Exciton hopping in $In_xGa_{1-x}N$ multiple quantum wells

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The dynamics of photoexcited excitons in thin InGaN/GaN multiple quantum wells (QW's) with different In contents was studied by comparing the experimental data obtained by photoluminescence (PL), PL excitation, and photoreflectance spectroscopy techniques with the results of Monte Carlo simulations of exciton hopping. The temperature dependence of the PL linewidth was demonstrated to be in a fair agreement with the model of phonon-assisted exciton in-plane hopping within In-rich regions with inhomogeneous broadening taken into account. The band potential fluctuations, which scale the dispersion of localized states the excitons are hopping over, were attributed to compositional disorder inside the In-rich regions. Meanwhile, the inhomogeneous broadening was explained by variation in mean exciton energy among the individual In-rich regions. For typical 2.5-nm-thick $In_xGa_{1-x}N$ ($x \approx 0.22$) QW's, the simulation revealed fluctuations of the band potential (31 meV) with additional inhomogeneous broadening (29 meV) and a crossover from a nonthermalized to thermalized exciton energy distribution at about 150 K. Both the fluctuations and inhomogeneous broadening showed an enhancement with increasing of In content. Simultaneously, a Bose-Einstein-like temperature dependence of the exciton energy in the wells was extracted using data on the PL peak position. The dependence exhibited a fair conformity with the photoreflectance data. Moreover, the density of localized states used in the simulation was found to be consistent with the PL excitation spectrum.

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InGaN/GaN multiple quantum wells (MQW's) are the key components of many commercial devices emitting green, blue, near-UV, and white light. The widely accepted paradigm is that the inhomogeneous distribution of indium facilitates high quantum efficiency of nitride-based light emitting devices in spite of the tremendous density of dislocations peculiar to InGaN/GaN structures grown on lattice-mismatched substrates.[1] The formation of In-rich regions in InGaN is proved by high-resolution microscopy and x-ray microanalysis,[2,3] spatially resolved cathodoluminescence,[4] and near-field optical microscopy.[5,6] However, despite an impressive commercial success, the physical origin of efficient light generation in this partially disordered system is unveiled incompletely. In particular, further effort is required to link the intricate structure of InGaN with its electrical and optical properties.

It is generally believed that the unique optical properties of InGaN are related to the specific nature of carrier motion that is governed by fluctuations of the band potential due to compositional disorder. In particular, carrier and exciton localization in fluctuation minima should prevent them from reaching nonradiative recombination sites. However, the character of carrier and exciton motion and the relevant process of establishing of their distribution over the localized states in InGaN are not completely understood. Meanwhile, an anomalous temperature behavior of photoluminescence (PL) in group-III nitride alloys and relevant quantum wells designated as an S-shaped peak position dependence and W-shaped linewidth dependence[7–13] indicate that exciton and carrier motion and the thermalization process occur through phonon-assisted hopping over localized states.[14–16] Such PL behavior related to exciton hopping was initially revealed in InGaAs/InP and ZnCdSe/ZnSe quantum wells[17,18] and was accounted for in terms of incomplete thermalization of localized excitons at low temperature. Recently, an evolvement of the S-shaped and W-shaped temperature dependences of the PL peak position and linewidth, respectively, was observed with gradual introduction of indium into thick layers of AlGaN alloy.[19] By using Monte Carlo simulations of exciton hopping, this observation resulted in unveiling of an intricate pattern of the band potential, containing fluctuations both within the In-rich regions and among the regions (double-scaled potential profile).

Here we generalize that exciton hopping can universally account for PL temperature dynamics in group-III nitride alloys, including quantum well structures. This is evidenced by comparison of the experimentally obtained temperature dependence of the PL parameters with the corresponding Monte Carlo simulation results in thin InGaN/GaN MQW's with different In contents. To provide more proof, the results were shown to be in quantitative agreement with extended data on the localized states obtained from photoreflectance (PR) and photoluminescence excitation (PLE) spectra.

Since the extraction of spectroscopic signatures of exciton hopping relies on precise measurements of the PL linewidth,[19] our study was performed in narrow quantum

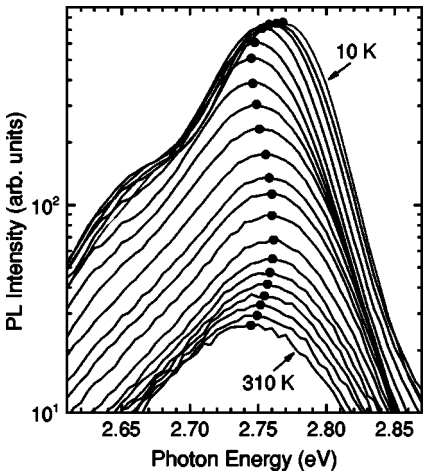

FIG. 1. Evolution of the PL spectra with temperature in $In_{0.22}GaN_{0.78}/GaN$ MQW's. The temperature is incremented by 15 K starting from 10 K (the uppermost spectrum) and ending with 310 K (the lowermost spectrum). The band peak positions are indicated by dots.

wells, where the inhomogeneous broadening of the PL line due to fluctuations of the built-in electric field via the quantum-confined Stark effect (QCSE) is small enough to allow measurements of the PL linewidth with sufficient accuracy. Here we employed MQW structures containing 2.5-nm-thick $In_xGa_{1-x}N$ quantum wells. The structures were grown by metal-organic chemical vapor deposition over a sapphire substrate and consisted of five $In_xGa_{1-x}N$ quantum wells separated by 9-nm-thick GaN barriers deposited on a 2.5-μm-thick GaN buffer layer.

Structures with different In content were under study. To ensure identical growth conditions, we fabricated a set of samples in a comparatively narrow range of In content from 22% to 27%. Below we focus our description of the study on the sample containing $In_{0.22}Ga_{0.78}N$ MQW's and summarize the results on an identical investigation carried out on samples containing quantum wells with different In content.

A continuous-wave He–Cd laser emitting at 325 nm was used for the excitation of PL, whereas a broadband Xe lamp was exploited in the PLE measurements. The PL signal was dispersed by a double monochromator (Jobin Yvon HRD-1) and recorded by using a photomultiplier (Hamamatsu R1463P) in the photon counting regime. To avoid distortions of the PL line shape due to Fabry-Perrot interference caused by multiple reflections of light between the substrate and sample surface (which are $\sim$2.5 μm apart), we collected the PL signal propagating through the transparent substrate that was frosted to randomize the angles of the escaping photons. The PR spectra were measured using a chopped excitation beam of the same He–Cd laser. The modulated constituent of reflected halogen-lamp radiation was detected by means of a lock-in amplifier (Signal Recovery 7265). A closed-cycle helium refrigerator was employed to perform the measurements at temperatures down to 10 K.

The near-band-edge PL spectra measured at different temperatures are presented in Fig. 1. The spectra contain a single band with a hump on the low-energy slope separated by approximately 90 meV. We attribute these features to direct

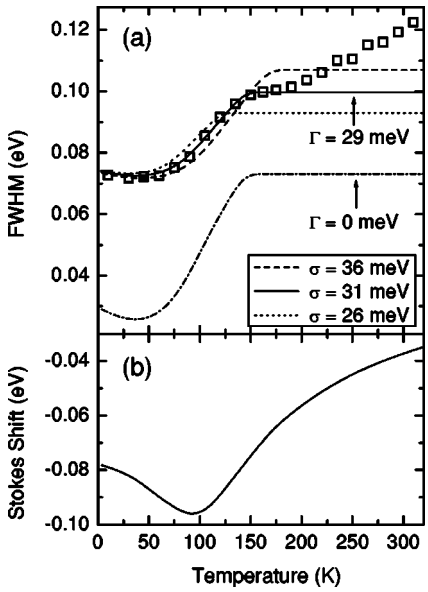

FIG. 2. (a) Temperature dependence of the full width at half maximum of the photoluminescence band in 2.5-nm $In_{0.22}GaN_{0.78}/GaN$ MQW's. Points depict experimental data; dashed, dotted, and solid lines show results of the Monte Carlo simulation of exciton hopping for different scales of random potential fluctuations σ (indicated) with the inhomogeneous broadening Γ taken into account; dash-dotted line represents results for $\sigma = 31$ meV and $\Gamma = 0$. (b) Simulated temperature dependence of the Stokes shift of the PL band peak position in respect of the mean exciton energy corresponding to the best-fitted linewidth dependence.

and longitudinal-optical-phonon-replicated recombination of localized excitons, respectively. The PL intensity maintains an almost stable value below 50 K and decreases at elevated temperatures, most probably due to enhanced influence of nonradiative recombination. The PL band peak position is highlighted by dots in Fig. 1. The peak exhibits a well-established S-shaped temperature behavior:[7–9] it slightly redhifts in the range from 10 K to 100 K, then blueshifts in the range of up to 180 K, and redshifts again afterwards.

The points in Fig. 2(a) show a W-shaped temperature dependence of the full width at half maximum (FWHM) of the PL band with a characteristic kink at about 150 K. The S-shaped temperature behavior of the PL band peak position and the W-shaped temperature behavior of the linewidth are known to be a signature of exciton hopping over randomly dispersed localized states with a crossover from a nonthermalized to a thermalized distribution function of the excitons.[19]

The observed temperature behavior of the PL linewidth was simulated by using a two-dimensional (2D) Monte Carlo procedure[16] with the Miller-Abrahams rate for phonon-assisted exciton tunneling between the initial and final states i and j with the energies E_i and E_j, respectively:

$$\nu_{i\to j} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha} - \frac{E_j - E_i + |E_j - E_i|}{2k_BT}\right). \qquad (1)$$

Here r_{ij} is the distance between the states, α is the decay length of the exciton wave function, and ν_0 is the attempt-

to-escape frequency. Hopping was simulated over a randomly generated set of localized states with the sheet density N. Dispersion of the localization energies was assumed to be in accordance with a Gaussian distribution

$$D'(E) \propto \exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right], \tag{2}$$

with the peak positioned at the mean exciton energy E_0 and the dispersion parameter (the energy scale of the band potential profile fluctuations) σ. For each generated exciton, the hopping process terminates by recombination with the probability τ_0^{-1} and the energy of the localized state, where the recombination has taken place from, is scored to the emission spectrum $S_0(h\nu)$.

Fitting of the temperature dependence of the simulated PL linewidth to the experimental results reveals the important peculiarities as follows. In the initial temperature range from 10 K to 150 K, the variation of the linewidth is due to thermal enhancement of exciton hopping within the nonthermalized energy distribution and the shape of the dependence is basically a function of the spatial (the product $N\alpha^2$) and temporal (the product $\nu_0\tau_0$) parameters of the hopping process. The kink in the temperature dependence of the linewidth at about 150 K represents a crossover from a nonthermalized to thermalized energy distribution of excitons. The crossover temperature is related mainly to the energy scale of the band potential fluctuations, σ. Finally, an almost constant linewidth right above the crossover temperature (150–180 K) indicates an occurrence of a thermalized exciton energy distribution. However, to achieve a quantitative agreement with the experimentally determined low-temperature linewidth, additional inhomogeneous broadening Γ should be introduced. The simulated initial emission spectrum $S_0(h\nu)$ transforms to

$$S(h\nu) = \int S_0(h\nu')G(\Gamma, h\nu - h\nu')dh\nu', \tag{3}$$

where $G(\Gamma, h\nu)$ is a standard Gaussian function with dispersion Γ^2. The further increase of the linewidth above 180 K is attributed to the participation of phonons in the radiative transitions and to the influence of delocalized excitons that are not taken into account in the model used.

The solid line in Fig. 2(a) represents the best fit obtained for the following values of the parameters: $N\alpha^2=1$, $\nu_0\tau_0=3\times10^5$, $\sigma=31$ meV, and $\Gamma=29$ meV. The dashed and dotted lines demonstrate the sensitivity of the simulation results with respect to the hopping energy scale σ, while the dash-dotted line shows the simulated dependence without inhomogeneous broadening.

The same fitting procedure was applied (with the same parameters $N\alpha^2=1$, $\nu_0\tau_0=3\times10^5$) to the set of InGaN samples with different In content. Both potential fluctuation scales σ and Γ have a general trend to increase with increasing indium molar fraction (see Fig. 3). Namely, σ increases from 31 to 38 meV, whereas Γ increases from 29 to 47 meV for x ranging from 0.22 to 0.27. This result is in good agreement with the well-established fact that in group-III nitrides increased In content facilitates an enhancement of band potential fluctuations.[20]

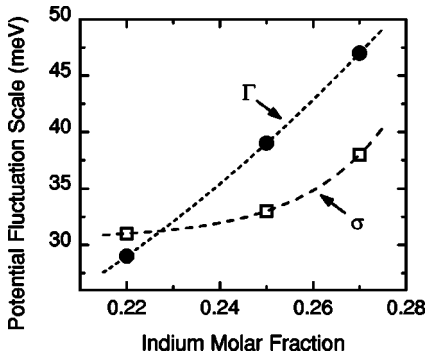

FIG. 3. Potential fluctuations within individual In-rich regions (σ) and inhomogeneous broadening due to fluctuations in the average exciton energy among individual In-rich regions (Γ) as a function of In molar fraction in $In_xGa_{1-x}N$ MQW's with a fixed well width of 2.5 nm.

Thus, our Monte Carlo–simulation-based analysis reveals a double-scaled band potential profile in InGaN quantum wells similar to that deduced in AlInGaN bulklike layers.[19] Such a band potential profile implies hopping of excitons within isolated In-rich regions[3,21] with the band potential roughness σ, whereas the average exciton energy is different in each In-rich region and is dispersed over the scale Γ. In thick layers, the dispersion Γ can be attributed to band-gap fluctuations due to different average indium content within the In-rich regions.[19] In quantum wells, the PL line can be additionally broadened by the well-width fluctuations that modulate the quantum confinement energy and by fluctuations of piezoelectric polarization, which result in the inhomogeneous red shift due to the QCSE.[22]

Figure 4 depicts several PR spectra measured at temperatures above 200 K. (At lower temperatures, the PL background was too high to extract reliable data.) The spectra contain a double structure, probably due to phase separation in InGaN (Ref. 23) or an admixture of the symmetry-forbidden optical transition involving first excited hole level.[24] The arrows in Fig. 4 denote the energy of the lower PR resonance deduced by fitting to Lorentzian line-shape functional form. This energy represents the mean exciton en-

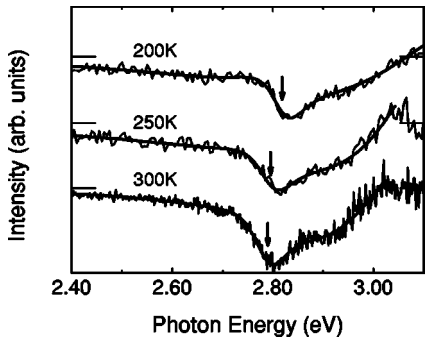

FIG. 4. PR spectra in $In_{0.22}GaN_{0.78}/GaN$ MQW's at different temperatures (indicated). Bold lines represent the best fit with two-component Lorentzian functional form.

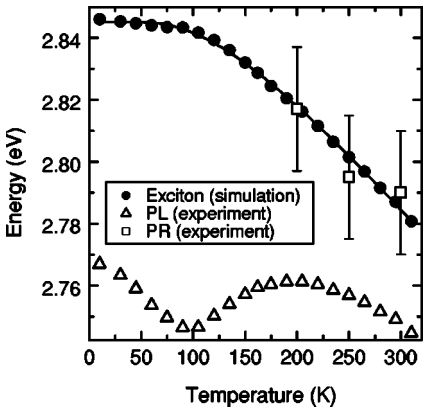

FIG. 5. Measured photoluminescence band peak position (open triangles) and the reconstructed mean exciton energy (solid dots) as a function of temperature. Solid line represents the best fit by using a Bose-Einstein-like formula. Open rectangles show the PR resonance energies.

ergy E_0,[25,26] which is inherently affected by the QCSE.[24]

To match the model of exciton hopping with the PR data, the results of the simulation were used to reconstruct the mean exciton energy. Here we exploited the fact that the simulated spectra are shifted to lower energies with respect to the exciton mean energy. The temperature behavior of the Stokes shift deduced from the peak position of the simulated spectra is depicted in Fig. 2(b). By adding the modulus of this shift to the energy of the measured peak positions of the PL band (open triangles in Fig. 5), the temperature dependence of the average exciton energy was reconstructed (solid circles in Fig. 5). The dependence is fairly well described by a Bose-Einstein-like expression

$$E(T) = E(0) - \frac{\lambda}{\exp(\theta/T) - 1}, \tag{4}$$

with the best-fit parameters $\lambda = 0.154$ eV, $\theta = 379$ K, and $E(0) = 2.845$ eV. The dependence obtained was collated with the energies of the PR resonance (rectangles in Fig. 5). Despite a large uncertainty of the PR data caused by broad PR features, a fair agreement with the data extracted using Monte Carlo simulations is obtained. In addition to proving of the model of exciton hopping, this suggests that the simulation provides us with unique data on the fundamental optical transition energy, especially at lower temperatures, where PR can be difficult to measure. Although obtained in a rather indirect way, these data can be useful for the characterization of thin quantum wells with a relatively high In molar fraction, where the exciton energy is difficult to precisely determine by other means.

An additional proof of the exciton hopping model is provided by comparison of the PLE spectra with the actual density of localized states used in the simulation,

$$D(E) \propto \exp\left[- \frac{(E - E_0)^2}{2(\sigma^2 + \Gamma^2)} \right], \tag{5}$$

where the inhomogeneous broadening is taken into account by introduction of Γ.

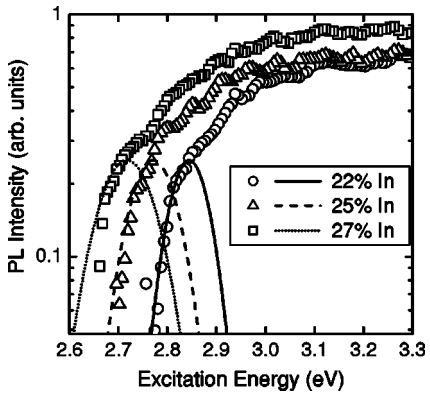

FIG. 6. PLE spectra (points) of 2.5-nm-thick InGaN/GaN MQW's with different In contents (indicated) at 77 K. Lines show the density of band-tail states used in the simulation with the inhomogeneous broadening taken into account.

The points in Fig. 6 present the PLE spectra of 2.5-nm-thick InGaN/GaN MQW samples with different In content, measured at 77 K. The long-wavelength slope of the PLE spectra is flat and temperature insensitive. This indicates the dominant contribution of disorder due to the compositional fluctuations and interface roughness over the contribution of thermal broadening. The lines in Fig. 6 depict the densities of band-tail states resulting from the Monte Carlo simulations [Eq. (5)] for the QW's with different In content. These densities of band-tail states are centered at the average exciton energies obtained by the reconstruction procedure described above and are collated with their respective PLE spectrum for each sample. The long-wavelength slopes of the densities of localized states are seen to be in a fair coincidence with the far long-wavelength tails of the corresponding PLE spectra. Furthermore, one can resolve that the peaks of the density-of-states functions coincide with the tiny kinks in the PLE spectra. This strongly supports the simulation-based quantitative estimates of the potential fluctuation scales and the reconstructed average exciton energies in the InGaN MQW's with various In content. The presented analysis not only provides additional evidence for the model of exciton hopping but also improves our understanding of the PLE spectra in partially disordered InGaN alloy, where quantitative characterization of the absorption edge is difficult to perform.

In conclusion, we have demonstrated an analysis of the temperature behavior of the PL linewidth in InGaN/GaN MQW's with various In contents by using Monte Carlo simulations of exciton hopping. The simulations revealed band potential fluctuations within individual In-rich regions and inhomogeneous broadening due to fluctuations in the average exciton energy among individual In-rich regions. Simultaneously, we deduced the Stokes shift of the PL band and reconstructed the Bose-Einstein-like temperature dependence of the average exciton energy in our MQW structures using the measured PL peak positions. These data were shown to be in a fair agreement with the PR data. Furthermore, the density of localized states employed in the simulation appeared to be in a fair agreement with the far long-wavelength region of the PLE spectra.

The present extended data on InGaN MQW's with different In content, as well as the preliminary data on thick AlInGaN layers,[19] infer that exciton motion in group-III nitride alloys can be universally described in terms of exciton hopping through localized states within relatively large In-rich regions (e.g., "quantum disks" within quantum wells[1]). The average exciton energy of these regions is subject to a considerable dispersion due to fluctuations in In content and, in quantum wells, additionally due to fluctuations of the well width and built-in field. Our results also imply that the hopping is the main route of the buildup of thermalized distribution of excitons over localized states.

Finally, simulations of exciton hopping in group-III nitride epilayers and MQW's not only improved our understanding of exciton dynamics in these intricate alloys, but also turned out to be a useful tool for the characterization of nitride structures by such important parameters as the format and magnitude of band potential fluctuations, the mean exciton energy, and the density of the localized states.

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