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Spectroscopy and Modeling of Carrier Recombination in III–N Heterostructures

P. M. Sweeney (a), M. C. Cheung (a), F. Chen (a), A. N. Cartwright[1]) (a), D. P. Bour*) (b), and M. Kneissl (b)

(a) Department of Electrical Engineering, 201 Bonner Hall, Box 60-1900, University at Buffalo, State University of New York, NY 14260, USA

(b) Xerox-Palo Alto Research Center, Electronic Materials Laboratory, Palo Alto, CA 94304, USA

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Time-resolved temperature dependent PL measurements of InGaN quantum wells are presented. The effects of quantum well-like and localized state emission in similar p–i(MQW)–n structures are discussed. A phenomenological model is presented to explain the observed dynamics.

Introduction The future development of visible optoelectronic devices such as LEDs, lasers, and visible modulators depends critically on a more complete understanding of the growth and emission processes in III–N quantum well structures. Much recent research has incorporated piezoelectricity, indium segregation, localized strain relaxation, quantum well width fluctuations, and spontaneous polarization to explain the complicated emission processes in these materials. Here, we present how time-resolved spectroscopy of nearly identical InGaN quantum well structures provides insight into the role of indium segregation in these structures. Moreover, we discuss how these localized fluctuations result in spatially distributed regions of highly efficient emission and drastic shifts in the emission wavelength, and how time-resolved spectroscopy can be used to estimate the relative percentage of phase segregation.

Indium Segregation and Piezoelectricity The solid phase immiscibility gap in InGaN results from the large difference in interatomic spacing between GaN and InN [1, 2]. One method to reach longer emission wavelengths in III-N heterostructures is to increase the indium concentration of the InGaN layer that is typically used as the quantum well material. High indium concentrations have been difficult to obtain primarily because of the effects on crystalline quality. Attempts to improve epilayer quality by raising the growth temperature have resulted in lower InN concentrations because of the volatility of nitrogen [3]. Moreover, in low temperature growth it is possible to get two separate phases of material within the same quantum well [1, 2, 4]. As a further complication to the emission dynamics in these materials, the observation of piezoelectricity in wurtzite $In_xGa_{1-x}N$/GaN heterostructures [5–7] has changed our understanding of the behavior of these materials under optical or electrical excitation. These piezoelectric fields are quite large (reported from 300 kV/cm to 1.1 MV/cm for 20% indium)

[1]) Corresponding author; Phone: (716) 645-3115x1205; Fax: (716) 645-5964;
e-mail: anc@eng.buffalo.edu
*) Now at Agilent Laboratories.

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[5, 6]. The magnitude of the in-well and barrier fields and the resulting band-structures of InGaN/GaN samples, as well as the accompanying spectral shifts, have been reported [7]. Of course, carrier recombination and transport dynamics in these materials are quite complicated due to the strong interaction between indium segregation and piezoelectricity [8].

Consistent with Stringfellow's theoretical calculation [1, 2], in this paper, we will provide data that is indicative of both a low indium phase and a high indium phase in the same sample. We discuss how these indium rich regions act as highly efficient radiative centers that increase device efficiency by attracting carriers away from non-radiative defect dislocations. To do this, we present the results of time-resolved photoluminescence (PL) of two samples with similar well widths and indium concentrations grown under different conditions (additional measurements have shown similar behavior in a number of other samples). Both samples were grown by organometallic vapor phase epitaxy (OMVPE). Initially, a 4 μm thick layer of GaN : Si was deposited on a *c*-plane sapphire substrate, followed by the MQW region. The MQW region consists of the GaN barrier and the 2 nm thick $In_{0.2}Ga_{0.8}N$ quantum well region. This barrier and quantum well layer was repeated to achieve the desired number of quantum wells (2 and 20). The last quantum well in each sample was capped with a GaN barrier region followed by a GaN : Mg p-contact layer. For simplicity we refer to these samples as M2 (2 quantum wells) and M20 (20 quantum wells). The frequency doubled, ~200 fs pulses, from a tunable mode-locked Ti : sapphire laser at the repetition rate of 80 MHz served as the excitation source for time-resolved photoluminescence (TRPL). The wavelength of the incident light was varied to effectively pump directly within the quantum well without exciting the higher bandgap barrier material. The resulting PL was spectrally and temporally resolved using a Hamamatsu streak camera with a 20 ps response time.

As can be seen from Fig. 1, the observed spectra for each sample at 15 K is quite different. The M20 spectrum consists of a single emission peak at 412 nm with a spectral width of 67 meV that decays with a time constant of approximately 5 ns. In contrast, M2 is seen to have two distinct peaks, a strong emission peak at 370 nm that decays with a time constant of 800 ps and a second peak at 463 nm that has an exceptionally long lifetime that is beyond the resolution of the interpulse spacing of our Ti : sapphire laser system. A quantum mechanical calculation of the expected excitonic

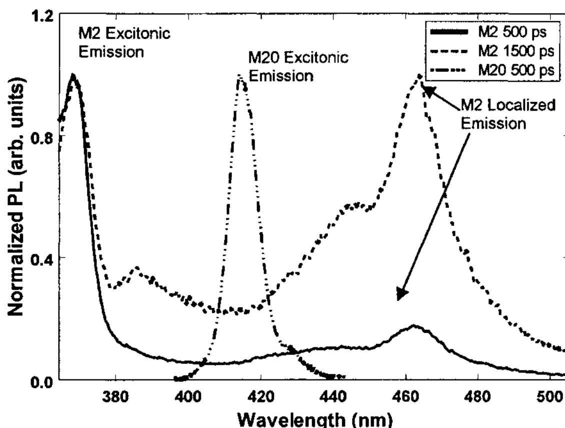

Fig. 1. Normalized time-resolved PL spectra of M2 (at 500 and 1500 ps) and M20 (at 500 ps) at 15 K

emission within the well (including piezoelectricity, the internal p–i–n field, and assuming 20% InGaN) is in excellent agreement with the peak emission energy of sample M20. However, the peak emission energies from sample M2 suggests that sample M2 is not behaving as a traditional quantum well at all. Clearly there are several different recombination states in M2, evidenced from the multiple peaks in the spectrum. The primary peak at short times (370 nm) behaves like a classic quantum well emission and the other very broad peak exhibits a Stokes shifted localized emission. Emission at this low energy (2.68 eV) would require either a much higher indium concentration or the presence of localized states due to phase segregation. The indium concentration within the quantum wells of M2 and M20 have both been estimated to be approximately 20% by X-ray diffraction. Although longer wavelength emission can be explained by several different theories including interface roughness, piezoelectricity, and localized strain, the 200 meV shift from the expected energy, and the broad emission, observed in sample M2 is consistent with a distribution of localized regions of varying size and indium concentration [8, 9]. Moreover, the observed increased lifetime of the low energy emission peak in M2 is consistent with stronger confinement due to localization of carriers in nanometer scale regions [10].

Model These studies are consistent with phase segregation producing regions of radiative recombination centers observed at lower emission energies. In other words, in InGaN the presence of the indium rich regions, which reduces crystalline quality, provides an efficient alternate, radiative trap for carriers in the quantum well [8, 9]. Although space limits full treatment here, Fig. 2 shows an energy level diagram with representative levels for the quantum well emission, for a spatially localized lower energy emission region, and finally a level that represents the defects within the system. For sample M20, there are very few localized low energy emission centers, and the emission spectrum is dominated by a single exponential decay representative of the excitonic emission, and the non-radiative recombination, from a fairly uniform alloy within the quantum well. Sample M2, on the other hand, is observed to have two distinct emission paths. The first (short wavelength) emission is a quantum well-like emission that rapidly decays as the carriers in the conduction band recombine radiatively through excitonic emission and also diffuse in the plane of the quantum well to the regions with lower potentials. Since the in-plane transport process can be very fast, the observed emission decay and the extracted lifetime from this high-energy state is probably more indicative

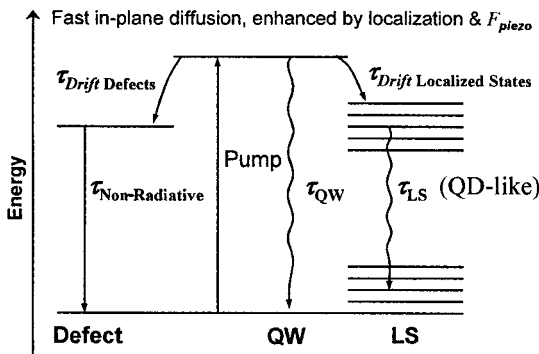

Fig. 2. Simple carrier dynamics model. Efficiency is affected by diffusion and drift to both defect dislocations and indium rich localized regions

of the in-plane transport. The second (long wavelength) emission appears to be strongly localized and has a very long lifetime (>13 ns), which is also representative of the typical emission observed from commercially available long wavelength emitting LED structures [10]. Moreover, this emission is well characterized by a disordered system with a large characteristic confinement potential. This disorder can be explained by phase segregation in M2 resulting in the formation of indium rich regions. Consistent with phase segregation, we should expect regions of high (>20%) indium concentrations and regions of low (< 20%) indium concentrations.

The emission spectrum near zero delay (the solid curve in Fig. 1) is extremely useful for estimating the relative areas of the efficient emission centers and the lower indium concentration material. At short times, before diffusion has taken place, carriers should be fairly uniformly distributed locally in the excitation region. Therefore, since the short wavelength emission represents quantum well emission and the long wavelength emission represents localized state emission in indium rich regions, the relative ratio of the area under the curve should be approximately representative of the area of each region. The ratio of the two peaks (quantum well-like emission and quantum dot-like emission) in M2 at short times is roughly 6 : 1. Based on Stringfellow's calculations [1, 2], a possible explanation of this would be that nearly 86% of the material produced was a true alloy of approximately 12% indium (estimated from a fit of the observed emission energy to the expected excitonic emission energy of this quantum well), while the other 14% is composed of indium rich regions that vary in size and concentration with an estimated average indium concentration of 62%. This is evident in the broad emission at long wavelengths. As diffusion starts to take place, carriers will be attracted to the lower energy localized potential minima, where they will recombine radiatively. In addition, the lifetimes of the longer wavelength emission will be enhanced, not only by the localization, but also due to the spatial separation of carriers resulting from the large piezoelectric fields generated in these indium rich regions.

Summary In this paper, we have presented experimental studies of two InGaN/GaN MQW structures and provided a description of phase-segregation as well as the resulting carrier dynamics. Moreover, we have demonstrated the use of time-resolved photoluminescence to estimate the segregation in these materials. Structural analyses are necessary to verify the accuracy of this simple technique. There are many more complications in these III–N materials that contribute to changes in emission energy, linewidth, and the lifetimes of the carriers. Moreover, the development of composite structures that can accurately control the in-well field and reduce defect densities should result in device geometries for high quality visible LEDs, lasers, and modulators.

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