# Origin of Luminescence from InGaN Diodes

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We report the first direct observation of phase decomposition in a luminescent alloy and show that this decomposition, allied to quantum confinement enhancements, accounts for the surprisingly high efficiency of InGaN-based diodes manufactured by Nichia Chemical Industries. Hence nanostructure, rather than composition, is responsible for the success of these devices. A common nanostructure, in the form of nearly pure InN quantum dots, occurs across a large range of average indium content in InGaN and leads to a universal scalability of the optical spectra. [S0031-9007(98)08055-7]

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While Nichia Chemical Industries have recently commercialized blue and green light-emitting diodes (LEDs) based upon InGaN quantum wells [1,2], and demonstrated long-lived blue lasers at room temperature [3], rather little is known about the origin of the luminescence from such devices, or its apparent indifference to a huge density of structural defects [4]. Much of the discussion of the operational characteristics of Nichia diodes contradicts a theoretical demonstration [5] that In is, to a large extent, *insoluble* in GaN at typical growth temperatures. Hence the emission spectrum of, say, a "50% alloy of InGaN grown at 700 °C" should actually contain two components at high and low energy, corresponding to the two-component phase decomposition demanded by thermodynamics. This decomposition of the emission spectrum has been observed for the first time in Nichia diode electroluminescence spectra. In addition, we observe a shift of the low-energy component due to quantum confinement in nanocrystalline inclusions of nearly pure InN, which leads to a dominant emission band in the blue or green spectral region.

Although (partial) phase segregation has been shown to be present in InGaN alloys by a number of authors [6–8], we argue here that cation segregation takes an extreme form in Nichia diodes, and find that the origin of the luminescence in these devices is best described as emission from quantum dots of approximately constant composition—approaching InN—and having radii that increase monotonically with the average In incorporation.

The intimate connection between exciton localization and luminescence in semiconductors is now well established. Luminescence occurs when the dwell time of an exciton in a localized site exceeds its radiative decay time. The process of luminescence therefore involves an exchange of energy between a massive stationary particle (the exciton) and a massless particle traveling out of the semiconductor at the speed of light (the photon). The interaction is well described in systems without disorder by the polariton model, but it should be noted that each luminescence event involves at least one defect, in the form of a surface. Since excitation, in contrast to luminescence, maps the joint density of states (JDOS), there is an energy shift (usually called the Stokes' shift) between peaks of luminescence and absorption in solid state systems with spatial energy disorder (see, for example, Ref. [9]). The magnitude of this shift scales in a universal way with the classical localization in one dimension [10] and two [11]. No analysis for three-dimensional localization, such as in disordered alloys, is available but, experimentally, the Stokes' shift has been shown to be proportional to the emission linewidth (these quantities being approximately equal in magnitude) [12]. In this paper we examine, with a large dynamic range, the electroluminescence (EL) and photocurrent (PC) spectra of commercial Nichia diodes. We thereby demonstrate the extent of localization in the active regions of these devices, and relate the experimental results to a model that attributes the luminescence almost exclusively to quantum dots.

Emission and absorption data were measured, at temperatures between 300 and 4.2 K, for blue and green Nichia LEDs. These devices contain a single InGaN quantum well (about 3 nm wide), sandwiched by several $\mu$m of $n$-GaN and a thin $p$-AlGaN cladding layer. The emission wavelength is tuned by increasing the indium level within the quantum well, with nominal indium mole fractions between 0.2 and 0.45 for blue and green devices. The EL was detected by using a GaAs:Cs photomultiplier tube while the PC spectroscopy involved measuring the photocurrent generated within unbiased LEDs illuminated by monochromated light from a tungsten lamp. Figure 1 shows low temperature spectra from blue and green emitting devices at 4.2 K, plotted on a logarithmic scale to emphasize the large dynamic range of the measurements.

The EL spectra show the main blue and green peaks with nearly exponential tails at both high and low energy [13]. A shift to higher energy is observed with increasing drive current due to the saturation of the lowest energy states. To faithfully represent the energy distribution of the localized states, measurements are made with rather low drive currents—typically, 50 $\mu$A. At a higher drive current, of order 5 mA, the linear EL spectrum (Fig. 2) highlights the relative weakness of the second,

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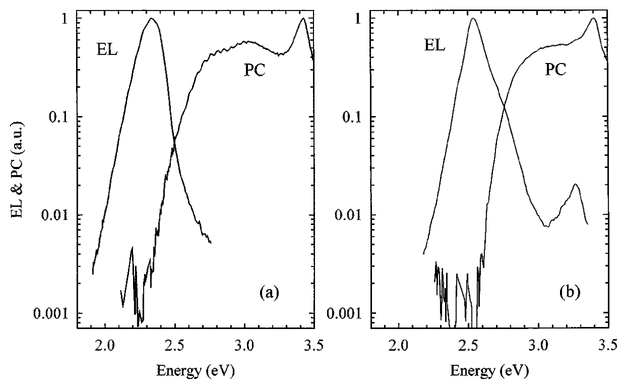


FIG. 1. EL and PC spectra at 4.2 K from (a) green and (b) blue Nichia diodes.

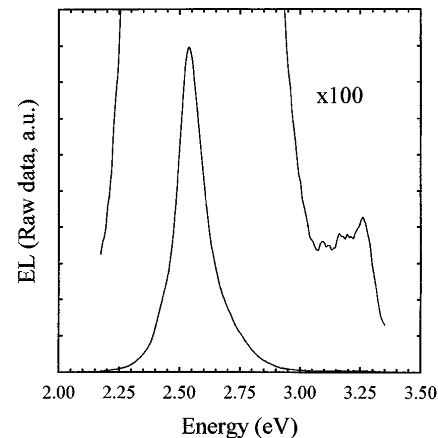


FIG. 2. Expanded 4.2 K EL data from a blue diode, highlighting the high-energy peak.

high-energy emission peak at 3.25 eV. The PC spectra consist of an absorption edge with a low-energy tail, rising to a plateau which terminates with a peak at approximately 3.4 eV, slightly below the low temperature band gap of GaN.

Our analysis of the light emission from Nichia diodes rests upon an evaluation of the Stokes' shifts for the luminescence peaks in Figs. 1 and 2. While the smaller, high-energy peak is related to the corresponding absorption transition in exactly the way predicted for a random alloy [12], the larger peak shows an anomalous relaxation, entirely consistent with our present knowledge of the excitation cycle of quantum dots. Taking into account their very different half-widths, the ratio of the emission intensities of the low- and high-energy peaks is approximately 1000:1.

It is immediately apparent that the dominant EL peak for both blue and green diodes coincides with the low-energy asymptote of the PC, indicating that the distribution of localized excitons peaks at an energy for which the JDOS of delocalized excitons is in fact vanishingly small. States at still lower energy, viz., the whole lower half of the emission spectra, do not overlap with the JDOS and are therefore *more localized* than is classically possible. To extend the comparison of EL and PC it is essential to provide a consistent description of the absorption edge, $\alpha(E)$. This involves an average energy gap ($E_B$) for the InGaN layer and a broadening parameter ($\Delta E$) which reflects the energy gap fluctuations resulting from In-Ga segregation. The following sigmoidal formula has been used [14] with $\Delta E$ equivalent to the Urbach tailing energy [15]:

$$\alpha(E) = \alpha_0 \left( \frac{1}{1 + \exp(\frac{E_B - E}{\Delta E})} \right). \tag{1}$$

The Stokes' shift, defined as the energy difference between $E_B$ and the peak of the emission spectrum, is plotted against the emission peak energy in Fig. 3. Results from photoluminescence and optical density measurements on a range of InGaN epilayers [14,16] are included to demonstrate the general linear relationship between Stokes' shift and luminescence peak energy. Extrapolating to the GaN band-gap energy reduces the Stokes' shift to zero, as expected. The energy shift between the delocalized excitonic states and the localized states responsible for light emission is seen to increase with increasing indium incorporation, demonstrating a deepening of the level of localization. In addition, data from large numbers of InGaN diodes and epilayers reveal similar linear dependencies on the emission peak energy for the width of the EL peak [17] and the broadening ($\Delta E$) of the PC or optical absorption spectra [14].

Having demonstrated these scaling relationships, we are able to offer a complete description of the origin of the luminescence in InGaN epilayers and Nichia LEDs. Rather than form a conventional alloy, the highly restricted solubility of In in GaN (less than 6% at typical growth temperatures according to the theoretical estimate) leads to an InGaN active layer composed of quantum dots of nearly uniform composition (approaching InN) embedded in an indium deficient matrix ($In_xGa_{1-x}N$, with $x < 0.06$). Increasing the indium incorporation merely increases the mean size of the quantum dots, while the composition stays pinned. These quantum dots provide highly efficient centers for radiative recombination of excitons, free from the deleterious effects of the numerous dislocations present. A sharp drop in efficiency has been reported at a low indium level in ultraviolet InGaN LEDs [18], which can be explained by the requirement of a minimum level of indium for quantum dot formation. The emission energy is determined by quantum confinement within the dots. Although a number of material parameters are not well established for InN, preliminary estimations using electron (hole) masses of $0.2m_0$ ($1.0m_0$) indicate that the entire observed spectral range can be accounted for with dot sizes ranging from the logical minimum (of order 0.6 nm) to approximately 2 nm. Thus, the energies of

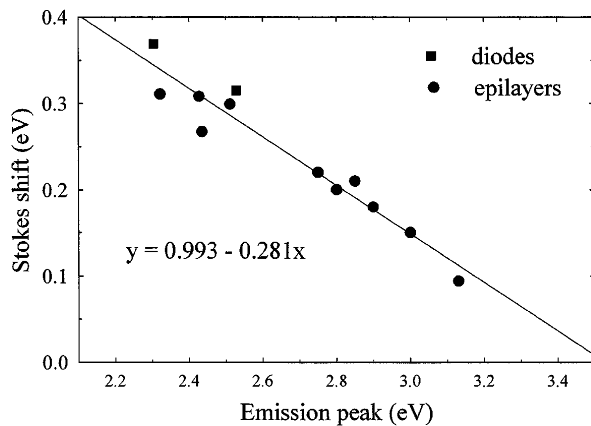


FIG. 3. Stokes shift plotted against emission peak energy for the Nichia diodes and a range of InGaN epilayers.

the main EL peaks in Figs. 1 and 2 correspond to intrinsic emission from nearly pure InN, enhanced by quantum confinement, while the higher energy of the subsidiary peak reflects the band gap of the nearly pure GaN matrix, saturated with a few percent of indium. According to the calibration of Middleton *et al.* [19], this peak corresponds to a saturated indium concentration of 4%.

A 4% solution of In in GaN may of course occupy more (or less) than 4% of the total volume. The filling of the available space in the decomposed InGaN mixture depends upon the initial In:Ga ratio. For example, a layer of $\ln_{0.53}Ga_{0.47}N$ may consist of a connected percolation tree of $\ln_{0.04}Ga_{0.96}N$ which takes up 49% of the total volume, InN dots which occupy 51%, and microdispersed metallic clusters which constitute the remainder of the material. Direct observation of the quantum dots using transmission electron microscopy would be desirable but is rendered extremely difficult by their small size (estimated to be of order 1 nm). Analysis of x-ray absorption fine structure oscillations can provide structural information on the nanometer scale. When used to probe the local environment of indium atoms within InGaN layers on a next-nearest-neighbor scale, this technique has indicated phase segregation into nanometer size quantum dots and metallic clusters [20,21].

The indium composition of InGaN "alloys" is usually extracted from x-ray diffraction experiments by using Vegard's law. This states that the lattice constant of a ternary compound varies linearly between those of the two constituent binaries as the composition changes. The broad peaks obtained by experiment are interpreted as resulting from an InGaN layer of varying composition, and a mean value for the composition is then calculated using the peak of the scattering curve. The InGaN peaks are found to broaden as one attempts to grow layers of higher indium concentration. This broadening is attributed to the deterioration of layer quality as the lattice mismatch between adjacent layers becomes an issue.

Our results suggest an alternative account: What is recovered in x-ray diffraction is a product of the distribution of nearly pure InN quantum dot sizes within the layer. At low levels of indium incorporation, the dots are small and therefore constrained to the GaN lattice constant by the surrounding matrix. Small variations in dot size, and hence local lattice constant, lead to a minimal broadening of the x-ray diffraction peak. However, as one introduces increasing amounts of indium to the system, the dots become larger and exert a greater influence over their local environment, gradually approaching the lattice constant of pure InN as the matrix effects weaken. The increased linewidth of the shifted diffraction peak is then explained by an increasing variation in the sizes of the nearly pure InN dots as the average indium content increases.

The anticorrelation between crystal perfection, assessed by detecting nonequilibrium single-phase material, and luminescence efficiency has an obvious explanation in the quantum dot picture. Material that shows sharp InGaN diffraction peaks may be devoid of nearly pure InN quantum dots and therefore show no, or very weak, luminescence. This matter will be explored elsewhere.

In summary, we have shown that InGaN is a truly quantum material. Perhaps only one other luminescent system, that of porous silicon, shows comparable characteristics [22]. There, too, it is the nanostructure, rather than the composition, which defines the material properties. The scalabilities of the Stokes shift, absorption edge broadening, and luminescence peak width with emission peak energy reveal a common factor controlling the spectroscopic properties of InGaN layers. This commonality is shown to arise from the presence of quantum dots whose composition does not change with the level of indium incorporation. The InGaN system acts as an extremely sophisticated quantum capture system: Charge carriers formed by electrical or photoexcitation are captured by nearly pure InN quantum dots before they can be destroyed in the network of dislocations that plague even the best materials. Once trapped, they have no choice but to convert into photons and contribute usefully to device output. Thus, it is not the perfection of layer structure that will provide a route to superior device performance, rather it is the utilization of the very impossibility of perfect material that is the key to future improvements in InGaN-based devices. The task for nitride research must now be to fully exploit the as-yet unrealized potential of the self-formed quantum dots.

[1] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Appl. Phys. Lett. **67**, 1868 (1995).
[2] S. Nakamura, Mater. Res. Soc. Symp. Proc. **395**, 879 (1996).
[3] S. Nakamura, Mater. Sci. Eng. B (to be published).
[4] S.D. Lester, F.A. Ponce, M.G. Craford, and D.A. Steigerwald, Appl. Phys. Lett. **66**, 1249 (1995).
[5] I. Ho and G.B. Stringfellow, Appl. Phys. Lett. **68**, 2701 (1996).

[6] S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, Appl. Phys. Lett. **70**, 2822 (1997).
[7] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **70**, 981 (1997).
[8] M. D. McCluskey, L. T. Romano, B. S. Krusor, D. P. Bour, N. M. Johnson, and S. Brennan, Appl. Phys. Lett. **72**, 1730 (1998).
[9] F. Yang, B. Henderson, and K. P. O'Donnell, Physica (Amsterdam) **185B**, 362 (1993).
[10] K. P. O'Donnell, F. Yang, and E. J. Austin, *Optical Properties of Low Dimensional Silicon Structures,* edited by D. C. Bensahel *et al.,* NATO ASI Ser. E, Vol. 244 (Kluwer, Dordrecht, 1993), p. 235.
[11] F. Yang, M. Wilkinson, E. J. Austin, and K. P. O'Donnell, Phys. Rev. Lett. **70**, 323 (1993).
[12] S. Permogorov and A. Reznitsky, J. Lumin. **52**, 201 (1992).
[13] K. P. O'Donnell, M. Umlauff, M. Kraushaar, H. Kalt, and O. Briot, Mater. Sci. Eng. B **50**, 264 (1997).
[14] K. P. O'Donnell, R. W. Martin, P. G. Middleton, S. C. Bayliss, I. Fletcher, W. Van der Stricht, P. Demeester, and I. Moerman, Mater. Sci. Eng. B (to be published).
[15] F. Urbach, Phys. Rev. **92**, 1324 (1953).
[16] W. Van der Stricht, K. Jacobs, I. Moerman, P. Demeester, L. Considine, E. J. Thrush, J. A. Crawley, and P. Ruterana, Mater. Res. Soc. Symp. Proc. **482**, 107 (1998).
[17] K. P. O'Donnell, T. Breitkopf, H. Kalt, W. Van der Stricht, I. Moerman, P. Demeester, and P. G. Middleton, Appl. Phys. Lett. **70**, 1843 (1997).
[18] T. Mukai, D. Morita, and S. Nakamura, J. Cryst. Growth **190**, 778 (1998).
[19] P. G. Middleton, K. P. O'Donnell, T. Breitkopf, H. Kalt, W. Van der Stricht, I. Moerman, and P. Demeester, Mater. Sci. Eng. B **50**, 285 (1997).
[20] S. C. Bayliss, P. Demeester, I. Fletcher, R. W. Martin, P. G. Middleton, I. Moerman, K. P. O'Donnell, A. Sapelkin, C. Trager-Cowan, W. Van der Stricht, and C. Young, Mater. Sci. Eng. B (to be published).
[21] S. C. Bayliss and A. Sapelkin (unpublished).
[22] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).