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Original Publication:

Chih-Wei Hsu, Evgenii Moskalenko, Martin Eriksson, Anders Lundskog, Fredrik K. Karlsson, Urban Forsberg, Erik Janzén and Per-Olof Holtz, The charged exciton in an InGaN quantum dot on a GaN pyramid, 2013, Applied Physics Letters, (103), 1.
http://dx.doi.org/10.1063/1.4812984

The charged exciton in an InGaN quantum dot on a GaN pyramid

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(Received 22 April 2013; accepted 16 June 2013; published online 2 July 2013)

The emission of a charged exciton in an InGaN quantum dot (QD) on top of a GaN pyramid is identified experimentally. The intensity of the charged exciton exhibits the expected competition with that of the single exciton, as observed in temperature-dependent micro-photoluminescence measurements, performed with different excitation energies. The non-zero charge state of this complex is further supported by time resolved micro-photoluminescence measurements, which excludes neutral alternatives of biexciton. The potential fluctuations in the vicinity of the QD that localizes the charge carriers are proposed to be responsible for the unequal supply of electrons and holes into the QD. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4812984]

Besides the exploration of new physical properties in quantum dots (QDs), the proposed quantum information applications (QIA), which make use of the quantum states of particles to transmit and encode information, also motivate the research on QDs. QDs are considered as a promising photon source which fulfill the essential demand for QIA: the generation of photons with specific energy polarization- and time-correlations.[1] A quantum photon source relies on the realization and engineering of specific excitonic states of various charge configurations of the QD. From the perspective of materials, III-nitrides QDs can be advantageous over III-arsenide counterparts due to their very wide spectral tunability of the photon energy and possible deep confining potentials for high temperature operation.[2] However, the development of high-quality III-nitride-based QDs today is well behind III-arsenide-based QDs. Regarding the fundamental identification of excitonic states, single excitons and biexcitons have been identified in the micro-photoluminescence (μPL) spectra of GaN and InGaN QDs, mainly based on their expected linear and quadratic intensity dependencies on the excitation power.[3–5] In some reports, this identification was further strengthened by more robust signatures of the exciton/biexciton pair, such as congruent fine structure splittings[6] or photon bunching characteristics.[2] The trion states have so far not been identified for the nitride-based QDs.

Direct growth of QDs on pre-fabricated templates of micro-/nano-structures has been demonstrated as an effective approach for controlling the position of the QDs for various systems.[4,7–9] By employing such spatially isolated QDs, the typical large inhomogeneous broadening, as well as dot-to-dot interactions, can be avoided.[10] This facilitates the spectral identification,[11] and a detailed polarized fine structure has been revealed in III-As QDs.[12] The InGaN QDs presented in this letter, exhibiting sub-meV emission lines in μPL, were formed individually on top of GaN pyramids. One emission line of a single InGaN QD in this work is consistently attributed to a trion, despite its quadratic excitation power dependence revealed at low temperatures (~4 K). It is demonstrated that the power dependence solely is not sufficient for reliable identification and that the temperature dependence is an important complement to enable a conclusion about the origin of the excitonic emission lines.

A low-temperature μPL system with two continuous-wave (cw) lasers, providing two excitation energies at $h\upsilon_{ex} = 4.66$ eV and $h\upsilon_{ex} = 3.49$ eV, respectively, was employed to perform the power (P_{ex})- and temperature (T)-dependent μPL measurements. Since the InGaN layer was sandwiched between GaN layers, the band gap of GaN (3.51 eV) represents the maximum energy of the barrier material confining the InGaN QDs, i.e., $h\upsilon_{ex} = 4.66$ eV and $h\upsilon_{ex} = 3.49$ eV correspond to above and near-resonant barrier excitation, respectively. A Ti:sapphire laser coupled in series with a second harmonic generator was applied to perform the μPL excitation (μPLE) spectroscopy in the energy range of 3.13–3.51 eV. Time resolved μPL (TRμPL) experiments were performed with excitation pulses (200 fs pulse width and 75 MHz repetition rate) at $h\upsilon_{ex} = 4.66$ eV generated by a frequency-tripled Ti-sapphire laser. A streak camera was used to acquire the transient PL signal with a time resolution of 10 ps.

Two individual QDs (QD1 and QD2), located at two different pyramids with different emission features, are presented for comparison. For QD1, only one emission line, denoted as X_0, is observed, and no other emission line appears when varying P_{ex} and T (Figs. 1(a) and 1(b), respectively). P_{ex}-dependent μPL performed on QD1 at 4 K reveals that the intensity of X_0 is directly proportional to P_{ex}, as characteristic for the single exciton. It should be noted that most QDs we studied exhibit only the single exciton emission. The presence of merely a single exciton can be ascribed to a shallow confinement potential in which solely the single neutral exciton state is bound.[9] Other excitonic complexes in III-nitride QDs, like the charged exciton and biexciton, are expected to appear at higher energies than the single exciton due to the strong repulsive Coulomb interactions, thus being unbound for the case of shallow barriers.[13]

In QD2, only one emission line, denoted as X_A, is recorded at low P_{ex} and/or T. However, an additional emission line, denoted as X_B, appears with increasing P_{ex} and/or T (Fig. 1). According to our polarization-dependent

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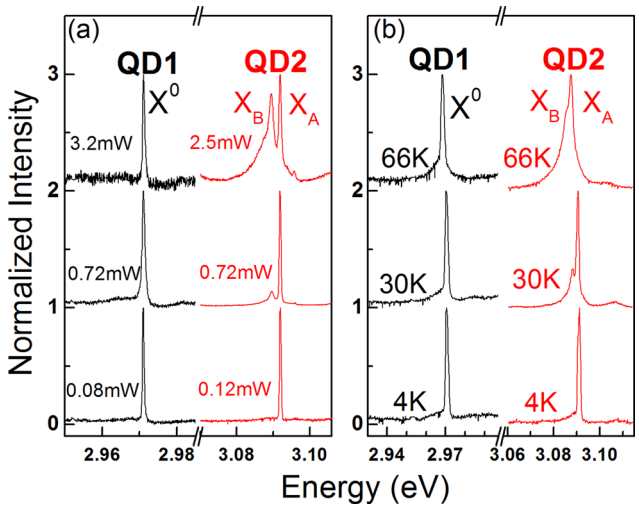

FIG. 1. μPL spectra of QD1 and QD2 employing the excitation energy $h\upsilon_{ex} = 4.66$ eV at (a) varying excitation power at constant temperature, 4 K, (b) varying temperature at constant excitation power of 0.7 mW. The spectra of QD1 are normalized to the intensity of X_0 while the spectra of QD2 are normalized to the intensity of X_A. They are all shifted along the y-axis for clarity.

measurements, X_A and X_B, are linearly polarized in the same direction and with a similar degree of polarization,[14] which can be interpreted as two different exciton complexes originating from the same QD involving the same hole state.[15] The intensity of X_A (I_{XA}) is linearly dependent on the P_{ex} at 4 K (Fig. 2(a)), by which X_A can be ascribed to the single exciton. The intensity of X_B (I_{XB}) exhibits a superlinear (quadratic) dependence on P_{ex} (Fig. 2(a)), suggesting that X_B is associated with an exciton complex consisting of more than one electron and one hole. The superlinear P_{ex} dependence is another indication that X_A and X_B originate from the same QD; If X_B would be a single exciton of another neighboring QD, a linear dependence on P_{ex} would be expected.

A quadratic P_{ex} dependence is commonly understood as the signature of the biexciton. However, we will argue that X_B should not be identified as the biexciton despite the

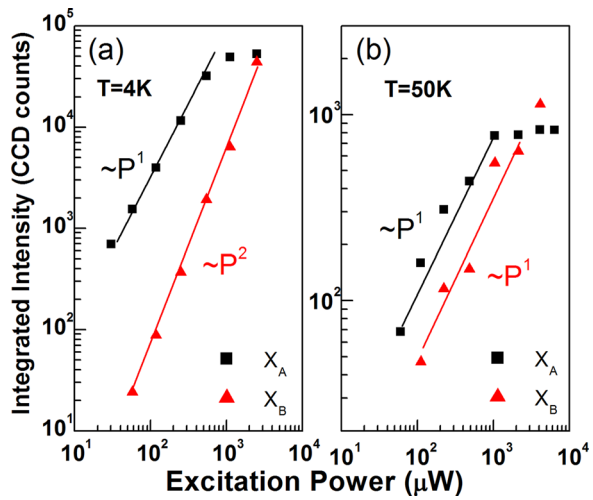

FIG. 2. The integrated emission intensities of X_A and X_B as a function of applied excitation powers plotted in logarithmic scales performed at (a) 4 K, (b) 50 K. The excitation energy was $h\upsilon_{ex} = 4.66$ eV. The experimental results are shown in scatters. The solid lines with indicated slopes are shown for visual clarity.

quadratic power dependence of I_{XB} observed at 4 K. First, the quadratic P_{ex}-dependence of X_B at 4 K turns into an almost linear dependence at 50 K (Fig. 2(b)) whereas the linear P_{ex}-dependence of X_A at 4 K remains linear at 50 K (Figs. 2(a) and 2(b)). Thus, the experimental observation of linear P_{ex}-dependence for both I_{XA} and I_{XB} at 50 K contradicts the arguments of I_{XB} being the biexciton. Moreover, for a biexciton-exciton cascade recombination under pulsed excitation, the recombination of a biexciton will leave an exciton as the intermediate state, with subsequent exciton emission. If the probability of populating the QD with two *e-h* pairs (biexciton) is significantly high, a delayed transient profile for the exciton with respect to that for the biexciton is expected. According to reported models of the biexciton-exciton system, the decay curve of the single exciton can be quantitatively described by rate equations.[16,17] In our case, the measured time-dependent I_{XA} does not match well with the modeled decay curve, implying that the assumption of X_B being a biexciton is false.[14] Finally, due to the sequential recombination of the biexciton-exciton system, an additive rather than a competitive emission intensity dependence is expected. A pronounced competition in terms of recombination probability between X_A and X_B is observed in our *T*-dependent measurements, which accordingly is inconsistent with the interpretation of X_B and X_A as the signatures of a biexciton-exciton system.

Fig. 3(a) shows the full spectrum of the GaN pyramid hosting QD2; exhibiting features related to the GaN barriers, QD2 and the InGaN layers on the facets of the GaN pyramid. The low density of states of the QDs makes it highly unlikely for absorption of photons directly into the QD volume.[18] Consequently, the emission of the QD is mainly the result of an excitation, in which the carriers are subsequently trapped into the QD from its surrounding barriers. From the μPLE spectrum in Fig. 3(a), it is demonstrated that $h\upsilon_{ex}$ above ~3.1 eV can contribute to I_{QD2}. This threshold energy observed is likely originating from potential fluctuations present in the vicinity of QD2. The probability for carriers to become captured by QD2 could be reduced because the carriers may be localized in these potential fluctuations. Such effects could be qualitatively investigated by selective generation of excited carriers, performed by means of different excitation energies at different temperatures. With $h\upsilon_{ex} = 4.66$ eV, a progressive enhancement of the integrated emission intensity of QD2 ($I_{QD2} = I_{XA} + I_{XB}$) with increasing *T* is observed (Fig. 3(b)), indicating that QD2 receives additional carriers (*e* and *h*) from its vicinity via thermal excitation of localized carriers.[19] It should be noted that P_{ex} of the laser was tuned to acquire an intensity of X_B "just above the detectable limit" with an initial intensity ratio of $I_{XB}/I_{XA} \sim 0.07$ at 4 K (Fig. 3(c)), ensuring that I_{XA} and/or I_{XB} are not saturated by P_{ex}. The increasing ratio of I_{XB}/I_{XA} with increasing *T* (Fig. 3(c)) agrees with the interpretation of X_B as being an excitonic complex because the probability for QD2 to acquire more than a sole *e-h* pair should increase with increasing *T*. On the other hand, the I_{QD2} remains essentially constant with increasing *T* under $h\upsilon_{ex} = 3.49$ eV (Fig. 3(b)), indicating that QD2 does not receive extra thermally activated *e-h* pairs for enhancing I_{QD2}. The combination of an observed constant I_{QD2} and an increasing ratio of I_{XB}/I_{XA} with increasing *T* reveals that I_{XA} is suppressed and I_{XB} is

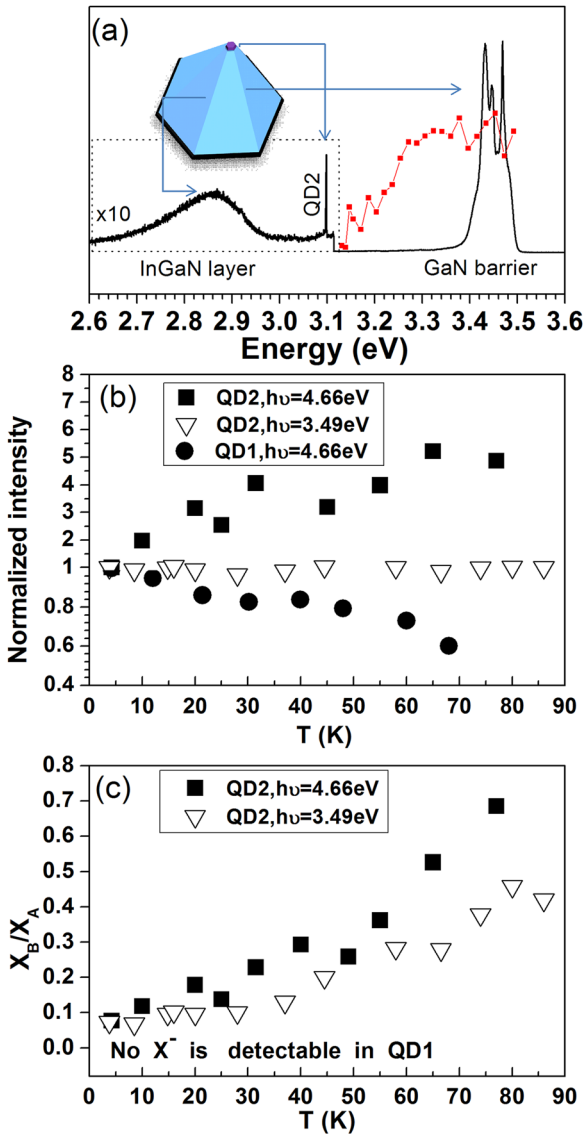

FIG. 3. (a) μPL spectra of QD2 together with its hosting pyramid and InGaN layer formed on the facets as indicated in the figure. The emission intensity within the dash-line frame is multiplied by a factor of 10 for clarity. The μPLE spectrum of the integrated emission intensity of QD2 is shown in red color. (b) Plots of the integrated emission intensity at different temperatures with two different excitation energies ($h\upsilon_{ex} = 4.66$ eV and $h\upsilon_{ex} = 3.49$ eV). The results are normalized to the intensity recorded at 4 K. Note that the y-scale changes for visual clarity when the value is smaller than 1. (c) Plots of the ratio of X_B/X_A at different temperatures with excitation energies both at $h\upsilon_{ex} = 4.66$ eV and $h\upsilon_{ex} = 3.49$ eV.

enhanced with increasing T. Such an observation is inconsistent with the general understanding of a biexciton-exciton recombination scheme in which the single exciton would increase together with the biexciton in an additive way for the case of low P_{ex}, well below the single exciton saturation as used in these experiments. Instead, the competing behavior observed for I_{XA} and I_{XB} strongly implies that both X_A and X_B originate from excitons involving just one e-h *pair*, but X_B should involve an extra charge carrier.

Charged excitons are formed due to unequal capture/supply rates of electrons and holes from the potential barrier into the QD. The difference in carrier relaxation times and diffusivities between electrons and holes, dopants/impurities and potential fluctuations in the vicinity of the QD can be

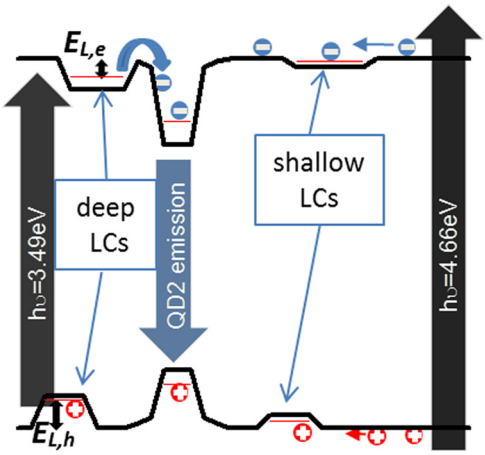

FIG. 4. A schematic figure illustrating the source of additional charge carrier involved in the recombination of X_B by considering the potential fluctuations in the vicinity of QD2. Upon excitation with $h\upsilon_{ex} = 3.49$ eV, only QD2 and deeper potential fluctuations are populated. Only electrons localized in the populated potential fluctuation can overcome the ionization energy (E_L) and then be recaptured by QD2 as illustrated in the figure.

utilized to manipulate the exciton charge states by means of varying the excitation energies, excitation power, and temperature.[11,20] Carriers localized in such potential fluctuations must acquire sufficient energy to overcome the energy barrier to become captured into the QD. The escape probability of carriers from the potential fluctuations is proportional to $\exp(-E_L/k_BT)$, where k_B is the Boltzmann constant and E_L is the ionization energy of the confined carriers. Given that the effective e mass is about 1/5 with respect to the effective h mass in GaN (Ref. 21) and assuming the potential depths are comparable for the e and the h, the e should have significantly larger probability to escape and subsequently be captured by QD2, implying a negatively charged exciton for X_B. A proposed recombination scheme involving the potential fluctuations (Fig. 4) can be explained in the following way: By $h\upsilon_{ex} = 4.66$ eV, the excited carriers gain sufficiently high energy to populate QD2, all potential fluctuations and the GaN barrier. The continuously enhanced I_{QD2} with increasing T (Fig. 3(b)) indicates a considerable enhancement of the escape probabilities for both e and h and a thermally facilitated diffusivity of carriers in the barriers at higher T. On the other hand, for $h\upsilon_{ex} = 3.49$ eV, only QD2 and the deeper potential fluctuations with energy gaps smaller than $h\upsilon_{ex} = 3.49$ eV are populated. The route for QD2 to acquire carriers in addition to the weak direct excitation is the thermally activated process of localized carriers from potential fluctuations. As stated above, X_B must possess an additional charge compared to X_A in order to explain the experimental observations, which is believed to be an e.

Theoretical models of strained III-nitride QDs with built in electric fields generally predict a certain order of the emission energies of the exciton complexes according to $E_{XX} > E_{X^+} > E_{X^-}$. The reason for this trend is that the repulsive Coulomb interaction between holes is larger than the corresponding repulsion between electrons, which in turn is larger than the attractive electron-hole interaction ($|J_{hh}| > |J_{ee}| > |J_{eh}|$).[13] All reported models predict negative binding energies of the complexes XX, X^+, and X^-, but Coulomb correlations are known to redshift the emission

energies with respect to the single exciton X. Thus, a plausible explanation to why the current models do not exhibit any positive binding energies, as sometimes observed experimentally, is that the correlation effects have not been taken into account in a realistic way in the models proposed. Under a successive redshift of XX, X^+, and X^- with respect to X, the negatively charged exciton X^- is the first one that turns from a negative binding energy into a positive binding energy. It should also be noted that the computational predictions on the polarization degree for exciton complexes predict a negligible difference in the polarization degree between the single exciton and the negatively charged exciton, whereas a small, but noticeable difference is typically found between the single exciton and the positively charged exciton and the biexciton.[14] Accordingly, the negatively charged exciton is the most likely interpretation of X_B.

In conclusion, several optical characterization techniques, including μPL, μPLE, and TRμPL, were employed to investigate the origins of two emission lines (X_A and X_B) from single InGaN QDs on a GaN pyramid. The emission lines are believed to be the single exciton and the negatively-charged exciton based on the following remarks: (i) Both X_A and X_B are verified to originate from the same QD. Power- and polarization-dependent measurements suggest that X_A and X_B are a single exciton and an exciton complex, respectively. (ii) The option of a biexciton for X_B is excluded and instead a three-particle configuration is suggested because the recombination of a biexciton is not expected to compete but rather be additive with the recombination of the single exciton. TRμPL results are not consistent with an interpretation of X_A and X_B as being biexciton-exciton, as the expected delay of the exciton relative to the biexciton is not observed. (iii) The negatively charged exciton is suggested based on the escape probability of localized carriers from the potential fluctuations in the vicinity of the QD and the comparison between our experimental results and theoretical predictions of emission polarization properties associated with various exciton complexes from a QD.

The authors would like to thank for the financial support from the NANO-N consortium funded by the Swedish Foundation for Strategic Research (SSF).

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