Probing Individual Localization Centers in an InGaN/GaN Quantum Well

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Photoluminescence (PL) spectroscopy with subwavelength lateral resolution has been employed to probe individual localization centers in a thin InGaN/GaN quantum well. Spectrally narrow emission lines with a linewidth as small as 0.8 meV can be resolved, originating from the recombination of an electron-hole pair occupying a single localized state. Surprisingly, the individual emission lines show a pronounced *blueshift* when raising the temperature, while virtually no energy shift occurs for increasing excitation density. These findings are in remarkable contrast to the behavior usually found in macro-PL measurements and give a fundamental new insight into the recombination process in semiconductor nanostructures in the presence of localization and strong internal electric fields. We find clear indications for a biexciton state with a negative binding energy of about -5 ± 0.7 meV.

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The development of light-emitting diodes (LEDs) and lasers based on InGaN quantum films [1] surely has to be considered a milestone in optoelectronics. Despite a poor crystalline quality due to a high density of threading dislocations, the quantum efficiency can be quite large. This has generally been attributed to the existence of localized or even quantum-dot-like states potentially formed by In-rich nanoislands [2,3], and monolayer or compositional fluctuations [4]. Besides the formation of such localization centers, there is another important effect that has a strong impact on the optical properties and therefore on the device functionality of nitride heterostructures: the internal electric field. In particular, there is still an intense and controversial debate on how to interpret the commonly observed strong blueshift of the photoluminescence (PL) signal when increasing the excitation power [5–8]. Screening of the internal electric field by photogenerated carriers is believed to play an important role here, while other authors emphasize the importance of a successive filling of localized states.

To address this fundamental issue, spatially resolved PL spectroscopy is expected to be a powerful experimental tool. In fact, various studies on thin InGaN/GaN quantum wells by scanning near-field optical microscopy (SNOM) [9,10], cathodoluminescence measurements [11,12], and PL spectroscopy using nanoapertures [13] have been reported. However, no spectrally narrow emission lines, which are typical fingerprints for individual localization centers, could be observed until now. This seems to be in clear contrast to experimental findings that indicate strong localization effects, e.g., large Stokes shifts [14] or sharp photoluminescence peaks on resonant excitation [2]. Only recently, Kaneta *et al.* [15] reported on SNOM measurements with 30 nm spatial resolution, revealing pronounced features in the PL spectra with emission linewidths down to 11.6 meV. This value is more than 2 orders of magnitude larger than what is typically obtained for III-V or II-VI structures and therefore unlikely to originate from a single localization center. The only observation of spectrally narrow emission lines in nitride heterostructures with linewidths down to 0.1 meV is reported by Moriwaki *et al.* on self-assembled InGaN/GaN quantum dots [16]. However, due to an intense, unidentified background signal, their contribution to the overall luminescence is quite unclear.

In this Letter, we present PL data on a thin InGaN/GaN quantum well recorded with subwavelength spatial resolution. The appearance of individual spectrally narrow emission lines with linewidths down to 0.8 meV clearly demonstrates the existence of three-dimensionally localized, quantum-dot-like states. Comparing macro-PL data and "single dot" measurements gives fundamental new insights into the interplay between internal electric fields and the filling of localized states in nitride semiconductor nanostructures.

The samples were grown by metal organic vapor phase epitaxy (MOVPE) on a 6H-SiC substrate. After a 300-nm AlGaN buffer layer and a 700-nm GaN barrier, a 3-nm-thick $In_xGa_{1-x}N$ quantum well with a nominal In content of $x = 0.15$ was grown, capped by 40-nm GaN. Microphotoluminescence spectroscopy with a numerical aperture of N.A. $= 0.6$ was used for the measurements. In order to increase the spatial resolution beyond the diffraction-limited spot size, an opaque metal mask with nanoapertures down to 100 nm in diameter has been defined lithographically on top of the semiconductor structure. The sample was mounted in a helium flow cryostat ($T \geq 3.5$ K) and excited by the UV lines

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(351–364 nm) of an argon ion laser. A 0.55-m-monochromator and a charge-coupled-device camera were used to disperse and to detect the photoluminescence signal.

Figure 1 displays low temperature ($T = 4$ K) PL spectra of the InGaN/GaN quantum well measured using apertures with different diameters. The uppermost trace corresponds to an aperture with a diameter of 25 μm. The inhomogeneously broadened PL spectrum is centered at an energy of 2.84 eV and has a full width at half maximum (FWHM) of 43 meV. Decreasing the aperture size, the PL signal splits more and more into individual, spectrally narrow emission lines, which we attribute to the recombination of electron-hole pairs in single localization centers. It is important to note that no background was subtracted; i.e., for the smallest apertures, background-free single lines are observed. The single lines exhibit linewidths with a FWHM down to 0.8 meV, which is more than 1 order of magnitude smaller than what has been obtained thus far in spatially resolved PL studies on InGaN/GaN quantum wells [15].

In Fig. 2, the typical evolution of the micro-PL spectra with increasing temperature is depicted. While in the low temperature regime (up to ≈ 10 K) the energy of the individual PL lines changes only weakly, a pronounced *blueshift* within a quite small temperature range is obtained for $T > 10$ K. In addition, the lines become dramatically broadened (e.g., by a factor of 2 within a temperature change of 6 K, see dashed box). Further increasing the temperature results in a spectral redistribution of intensity between the individual lines, and the low-energetic part of the spectrum becomes more and more intense. In addition, the energy of the peaks starts to shift to the red due to band gap shrinkage. Studies on a variety of different apertures show qualitatively the same behavior.

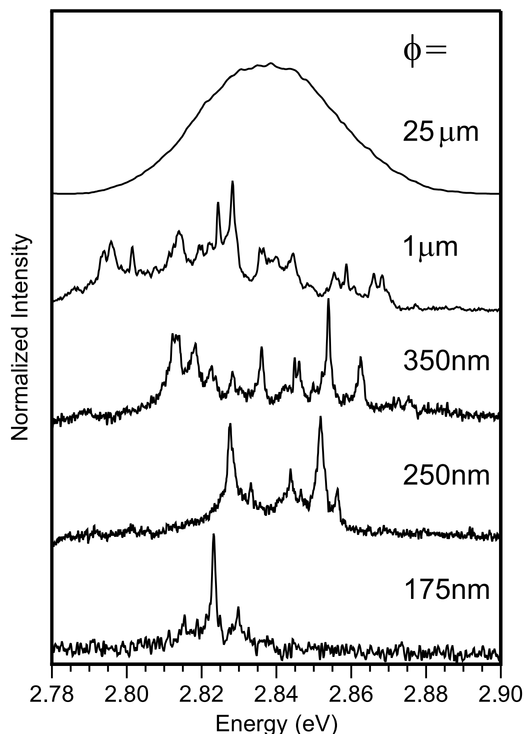

FIG. 1. PL spectra from apertures of different sizes at $T = 4$ K.

Figure 3 summarizes the temperature dependent PL energy shifts for an ensemble [Fig. 3(a)] and for an individual localization center [Fig. 3(b)]. In the case of macro-PL measurements obtained on a 25 μm aperture [Fig. 3(a)], a pronounced redshift of the PL signal, much stronger than expected from Varshni's law [17] (dashed line), is observed with increasing temperature, and above 50 K the PL signal even moves to higher energies. This "S-shaped" behavior is well known for InGaN/GaN quantum wells [19,20] as well as for III-V and II-VI quantum dots [21,22] and usually interpreted as a temperature-sensitive redistribution process transferring carriers between high-energetic and low-energetic localized states. In contrast, the PL peak originating from an individual localization center first exhibits a strong and continuous blueshift with temperature and only for temperatures above about 25 K follows Varshni's law. This characteristic blueshift indicates a quite unusual variation

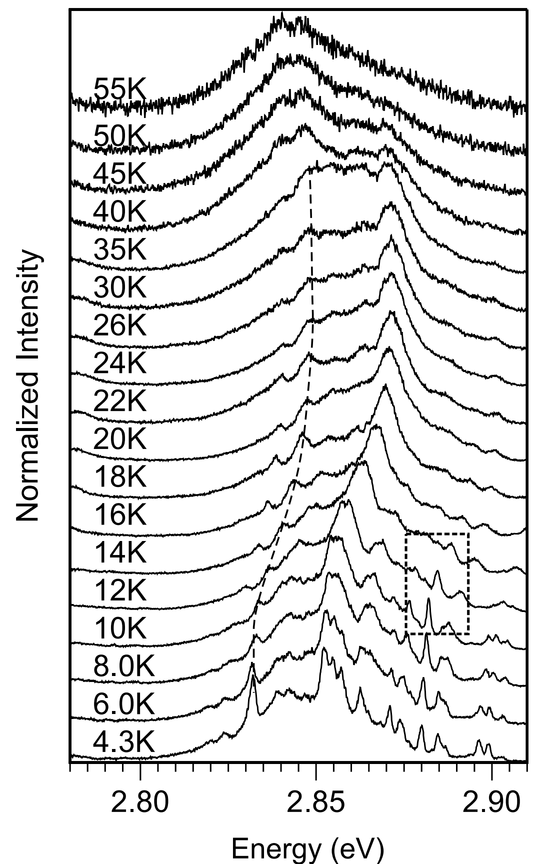

FIG. 2. PL spectra measured using an aperture of 350 nm for different temperatures. The dashed line indicates the energy shift of an emission peak originating from a single localized state.

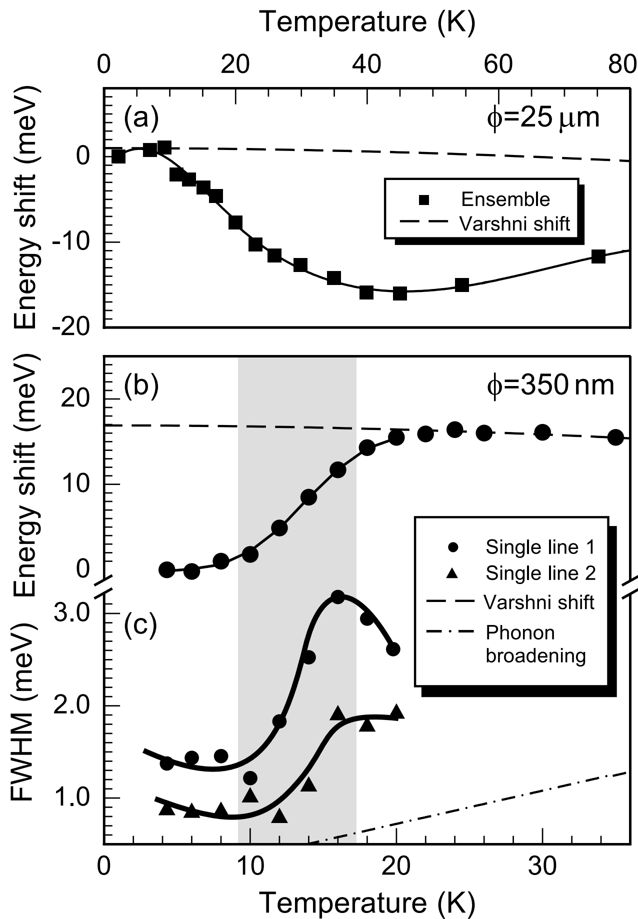

FIG. 3. Energy shift versus temperature (a) of macro-PL spectra (aperture size $\phi = 25\ \mu$m) and (b) of a single line (marked by the dashed line in Fig. 2). The dashed line corresponds to the expected Varshni shift of the band gap [17]. (c) Linewidth of two single lines versus temperature. The expected line broadening due to phonon scattering (after Xu *et al.* [18]) is marked by a dash-dotted line. The solid lines are guides to the eye.

of the ground state energy of each localization center with temperature, which thus far has been hidden by inhomogeneous broadening effects characteristic for ensemble measurements.

In order to understand these experimental findings, one has to consider that in InGaN/GaN-quantum well structures large internal electric fields are present, reaching values in the MV/cm range. The resulting quantum-confined Stark effect (QCSE) leads to a pronounced shift to lower energies for confined carriers as well as to an increase of the recombination lifetime [23]. We attribute the observed blueshift of the PL emission from a single localization center to a temperature dependent screening of the internal electric field, as an increase of the temperature may statistically release carriers bound to impurities or defects in the nanoenvironment of the localized state causing a quasicontinuous energy shift with temperature [24]. This interpretation is strongly supported by the obvious correlation between the energy shift and the linewidth of the PL emission. In Fig. 3(c), the FWHM of two different localization centers is plotted versus temperature. The strong increase of the PL linewidth for $T >$ 10 K goes hand in hand with a distinct blueshift of the peak energy [see shaded area in Figs. 3(b) and 3(c)]. Indeed, the thermal release of trapped carriers is a statistical process, which is expected to result in statistically fluctuating charges in the nanoenvironment of the localized state and therefore in a line broadening due to spectral diffusion as discussed, e.g., by Seufert *et al.* [25].

An increase of the excitation density usually results in a pronounced and continuous blueshift of the inhomogeneously broadened PL spectrum of InGaN/GaN heterostructures, and in the literature there is still a controversial discussion concerning the relative importance of screening of internal electric fields and bandtail filling, respectively. Indeed macro-PL measurements on our samples do exactly show the expected behavior, namely, a blueshift of more than 60 meV when increasing the excitation power by about 3 orders of magnitude (not shown). The situation appears completely different, if one looks at the power dependent PL spectra obtained with a small nanoaperture. As shown in the inset of Fig. 4, virtually no energy shift is found for each individual line. Increasing the excitation power instead leads to an occurrence of new, discrete PL peaks at the high energy tail of the PL spectrum. As a consequence, integrating over lots of localization centers just results in a continuous blueshift with increasing power, as obtained in macro-PL measurements. Figure 4 representatively summarizes these findings for an aperture with a diameter of 1 μm: While each single PL peak does not shift (open circles), the spectral weight of the total PL signal clearly shifts to the blue with increasing excitation power (closed circles). Qualitatively, the same behavior is found for each nanoaperture studied.

Screening of the internal electric field in InGaN/GaN quantum wells is usually explained as follows: Photogenerated carriers occupy quantum well states and, due to the internal field, electrons and holes become spatially separated. This results in a screening of the internal field and, consequently, in a blueshift of the characteristic PL signal with increasing excitation power. In contrast, the single exciton recombination peaks do not show any energy shift with increasing power, demonstrating that no variation of the ground state energy due to screening by free carriers occupying delocalized states occurs. We thus have to suggest an alternative microscopic picture: At low excitation, mainly the ground state of low-energetic localization centers will be populated with a single electron-hole pair. An increase of the excitation power results in a change of the electron-hole population within the localized state without modifying the charge configuration in the nanoenvironment of the localization center. Thus, no continuous energy shift of the PL line with excitation power can be expected, while, however, the successive population of localized states

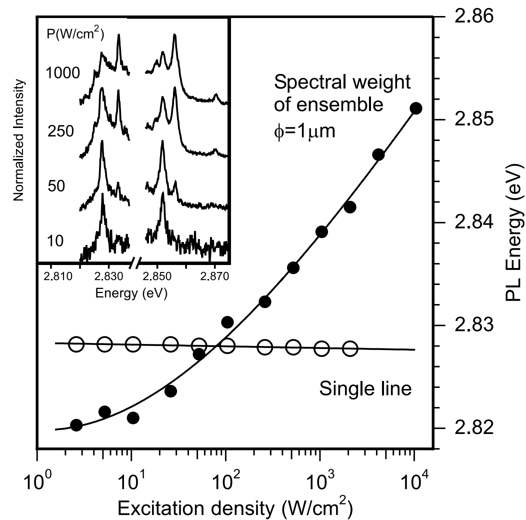

FIG. 4. Energy shift of a single PL line versus excitation density compared to the energy shift of the spectral weight of an ensemble ($\phi = 1$ μm). The temperature is 4 K. Inset: Power-dependent evolution of PL spectra obtained with an aperture size of 250 nm at $T = 4$ K.

with electron-hole pairs should result in the occurrence of discrete new lines in the PL spectrum. Increasing the excitation power can result in (i) the formation of biexciton or other multiexciton states and (ii) an enhanced occupation of high-energetic localization centers with single electron-hole pairs.

Indeed new PL peaks appear at the high energy tail as the excitation power is increased. While some of these lines show a linear increase in intensity, suggesting mechanism (ii) as a possible origin, other lines clearly display a superlinear increase of the PL emission (see inset of Fig. 4). Below saturation, we obtain, e.g., $I \sim P^2$ for the peak at $E = 2.8562$ eV in contrast to $I \sim P^1$ for the corresponding single exciton peak at $E = 2.8518$ eV, exactly what is expected for a biexciton-exciton pair [26,27]. Surprisingly, these biexciton PL peaks occur at the *high* energy tail of the single exciton peak. We attribute this to the influence of the internal electric field: In a field-free environment, the biexcitonic charges usually arrange themselves in a way that results in a net attractive Coulomb term, i.e., a positive biexciton binding energy. In the presence of a strong electric field, in contrast, electrons and holes are spatially separated. This enhances the repulsive and decreases the attractive Coulomb interaction, which may even lead to a *negative* binding energy of biexcitons [28]. Indeed, we obtain a negative biexciton binding energy of about -5 ± 0.7 meV. In light of these results, the commonly observed blueshift of the PL signal in InGaN/GaN quantum wells with increasing power has to be considered as a consequence of the successive occurrence of high-energetic PL peaks rather than a continuous energy shift of each localized state with increasing power. Again, it becomes clear that macro-PL measurements performed thus far are intrinsically unable to uncover essential physical mechanisms responsible for the optical properties at various excitation levels.

In conclusion, we have successfully applied PL spectroscopy with subwavelength spatial resolution to address single localization centers in a thin InGaN/GaN quantum well. The usage of low temperatures and low excitation densities in combination with the high sensitivity of our setup (N.A. = 0.6) does allow one to resolve new effects, until now hidden by inhomogeneous broadening effects in macro-PL measurements. In particular, the unexpected findings of the energy shift of the PL peaks originating from single localized states with temperature and excitation power shed new light on the recombination mechanism in semiconductor nanostructures in the presence of localization and internal electric fields.

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