretical dynamical simulations. For cw and pw excitation PL, a Ti sapphire laser, in either cw mode or mode-locked mode, was used as the excitation source. The detection system includes an HR250 single-grating spectrometer and a liquid nitrogen cooled InGaAs photomultiplier tube. The spectral resolution was 0.4 meV. For the time-resolved PL, the Ti:sapphire mode-locked laser was used and the time-correlated signal

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FIG. 3. (a) 14 K time-resolved PL of No. 2658 sample which are detected at 20, 50, and 150 ps, respectively. (b) The decay PL decay curves of No. 2658 sample monitored at GaAs [not shown in Fig. 3(a)], E_b , NN_E , NN_D , and NC.

different evolution of the E_b emission and N-related bound emissions with increasing N composition shows again that the origin of the E_b emission could be completely different from N-related bound states. In the inset of Fig. 2 the peak energy of the E_b emission is plotted as a function of N concentration. E_b has approximately a linear dependence on x with $dE/dx \sim -200$ meV/N% in the N-concentration range of 0.1%–0.62%. Note that E_b follows closely with the excitonic band gap determined by the absorption¹⁰ or photoluminescence excited spectra (PLE),^{6,7} but with a small redshift, as in many conventional alloys.

In order to reveal the physical origin of the E_b emission, we have carried out time-resolved PL measurements for the samples. Figure 3(a) shows the low-temperature PL spectra of a $\text{GaN}_x\text{As}_{1-x}$ ($x=0.1\%$) sample at different delay times. It can be seen that the E_b emission dominates the PL spectrum immediately after the short pulse excitation (20 ps). With increase of the delay time, a number of N-related emissions appear. At 200 ps the PL spectrum is dominated by N-related emissions, labeled as NC, NN_E , NN_D , etc. PL decay curves monitored at different energies are plotted in Fig. 3(b). One can clearly distinguish two types of carrier dynamics. The decay time of the E_b emission is ~ 165 ps, comparable to that of the near band gap GaAs emission (170 ps). Whereas the carrier decay times of the nitrogen bound states are much longer: 3 ns for NN_E , 8 ns for NN_D , and more than 10 ns for NC (limited by the instrument). In general, excitons bound in potential minima, will be frozen up in mobility, resulting in a reduction of the spatial coherence,

and consequently have a longer lifetime. This happens in the cases of quantum dots and quantum wires where the decrease of the excitonic coherence extension is imposed by the lateral dimensional confinement.^{16,17}

In summary we have investigated a set of heavily doped $\text{GaAs}_{1-x}\text{N}_x$ with small N composition ($x < 1\%$) by PL and TRPL. In the PL spectra an extra transition located at the higher energy side of the reported N-related emissions was observed. We have taken advantages of short pulse excitation and PL decay time measurements to clarify the physical origin of the emission. Our experimental results strongly suggest that the PL peak is a band edge transition of the GaNAs alloy rather than a transition from N-related bound states. The GaAsN band edge states remain distinguished from N impurity states at least up to $x=0.62\%$. The importance of this work is to show how the change in the alloy band gap is manifested in its band edge PL in a similar fashion as that in conventional alloys.

The authors are grateful to Professor G. H. Li for his comments. This work was supported by the special funds of the Major State Basic Research Project through Grant Nos. G001CB3095, 19974045, and 10274081 from NSFC, Nanotech project of CAS, and Grant No. HKUST 6125/98P.

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