The true-color photoluminescence microscopy image of an InGaN alloy-based quantum-well LED shows the presence of highly localized emission centers which originate from modulation of the quantum-well potential landscape along lateral dimensions. On page 3828, Arindam Chowdhury and co-workers show that the carrier localization in efficient radiative traps with diverse transition energies results from both local indium compositional fluctuations (orange-red dots) as well as interface-morphology related inhomogeneities (green dots).
Two Distinct Origins of Highly Localized Luminescent Centers within InGaN/GaN Quantum-Well Light-Emitting Diodes

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The high light-output efficiencies of In$_x$Ga$_{1-x}$N quantum-well (QW)-based light-emitting diodes (LEDs) even in presence of a large number of non-radiative recombination centers (such as dislocations) has been explained by localization of carriers in radiative potential traps, the origins of which still remain unclear. To provide insights on the highly efficient radiative traps, spectrally resolved photoluminescence (PL) microscopy has been performed on green-light-emitting In$_{0.22}$Ga$_{0.78}$N QW LEDs, by selectively generating carriers in the alloy layers. PL imaging shows the presence of numerous inhomogeneously distributed low-band-gap traps with diverse radiative intensities. PL spectroscopy of a statistically relevant number of individual traps reveals a clear bimodal distribution in terms of both band-gap energies and radiative recombination efficiencies, indicating the presence of two distinct classes of carrier localization centers within the same QW sample. Disparity in their relative surface coverage and photoemission “blinking” characteristics suggests that the deep traps originate from local compositional fluctuations of indium within the alloy, while the shallow traps arise from nanometer-scale thickness variations of the active layers. This is further supported by Poisson–Schrödinger self-consistent calculations and implies that radiative traps formed due to both local indium content and interface-morphology-related heterogeneities can coexist within the same QW sample.

1. Introduction

Solid-state light-emitting devices (LEDs) that utilize In$_x$Ga$_{1-x}$N-based quantum-well (QW) heterostructures are widely used for lighting applications.$^{[1-4]}$ The use of In$_x$Ga$_{1-x}$N alloys as active layers allows tunability of the wavelength of emitted light in the visible spectral range, while maintaining high external quantum efficiencies.$^{[5]}$ In$_x$Ga$_{1-x}$N QW LEDs that emit light from blue, green, and yellow regions have been successfully developed by either altering the mole-fraction of indium$^{[6]}$ or by changing the thickness of the alloy layer.$^{[3]}$ However, high efficiencies of light output in In$_x$Ga$_{1-x}$N QW LEDs is somewhat of a surprise considering the presence of a tremendously large number of (threading) dislocations ($10^8$–$10^{10}$ cm$^{-2}$), which act as highly efficient centers of non-radiative recombination of carriers.$^{[2,3,7,8]}$ It has been speculated that incorporation of indium into gallium sites suppresses non-radiative recombination pathways by funneling excitons (carriers) through sites associated with highly efficient radiative channels.$^{[7,8]}$ Although the exact nature of these radiative recombination centers in unclear,$^{[10,11]}$ there is a general consensus that spatial localization of excitions along the in-plane dimensions prevents carrier migration to non-radiative dislocations, thereby enhancing internal quantum efficiencies in In$_x$Ga$_{1-x}$N based LEDs.$^{[6,8,12-17]}$ Therefore, understanding the nature of these localization centers is tremendously important for the development of higher efficiency InGaN-based optoelectronic devices.

The existence of inhomogeneities in the active layers have added to the complexity in understanding various In$_x$Ga$_{1-x}$N-based LEDs and, consequently, the origin of the carrier localization centers (traps) that facilitate radiative recombination is not unequivocal. Based on theoretical calculations$^{[15,18,19]}$ and experimental studies, such as cathodoluminescence (CL),$^{[20,21]}$ transmission electron microscopy (TEM)$^{[13,22]}$ and near-field scanning optical microscopy (NSOM)$^{[23,24]}$ it has been proposed that efficient radiative centers can result from variation of indium compositions, presumably due to spinoidal decomposition.$^{[18]}$ However, there is ambiguity in the literature regarding the degree of variation in indium fractions in alloy layers.$^{[7,25,26]}$ Even though TEM measurements have shown the presence of significantly higher indium fractions in nanometer-scale regions,$^{[13,26]}$ it has also been reported that high electron-beam irradiation can lead to the appearance of inhomogeneous locally strained regions that can be interpreted as self-assembled indium-rich clusters.$^{[27]}$ As an alternative mechanism, it has
been proposed that interface morphology of the active layers also plays an important role in the confinement of carriers.\textsuperscript{[6,28,29]} Using TEM\textsuperscript{[28,29]} and 3D atom probe tomography (3D-APT),\textsuperscript{[30]} it has been shown that there are fluctuations in the in-plane thickness of the alloy layers and it has been surmised that these may also lead to the formation of efficient radiative traps. However, there has been no prior report that conclusively shows evidences of both compositional and morphological fluctuations within the same QW sample, even though it is beyond doubt that spatial (in-plane) localization of carriers can arise either due to formation of nanometer-scale indium-rich regions within the alloy, or due to monolayer(s) fluctuations in QW thickness.\textsuperscript{[2,8,14–16,18,19,28,29]}

Photoluminescence (PL)\textsuperscript{[21,23]} and CL\textsuperscript{[20,21]} microscopy studies performed on In\textsubscript{x}Ga\textsubscript{1-x}N QWs has revealed the presence of energetically red-shifted localized luminescent centers spread inhomogeneously across in-plane dimensions. These localized luminescent centers, which arise due to efficient funneling of carriers through radiative potential traps, have been related to the formation of quantum-dot-\textsuperscript{[22,23]} or quantum-disk-like\textsuperscript{[20,32]} centers within the alloy, which spatially localize carriers (along lateral dimensions) in lower-energy potential wells. The band-gap energies and radiative recombination efficiencies in these carrier localization centers strongly depend on the nature of the potential wells that constitute individual traps. Therefore, to relate the optoelectronic properties associated with these radiative potential traps to physical parameters that are responsible for their formation, it is imperative that individual localized luminescence centers be probed in a noninvasive fashion, preferably by optical methods. Interestingly, the vast majority of prior experiments have focused on generating carriers in barrier layers and monitor recombination processes within the alloy.\textsuperscript{[12,23,24]} However, the avalanche of carriers originating in the barriers and culminating in the wells saturate (and hence obscure) the recombination processes via the trap states due to overwhelming recombination occurring through the alloy layers.

To understand the origins of these efficient radiative potential traps and the modulations within the QW potential landscape that leads to their highly inhomogeneous photoemission behaviors, we have performed energy-mapped PL imaging and spectroscopy of green-light emitting In\textsubscript{0.22}Ga\textsubscript{0.78}N/GaN LEDs. We have selectively excited QWs with relatively low-intensity light, which serves as a unique method not only to probe the most efficient radiative traps and the carrier dynamics occurring therein, but also gain detailed information on the potential landscape within the QWs. Spectrally resolved PL imaging performed on thousands of individual luminescent traps reveal distinct radiative recombination efficiencies and band-gap energies. In this report, we show that localized emission centers in the same InGaN/GaN QW-LED sample can originate from both indium content as well as interface-morphological fluctuations along in-plane dimensions of the active layers in the same QW sample. Our work therefore provides valuable insights into the origins of radiative traps that lead to carrier localization within In\textsubscript{x}Ga\textsubscript{1-x}N QW LEDs.

2. Results

2.1. Photoluminescence Band-Gap mapping of Quantum Wells

Figure 1 (inset B) shows a typical PL image of a 10 \( \mu \text{m} \times 14 \mu \text{m} \) area of the In\textsubscript{0.22}Ga\textsubscript{0.78}N/GaN QW LED, as observed by optical microscopy. This true-color image is obtained by selectively photoexciting the alloy layer and capturing the luminescence using a color camera. In such optical images, several spatially isolated and highly localized luminescent centers are clearly visible, in addition to a weak background due to radiative recombination processes near the QW band-edge. These highly localized photoemission centers (from now on referred to as dots) are diffraction limited (FWHM <200 nm) and have intensities more than the QW background in their immediate vicinity (Supporting Information, Figure S1). The abundance of the dots show the presence of a large number of localized radiative states, where optically generated excitons recombine more efficiently than in neighboring regions in the QWs. These dots are found to be spread out in an inhomogeneous fashion across the lateral axes of the entire LED wafer and exhibit considerable differences in their emission intensities. Additionally it is possible to distinguish the colors of emitted light originating from individual emission centers even by visual inspection. The wide range of colors between green and red spectral regions that emerge from spatially well-separated Dots therefore suggests significantly diverse optical transition energies for individual emission centers. Since the energies of the emitted photons in semiconductor crystalline matrices is a consequence of radiative
recombination of carriers present in the valence/conduction bands, this color image qualitatively portrays the spatial fluctuations of optical band-gaps along the lateral axes of QWs.

The PL intensity images of the QWs obtained by collecting the luminescence via a 500 nm long-pass filter using a cooled CCD detector is shown in Figure 2A and B. These images depict the presence of several weakly emitting localized luminescent centers against an inhomogeneous QW background emission, which are found to vary over several micrometers length scales. Additionally, there are some highly radiative (“bright”) luminescent centers, the intensities of which are often an order of magnitude higher compared to the weakly emitting dots (Supporting Information, Figure S1). It is possible, however, to separate the emission originating from the weak emitters and the QW background emission by collecting the PL beyond 530 nm, where the contribution from radiative recombination processes within the QWs is relatively small. This results in the identification of a large number of dots with varying intensities and demonstrates that almost all the dots have radiative recombination energies lower than that of QWs.

Figure 2C shows the pseudocolor intensity image generated by quantitatively superimposing individual PL intensity images of the same area as in Figure 2B. The emission was collected through a green-yellow and an orange-red band-pass filter (Supporting Information, Figure S2). The emission channels are chosen such that luminescence originating from the QW background is excluded effectively. Using this method the spatial distribution of both transition energies and intensities of individual dots could be obtained in a semiquantitative manner. In these energy-mapped PL images, the colors of dots range from green through red therefore portrayed decreasing band-gaps of the localized luminescent centers. Those dots with dominant intensity contributions in either the green or the red channels are designated as green dots or red dots, respectively.

Energy-mapped PL imaging therefore served as a high-throughput technique to obtain transition energy and intensity variations for thousands of dots spread along the lateral axes of the QWs. Moreover, this method directly provides semiquantitative information on the band-gap energy distributions within the QWs, without performing spectroscopic measurements. Upon analysis of several of such color images, each containing hundreds of dots, two interesting behaviors related to the emission energies can be noticed. First, as evident from Figure 2C, amongst the numerous observable localized emission centers, there is a predominance of green dots as compared to red dots, i.e., we observe a larger number of dots through the green channel than through the lower-energy red channel. This suggests that the majority of the localized radiative recombination centers exhibits relatively shallow states, while, additionally, there are fewer (but a non-negligible number) deep-trap states. Further, on comparing the intensity and color-mapped images of the same area, we observe that most of the bright dots (dotted circles) in Figure 2A appear as red dots in Figure 2C, while the majority of green dots are relatively weak emitters (Supporting Information, Figure S2).

### 2.2. Spectrally Resolved Photoluminescence Microscopy of Individual Dots

Using the spectrally resolved PL microscopy (PLM) setup, we have been able to obtain the emission spectra of individual dots by selectively exciting the QW alloy layers. Figure 3A shows typical single-dot PL spectra obtained for five different localized emission centers, along with the electroluminescence (EL) spectra for this sample. The emission profiles are typically found to be quite broad (line widths ≈240 ± 40 meV) for all the investigated dots with a single prominent peak. It is noted that the emission maximum ($\lambda_{em}^{max}$) positions do not show any spectral diffusion within our spectral resolution. More importantly, the emission profiles are found to alter significantly from one dot to another, especially in terms of their $\lambda_{em}^{max}$ positions. Since the transition energies ($\varepsilon_{em}^{max}$) of individual localized luminescent centers are directly related to their optical band-gaps, single-dot spectroscopy corroborates that these radiative traps
having a very wide spread (≈550 meV) of band-gap energies and are always energetically lower than those of the alloy layer (dotted line).

However, it is noticed that the $\lambda_{\text{em \ max}}$ of individual Dots are not uniformly distributed over the entire spectral range between 520 and 700 nm. Therefore, single-dot PL emission spectra were recorded and analyzed for a statistically relevant number of dots from various regions of the sample. Figure 3B shows the frequency distribution of optical band-gap energies generated from the spectral analysis of 1380 individual dots. This distribution of transition energies shows that the optical band-gaps associated with dots do not vary evenly. Instead, the $\lambda_{\text{em \ max}}$ distribution is bimodal in nature and can be nicely fitted with two Gaussians centered on $\approx 2.2$ and $\approx 2$ eV. Two other multiple QW LED samples grown independently under identical growth conditions also yielded very similar results. This shows that the band-gaps associated with these radiative centers are indeed localized in two distinct well-separated energetic domains, $\approx 200$ meV and $\approx 420$ meV below that of the QWs.

In addition to such a strong band-gap preference in two specific energetic zones, there is a marked dissimilarity in the radiative recombination efficiencies of dots depending on their band-gap energies. In Figure 3C, integrated intensities of the emission spectra for all 1380 individual dots are plotted against their corresponding $\lambda_{\text{em \ max}}$ positions. This scatter plot shows that a larger number of dots with low band-gap energies are very strong emitters and therefore highly efficient radiative recombination centers as compared to the higher band-gap luminescent centers. Interestingly, there is a clear demarcation at a band-gap of $\approx 2.08$ eV, below which the average intensity of light originating from individual dots ($<I_{\text{green}}>$ = 1080 cps) is more than twice that of the higher energy luminescent centers ($<I_{\text{red}}>$ = 440 cps). This illustrates that there is a rather dramatic change in the photo-emission behavior of dots depending on whether their optical band-gaps lie below or above $\approx 2.08$ eV, which is the minimum position in the band-gap distribution shown in Figure 3B. In effect, the distribution of luminescence intensities also displays an identical bimodal behavior indicating markedly diverse radiative recombination efficiencies for the green and the red dots.

### 2.3. Relative Surface Coverage of Dots

In view of the fact that the energy-mapped PL imaging reveals the same qualitative information on optical band-gaps and radiative recombination efficiencies as achieved by single dot spectroscopy (Figure 3), the surface coverage of the green and red dots across the lateral axes of the QWs was surveyed by changing the observation areas to very different locations of the LED wafer. Figure 4A and B shows energy-mapped PL images of the QWs obtained at two very different regions—one near the center of the wafer and the other farther away from it. These two images show that both color and intensity of dots in these two regions of the same sample are very dissimilar. Typically, the green dots are found to have almost identical surface coverage over the entire LED, irrespective of the area probed. However, the red dots are sparse in the central regions of the wafer, while near the periphery there is a 5–8 fold increase in their population. Images obtained in the individual channels additionally shows that the very bright dots, which typically emitted at lower energies, are much more abundant near the periphery of the wafer. This indicates that a larger number of dots with high radiative recombination efficiencies exist near the periphery of the wafer, and most of these are red dots.

![Figure 4](https://www.MaterialsViews.com)
2.4. PL Intermittency of Dots

In addition to vast the disparities in the surface coverage and quantum efficiencies of radiative recombination in the green and red dots, there is a striking difference in their photostabilities upon continuous irradiation. It was noticed that some of the dots show discrete fluctuations in luminescence intensities upon photoexcitation of the QWs. Figure 5 shows temporal emission intermittency or “blinking” characteristics typical for such unstable dots. An energy-mapped color image in Figure 5A shows a 3 μm × 3 μm region of the QWs with several green and red dots, a few being relatively strong emitters (marked within box). Figure 5B shows that the red dot within the highlighted area displays a frequent blinking phenomenon, while the PL intensities for the other dots essentially remain unchanged over the entire acquisition times (Supporting Information, movie 1). Several such optically unstable dots are found to be present at random locations over the entire sample. However, of all the localized emission centers that were monitored, those dots that show optical instabilities are always found to have significant intensity contributions in the red channel. We have been unable to identify even a single green dot that shows any discernable temporal fluctuation of emission intensities within our time-resolution of 20 ms, even after extensive search over the entire sample. In contrast, it is possible to locate blinking red dots, even if they are relatively weak emitters. Most of these optically unstable red dots show a discrete switching of photomission signals between a bright “on” and a dim “off” state (Figure 5B) with residence times between tens of milliseconds to several seconds, depending on the concentration of photogenerated carriers.

3. Discussions

The band-gap distribution obtained from single-dot spectroscopic measurements (Figure 3) reveals that carriers can recombine at energies up to ≈550 meV lower than those in QWs. More importantly the localized emission centers show an unambiguous bimodality in their band-gaps with two maxima positions separated by more than 200 meV. Furthermore, there is an abrupt change in the average PL intensities for dots with band-gaps above and below 2.08 eV (Figure 3C) which corresponds to the minimum in the band-gap energy distribution (Figure 3B, dashed line). The lack of gradual change in both their band-gap energies and radiative recombination efficiencies therefore suggests remarkably dissimilar optoelectronic properties of these dots.

Interestingly, there are a few reports on the presence of dual-luminescence peaks in In$_x$Ga$_{1-x}$N heterostructures. [17,33–36] Dual emission features, energetically separated by ≈100 meV, observed in (ensemble) PL spectroscopy of QWs has been ascribed to dual size-distribution of indium-rich self-formed nanoclusters. [33] The presence of a red-shifted (100–200 meV) shoulder emission has also been reported for relatively thick (30–100 nm) In$_x$Ga$_{1-x}$N alloy layers using both micro-PL spectroscopy and CL imaging measurements. [17,34–36] This lower-energy (shoulder) emission has been attributed to strain-relaxation in localized regions as compared to strained areas within the QWs, which emit at higher energies. [17,36] Although a correlation between nanometer-scale strain relaxation and band-gap energies of individual localized emission centers cannot be excluded, it is rather unlikely that shifts in transition energies larger than ≈300 meV are caused by inhomogeneous strain relaxation in In$_x$Ga$_{1-x}$N multiple QW structures. [17,36]

It should be mentioned that structural imperfections, such as V-shaped pits, can also lead to the formation of localized luminescent centers. [37,38] However, these highly effective radiative recombination sites have been shown to emit at energies a few hundred meV higher than those of the QWs. [37,39] Therefore, it is improbable that the dots observed in our measurements originate due to such structural imperfections.

The lowering of band-gaps for the radiative traps can be either a consequence of local compositional fluctuations in indium content within the QWS [17,13,14] or due to slight changes in the alloy-layer morphologies near the well-barrier interface. [28,29] Both these can create localization centers along the lateral axes that alters the QW potential surface in an inhomogeneous fashion, efficiently funneling carriers through radiative channels. The dots observed in our measurements can therefore arise due to fluctuations in either the interfacial morphology of the alloy or local indium content therein, or both. Evidently, the band-gap energies and carrier recombination efficiencies
in these radiative traps will depend on the extent of compositional or thickness variations within the alloy.\textsuperscript{11,24,25} It is highly improbable, however, that nonuniform fluctuation of either of these key structural or compositional parameters can result in such intriguing observations, i.e.: i) a clear bimodal distribution of band-gap energies for the radiative traps with a maxima positioned at 1.98 and 2.2 eV; ii) the average PL intensities of individual dots show a dramatic increase with decreasing band-gap energies at \textapprox 2.08 eV. It is therefore very unlikely that the same physical phenomena gives rise to the formation of both the green and the red dots.

For In\textsubscript{0.25}Ga\textsubscript{0.75}N QWs with an alloy layer thickness of \textapprox 3.4 nm, single-monolayer fluctuations (\textapprox 0.26 nm) has been shown to alter band-gap by \textapprox 58 meV.\textsuperscript{6} It is possible however, to have thickness fluctuations up to several monolayers at given spatial location.\textsuperscript{6,10} Large variation in thickness of 4--- monolayers, though not prevalent, can lead to lowering of the band-gap of \textapprox 250 meV. Indeed, there will be a distribution of thickness variations along the in-plane axes of the QWs and single or double monolayer deviations (shallower potential traps) would be much more frequent. Therefore, it is possible that the green dots, which have band-gaps lower than the QWs by up to 260 meV (Figure 3B), can originate from fluctuations in interfacial morphology. However, since the red dots emit at considerably lower energies (2.1--1.84 eV), it is highly unlikely that these also arise due to the same reasons.

Large red-shifts in transition energies for luminescent centers have been ascribed to local compositional fluctuations in indium content, since it is well known that the alloy-layer band-gap is very sensitive to slight changes in the indium fraction.\textsuperscript{12,21,22} It has been reported for In\textsubscript{0.20}Ga\textsubscript{0.80}N QWs of 3.4 nm well widths that every percent increase in the indium content reduces the band-gap of the alloy by \textapprox 40 meV.\textsuperscript{6} Inhomogeneous compositional fluctuations are known to occur in relatively high-indium-fraction (\textgtrsim 20\%) alloys, where local domains along in-plane dimensions can comprise indium-rich zones.\textsuperscript{7,12,13,20,40} An indium content of up to \textapprox 40\% have been shown to be present in nanometer domains within green-light-emitting In\textsubscript{0.25}Ga\textsubscript{0.75}N QWs,\textsuperscript{38} which can result in a lowering of the band-gap of radiative traps by \textapprox 600 meV. Therefore, it is highly conceivable that the red dots, with transition energies 300--550 meV lower than the QWs (Figure 3B), are related to inhomogeneous variations of local-indium-fractions within the In\textsubscript{0.25}Ga\textsubscript{0.75}N alloy.

To substantiate the feasibility of this suggestion, numerical simulations using the one-dimensional Poisson--Schrödinger equation were carried out to estimate band-gap energies of In\textsubscript{1-x}Ga\textsubscript{x}N alloy layers as a function of active layer thickness and indium content (Supporting Information, Figure S3).\textsuperscript{41} These calculations show that the reduction in QW band-gap due to an increase in alloy-layer thickness of 4 monolayers (\textapprox 1 nm) does not exceed 270 and 330 meV for indium content of 20\% and 25\%, respectively. On the contrary, for an alloy layer of 4 nm thickness, an increase of the indium content by \textapprox 10\% can result in a lowering of the band-gap by more than 700 meV. These calculations therefore strongly suggest that the green dots are likely to originate from thickness variations within the alloy layer, while an increase in the local indium-fractions can indeed give rise to the red dots observed in our measurements.

Further indications that the red dots originate from local compositional fluctuations in indium content stem from their optical instabilities upon continuous irradiation (Figure 5). Temporal intermittency in the PL emission has been reported from local domains within blue- and green-light-emitting InGaN QWs prepared using metalorganic vapor phase epitaxy (MOVPE).\textsuperscript{40} It has been shown that there was a prevalence of blinking emission zones for alloy layers with larger indium fractions (i.e., for green-light-emitting QWs).\textsuperscript{40} PL emission intermittency has also been observed from lower-band-gap domains spanning several micrometers along the lateral axes of In\textsubscript{0.15}Ga\textsubscript{0.85}N QWs, which has been ascribed to formation of indium-rich regions within the alloy layers.\textsuperscript{31} Of several thousand diffraction-limited luminescent spots investigated in our samples, only the red dots, with band-gaps below 2.1 eV, show discernable two-state blinking with emission switching rates between 0.1 and 100 Hz. Such discrete switching of emission signals and excitation-power-dependent variations in their residence times are very similar to those reported for In\textsubscript{0.4}Ga\textsubscript{0.6}As and In\textsubscript{0.5}Ga\textsubscript{0.5}P self-assembled quantum dots, where the relative content of indium was considerably high.\textsuperscript{42,43} It is therefore highly likely that the red dots originate due to a local increase of indium fractions within the alloy layer. However, the green dots never show PL intermittency in the entire range of excitation powers (0.1--10 KW cm\textsuperscript{-2}), suggesting these Dots do not originate due to the same reasons.

Additional evidence on the origin of the localized luminescent centers comes from the relative surface coverage of the red and green dots near the center and periphery of the wafer on which the QWs are grown (Figure 4). It is known that for epitaxially grown heterostructures (using MOVPE), the gradient in growth temperature from the center of the wafer to its periphery is responsible for the enhanced indium incorporation in the alloy near the edge of the wafer.\textsuperscript{44} This in turn can generate a higher number of deep-trap centers within the alloy. For the LEDs reported in this work, the density of green dots remains uniform throughout the sample, indicating that their formation is unaffected by changes in the indium fractions. However, an increasing number of red dots at locations further away from the centre suggest that these highly efficient radiative traps are extremely sensitive to the indium compositional variations resulting from inhomogeneities of growth temperature across the sample. These observations are consistent with our proposition that the red dots originate from local fluctuations in the indium fractions within the InGaN alloy layers, while the green dots do not.

Inhomogeneities in QW band-gap energies, i.e., local dips and crests in the potential profiles at random spatial locations can therefore indeed originate from both compositional variations in indium content as well as interface-morphology fluctuations within the alloy layers. Such modulation of the potential landscape results in a carrier localization in these radiative traps, which abates non-radiative recombination processes by preventing carrier diffusion to nearby dislocations. However, the potential wells formed due to alloy thickness and compositional variations are energetically distinct. Radiative traps formed due to local indium fraction changes are likely to be (energetically) deep, while those originating from thickness variation are relatively shallow.\textsuperscript{45} Carriers generated in the vicinity can diffuse
to either type of wells, depending on the surrounding potential landscape, and emit photons characteristic of band-gaps in the corresponding sites. In view of the fact that carriers trapped in shallow wells have a lower activation energy to surpass and migrate to non-radiative recombination centers, green dots have relatively modest photoemission intensities. However, energetic traps formed by a local increase of indium content confine carriers in a deeper potential minima resulting in more efficient rates of radiative recombination.

The observed optoelectronic properties of the dots are also a consequence of the nature of potential wells that spatially confine the photogenerated carriers along lateral dimensions. For instance, in-plane dimensions of the potential traps formed due to indium-rich regions may become larger with increasing indium content resulting in a weak confinement of carriers.\(^\text{[46]}\) Radiative traps with such wide potential wells leads to a reduction of the overlap integral of electron and hole-wavefunctions, culminating in lower radiative recombination efficiencies, in contrast to narrow wells. Therefore, depending on the degree of the increase in indium content as well as on the spatial extent of the nanometer-scale domains where such enhancements occur, the red dots can have varying well-widths. Moderate emission intensities are observed if the in-plane spatial dimensions of localization centers are relatively large, while carriers that are confined in narrow wells have considerably higher radiative recombination efficiencies. This is in agreement with our observation that emission intensities of the red dots have such a large spread (Figure 3C).

4. Conclusions

In conclusion, we have shown that spectrally resolved PLM serves as a non-invasive high-throughput, yet simple, technique to probe the optoelectronic properties of individual localized radiative potential traps within the active layers of InGaN/GaN QW LEDs. Our results show the presence of a large number of spatially localized red-shifted luminescent centers with varied radiative recombination efficiencies. The distribution of band-gaps and radiative intensities obtained from a statistically relevant number of individual dots not only suggests a highly heterogeneous potential landscape within the QWs, but also reveals the presence of two distinct types of radiative traps (green and red dots) with stark differences in their optoelectronic properties. There is little doubt that the red dots originate from compositional fluctuations in indium content within the alloy layers. However, it is highly improbable that the relatively less intense green dots are also formed due to the same reasons, and we argue that these shallow traps are related to thickness fluctuations of the active layer. This implies that both local indium content and interface-morphology-related heterogeneities can coexist within the same QW sample, either of which can act as efficient radiative recombination centers within InGaN QWs.

5. Experimental Section

Growth and Characterization of the Quantum Wells: The InGaN QW LED structures were grown on c-plane sapphire substrates using metalorganic vapor phase epitaxy (MOVPE) in a 3 in. × 2 in. close-coupled showerhead reactor. The active region consists of a 5 QW stack with InGaN wells separated by lightly n-doped GaN barrier layers. A standard two-temperature growth process under nitrogen carrier gas is used for the growth of the active region, with the InGaN QW grown at a lower temperature (660 °C) than the GaN barrier (720 °C) to enhance the indium incorporation into the QW. As the incorporation of indium depends critically on the temperature of the substrate, small inhomogeneities in the temperature profile across the reactor, as well as during the temperature ramps between the well and barrier growths lead to differential indium content across the wafer. Therefore the edges have a slightly higher average indium content relative to the center of the wafer. This allows us to probe QWs with a slightly varying indium content using the same sample, while keeping all other parameters constant. Structural characterization using high-resolution X-ray diffraction shows distinct superlattice fringes; simulation of the diffraction profiles for multiple reflections is used to estimate the average layer thickness and Indium content. From the X-ray data we estimate the active region to have 4-nm-thick In\(_{0.22}\)Ga\(_{0.78}\)N wells separated by 10-nm GaN barrier layers. EL spectra obtained from different regions of the wafer showed that this LED emitted green light, corresponding to a band gap of \(≈2.4\) eV.

Spectrally Resolved Photoluminescence Microscopy: Figure 1 shows the details of the home-built PL microscopy (PLM) set-up used for spectrally resolved imaging of the In\(_{0.22}\)Ga\(_{0.78}\)N multiple QW heterostructures. A 488-nm laser was used to selectively excite the alloy layers via a 60× objective (inset A) and the luminescence emerging from the sample was collected via the same objective lens and subsequently imaged (inset B) using a cooled charge-coupled device (CCD) or a color digital camera. In general, excitation powers between 0.2 and 5 mW were taken through the back-entrance of the objective lens to illuminate a \(≈30\) μm \(×\) 30 μm area of the sample. Dual-color imaging was performed by collecting the emission via a green-yellow (530–590 nm) and an orange-red (590–700 nm) bandpass filter. Individual images obtained in the two channels were quantitatively overlaid to generate a pseudo-color energy mapped image (see the Supporting Information).

To obtain temporal fluctuation of PL intensities, movies were collected at 20–50 Hz depending on the intensity of the luminescent centers. The dispersed emission spectra for individual diffraction limited spots (Figure 1, inset B) were collected in a high-throughput manner using a combination of slit and transmission grating (70 lines/mm) placed in front of the CCD camera. The spectrally resolved images were corrected for CCD detector response and calibrated using several laser lines. The emission spectrum obtained for each spatially separated spot was fitted to a single Gaussian to obtain their spectral maxima positions (\(λ_{\text{max}}\)) and integrated intensities. All measurements were performed at 295 K. Further details on spectrally resolved photoluminescence microscopy and data analyses procedures are provided in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Two distinct origins of highly localized luminescent centers within InGaN/GaN Quantum Well-LEDs

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Methods:

Spectrally Resolved Photoluminescence Microscopy. Home-built laser photoluminescence microscopy setup was used for spectrally resolved imaging of QWs. The 488 nm line of an Ar+ laser (Mellos Griot) was used to selectively excite the In$_{0.22}$Ga$_{0.78}$N QW in epi-fluorescence configuration through an inverted microscope (Nikon Eclipse 2000 U). The expanded and collimated laser beam was focused using a two Plano-convex lens on the back-focal plane of the 60X, 1.49NA oil immersion objective lens (Nikon) to a spot of adjustable diameter. In general, excitation powers between 0.2 and 5 mW was taken through the back-entrance of the objective lens to illuminate ~30x30 µm$^2$ area of the sample. The emerging photoluminescence was collected by the same objective and separated from the excitation beam by using 488nm dichroic mirror (Semrock) and a 488nm notch filter (Semrock) and subsequently imaged using cooled CCD camera (DVC-1412AM) operating at 5-50 Hz, or using a color digital camera (Nikon 4500) at 1 sec exposures. Dual-color imaging was performed by collecting the emission using two bandpass filters: green-yellow (530-590 nm) and orange-red (590-700 nm). Temporal fluctuation of PL intensities, i.e. blinking behaviors was obtained by acquiring movies at 20-50 Hz depending on the brightness of individual luminescent centers. To obtain single-dot emission profiles in a high-throughput manner, the emission was collected through a slit and a transmission grating (70 gr/mm, Optomerics) mounted in front of the CCD. Diffraction-limited spots randomly selected using an adjustable slit placed before the transmission grating allow us to image spatially well-separated (>300 nm) Dots and obtain their emission profiles concurrently. The distance between the transmission grating and the CCD was set such a way that zeroth-order diffraction, i.e., image and first-order diffraction, i.e. spectra (see Figure 1 inset B), would not spatially overlap and both the image and spectra would appear in the field of view of the same chip of the CCD with high enough spatial resolution. All spectral data were obtained at identical excitation powers (~500 W/cm$^2$) and exposure times of 500 ms. All the measurements are carried out under ambient conditions (T=295K).
Data Analyses: All images were analyzed after background flattening due to slight modulations in the excitation field unless otherwise mentioned. For band-gap mapping, individual images of the same area obtained in the two detection channels were quantitatively overlaid (16 bit image format) to generate a pseudo-color energy mapped image using the NIH ImageJ (exemplified in supplementary Figure S2). As a qualitative indicator of optical band-gaps for individual Dots, the higher and lower energy detection channels have been assigned green and red colors. It should be noted however that in order to compare the number of spots that emitted in either red or green detection channels (as in Figure 4), the brightness-contrast of the images were adjusted so as to make these spots visible (i.e. the intensities are not relative). All the analysis of the images, time traces and spectra were done by ImageJ (NIH), Matlab and Origin. The spectrally resolved images were analyzed after appropriate background subtraction and corrected for the CCD detector response over the entire wavelength range. The wavelength positions (with respect to CCD pixels) were calibrated using four laser lines (488 nm, 514 nm, 532 nm and 633 nm) for accurate estimation of $\lambda_{\text{em}}^{\text{max}}$ positions. The emission spectrum obtained for each spatially separated diffraction-limited spot was fitted to a single Gaussian to obtain their spectral maxima positions $\lambda_{\text{em}}^{\text{max}}$ and integrated intensities. Meticulous care was taken for estimation of $\lambda_{\text{em}}^{\text{max}}$ for all the spatially well-separated (>200 nm) individual spots resulting in a wavelength resolution of ~2.5 nm. The $\lambda_{\text{em}}^{\text{max}}$ as well as integrated intensities for all the 1380 randomly chosen spots were plotted in a frequency histogram at 5 nm bins, against transition energies ($\nu_{\text{em}}^{\text{max}}$) to obtain the band-gap energy and intensity distributions, respectively.
Supplementary Figures:

Figure S1. (A) PL image in a 10x10 µm² region of the active layer, where the total emission between 500-800 nm is collected, allowing the light from both QW background and the Dots. Line-profiles (B) of the intensity image showing that the various localized luminous spots are typically diffraction (arrow-heads separated by ~200 nm) irrespective of their intensities. A photoemission (relative) intensity distribution (C) of a typical image was obtained by constructing frequency histograms for the signal to background ratios of ~400 dots.
Figure S2. Energy-mapped PL Imaging: Dual-channel detection over the a 18x18 µm² area (shown in Figure 2) depicting diverse energies of emission from individual Dots. Entire photoemission (500-800 nm) (A), through a green (530-590 nm) (B), and through red (590-700 nm) (C) band pass filters. A Color-combined image (D) constructed by precisely and quantitatively overlaying actual intensity images of (B) and (C). A blowup of the 2x2 µm² area is used to show that some Dots don’t emit in both the channels. Note that several dots having comparable intensities in both (B) and (C) end up as yellow-orange dots in (D). Line profiles are shown on the top for comparison of the quantitative intensities observed in individual channels as well as in the energy mapped color image. It should be noted that the Green channel (B) intensities were multiplied by a factor of 3 to make the green dots visible in the same scale as the red channel (C).
Variation of band-gap energies of In$_x$Ga$_{1-x}$N alloy layers as a function of (A) Indium composition for a QW thickness of 3.5 nm (square), 4 nm (circles) and 4.5 nm (stars), and (B) active layer thickness for fixed Indium compositions of 20 and 25%. The calculated results are based on numerical solutions of 1D Poisson/ Schrödinger equation using a freely available computer program (Ref 34).

**Supplementary Movie**

**Movie M1:** Photoluminescence blinking of the Red-Dot depicted in Figure 5, for which the intensity time-traces are shown. This movie has been made to run at 15 fps.