Excitonic complexes in single zinc-blende GaN/AlN quantum dots grown by droplet epitaxy

S. Sergent,[1] S. Kako,[2] M. Bürger,[3] T. Schupp,[3] D. J. As,[3] and Y. Arakawa[1,2]
[1]*Institute for Nano Quantum Information Electronics, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo 153-8505, Japan*
[2]*Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo 153-8505, Japan*
[3]*Department Physik, Universität Paderborn, 33095 Paderborn, Germany*

(Received 18 July 2014; accepted 30 September 2014; published online 9 October 2014)

We study by microphotoluminescence the optical properties of single zinc-blende GaN/AlN quantum dots grown by droplet epitaxy. We show evidences of both excitonic and multiexcitonic recombinations in individual quantum dots with radiative lifetimes shorter than 287 ± 8 ps. Owing to large band offsets and a large exciton binding energy, the excitonic recombinations of single zinc-blende GaN/AlN quantum dots can be observed up to 300 K. © *2014 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4897993]

GaN quantum dots (QDs) have recently been under the scope of a lot of attention as high-temperature solid state emitters due to the demonstration of single photon emission up to 200 K in self-assembled wurtzite GaN QDs[1] and up to 300 K in site-controlled wurtzite nanowire QDs.[2] Less mature than their wurtzite counterparts, single self-assembled zinc-blende (ZB) GaN QDs already show good prospects in terms of high-temperature operation,[3–5] especially with the recent demonstration of single photon emission up to 100 K.[5] They even present several advantages over self-assembled wurtzite GaN QDs: shorter radiative lifetimes/larger oscillator strengths[4,6] as well as a reduced spectral diffusion[4] because of the non-polar aspect of ZB GaN, and also a better photon antibunching at low temperature.[5]

Most of the experimental studies carried out so far[3–7] dealt with ZB GaN QDs fabricated by plasma-assisted molecular beam epitaxy in the frame of the Stranski-Krastanov (SK) growth mode.[7] However as recently demonstrated, the fabrication of ZB GaN QDs can also be obtained by droplet epitaxy (DE).[8] This is a promising technique that allows for a greater control of the QD density,[8] but the optical properties of excitonic complexes in single ZB GaN QDs grown by DE are yet to be investigated.

In this letter, we study by microphotoluminescence (μPL) the optical properties of single ZB GaN QDs obtained by the DE growth mode. We investigate the radiative and non-radiative recombination processes in single QDs as a function of temperature, and we show that it is possible to obtain the photoluminescence of a single QD at room-temperature. We also show some evidence of biexciton recombinations.

The sample is grown on a 3C-SiC pseudo-substrate by plasma-assisted molecular beam epitaxy. A 30-nm ZB AlN buffer layer is first deposited on the pseudo-substrate, and self-assembled ZB GaN QDs are subsequently grown by the DE technique.[8] They are finally capped by a 30-nm ZB AlN layer. We estimate the QD density to be in the low $10^{10}\,cm^{-2}$ range, as confirmed by atomic force microscopy of uncapped samples. In order to limit the number of QDs probed by the μPL setup, we then process sub-micrometer mesas by electron-beam lithography of a spin-coated resist followed by Cl_2/Ar ion-coupled plasma reactive ion etching of the epilayer.

The sample is placed in a He-cooled cryostat at temperatures that can vary between 4 K and 300 K. The QDs are excited non-resonantly in grazing incidence geometry by a frequency-quadrupled continuous-wave (CW) laser emitting at 266 nm. The μPL signal is collected by a microscope objective (numerical aperture 0.4) aligned along the [001] crystal direction. The QD μPL signal is spatially filtered by a pinhole, dispersed on 300, 1200, or 2400 grooves/mm gratings and collected by a nitrogen-cooled charge-coupled device camera. The spectral resolution of the setup can be as good as 0.1 meV in the considered spectral range. QD decay measurements are carried out by time correlated single photon counting, using the third harmonic of a Ti-Sa laser emitting at 266 nm as the pulsed excitation source. The time-resolution of the setup is 200 ps. In order to bypass the spectrometer polarization response function, polarization measurements are carried out using a half-wave plate followed by a Glan-Taylor linear polarizer positioned after the microscope objective.

The μPL spectrum of the QD ensemble observed on a non-patterned area of the sample is centered at 3.7 eV with a 400 meV full width at half maximum (see dashed curve in Fig. 1(a)). When probing sub-micrometer mesas, individual μPL peaks can be observed between 3.5 eV and 4.0 eV. Most of the lines exhibit a linear behavior as a function of excitation power so that they are associated to excitonic recombinations in individual QDs. Their time-resolved decays are measured for 14 different single QDs and can be fitted with a single exponential function (Fig. 1(b)). The fitting leads to lifetimes at T = 4 K ranging from 225 ± 4 ps to 287 ± 8 ps (see open circles in the inset of Fig. 1(b)), and the average lifetime is 260 ± 23 ps. The decay lifetimes present no obvious energy dependence, most likely due to a distribution of the QD aspect ratio. When the temperature is increased, the lifetime exhibits a plateau up to 50 K (see closed circles in the inset of Fig. 1(b)), which is consistent with what one would expect from radiative recombinations. Such short radiative lifetimes are of the same order as SK ZB GaN QDs[4] and confirm that we are dealing with non-polar GaN

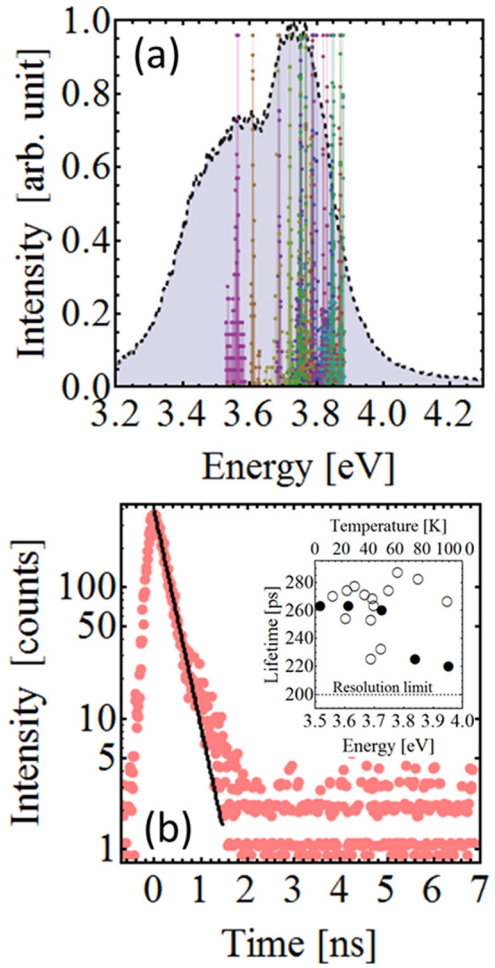

FIG. 1. (a) Normalized μPL spectra of single QDs from various mesas excited at T = 4 K by a CW laser at 266 nm. The dashed line represents the QD ensemble on a non-patterned area of the sample. (b) Typical time-resolved μPL decay of a single QD emitting at 3.70 eV and excited by a 266 nm pulsed laser at T = 4 K. The black line represents the fitting to a single exponential decay. The decay time is 264 ± 2ps. The closed circles in the inset represent the measured decay times of the same QD as a function of temperature. The open circles represent the low-temperature decay times for 14 single QDs as a function of emission energy. The 200 ps resolution limit is represented by the dashed line.

QDs. From 75 K, the decay lifetimes become even shorter and very close to the setup resolution as temperature-activated non-radiative recombination processes kick in. Despite such non-radiative processes and the subsequent intensity quenching, the photoluminescence of some single QDs can be followed up to 300 K (Fig. 2). This is a clear improvement over the 205 K limit observed for single SK ZB GaN QDs.[3,4] As the temperature increases, the single QD emission energy redshifts along with the ZB GaN bandgap, and due to phonon broadening the QD homogeneous linewidth increases from 3 meV at 4 K up to 28 meV at 300 K.

Despite their non-polar aspects, DE QDs are still sensitive to their electrostatic environment. Due to the short time-scale jittering, most of the QDs exhibit low-temperature homogeneous linewidths of several meV (Fig. 3(a)), very similar to SK QDs in the considered spectral range.[4] QDs with homogeneous linewidths as narrow as 0.6±0.07 meV at 3.87 eV can also be found, slightly larger than the narrowest linewidth found in SK QDs.[4] At high excitation power, some DE QDs present also significant long time-scale jittering

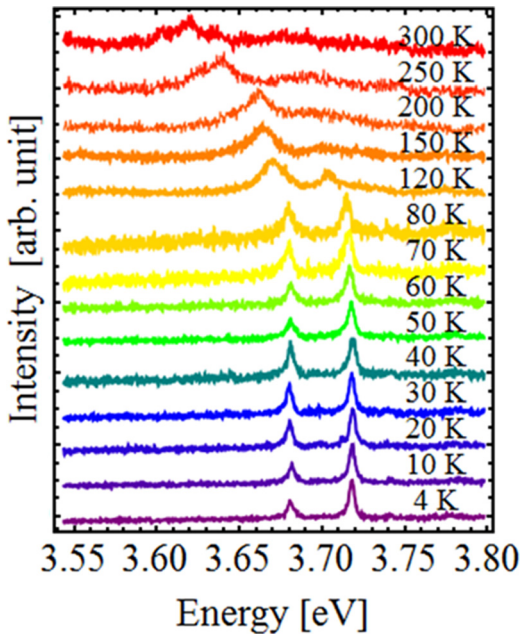

FIG. 2. Normalized μPL spectra of two individual QDs measured in the same mesa at various temperatures.

(Fig. 3(b)). In this work, we actually use the QD long time-scale jittering at high excitation as an advantage to identify peaks emerging from the same QD. This is typically the case of peaks X and XX of Fig. 3(b), the emission energies which exhibit a Pearson correlation coefficient close to 1 and are totally uncorrelated to higher energy peaks emerging from the same mesa (not shown here). The excitation power dependence of X and XX integrated intensities (Fig. 4(a)) can be fitted by a function of the form $\alpha.P^n$ with P being the excitation power. The exponents n of X and XX are respectively $n_X = 0.89$ and $n_{XX} = 1.99$, close to linear and quadratic

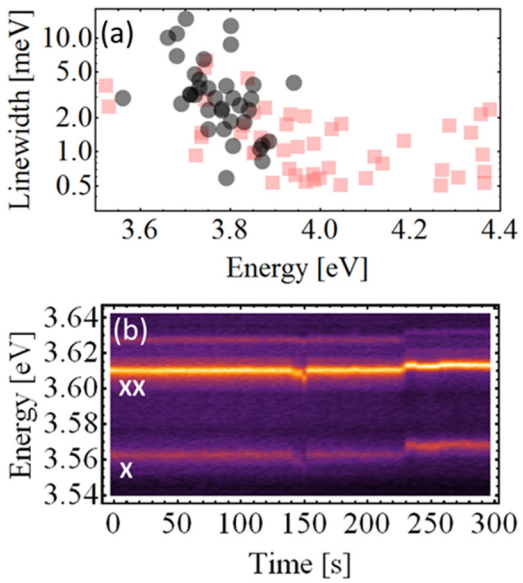

FIG. 3. (a) Homogeneous linewidth of various single QDs obtained at low CW excitation power and low temperature (black circles). Pink squares represent the homogeneous linewidths of single SK ZB GaN QDs extracted from Ref. 4 and completed. (b) Time-dependent spectrum of a single QD excited at 4×10^5 W cm^{-2} highlighting its long time-scale spectral diffusion. A spectrum is taken every 3 s.

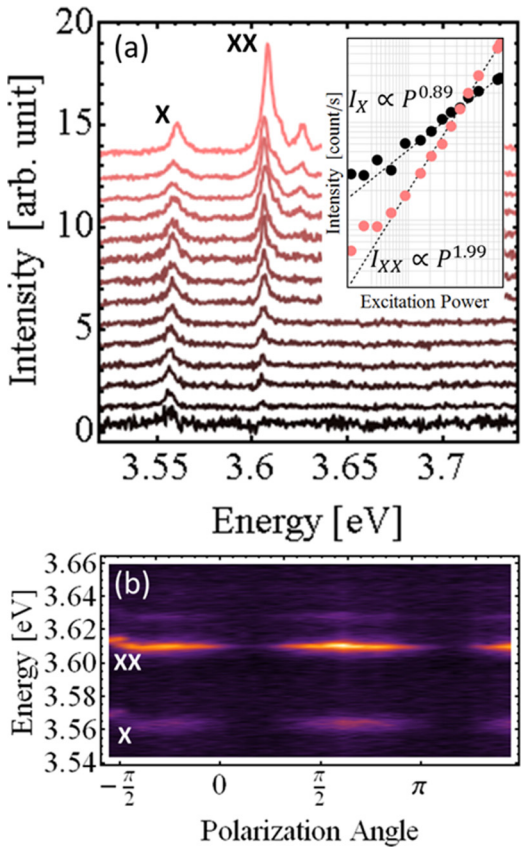

FIG. 4. (a) μPL spectra of the single QD from Fig. 3(b) measured at various CW excitation powers. The energies of X and XX peaks are respectively 3.561 eV and 3.608 eV. The inset shows the Log-Log plot of the X and XX integrated intensity as a function of excitation power. The dashed lines represent fitting curves of the form $\alpha.P^n$. (b) Polarization measurements of the same single QD excited at 4×10^5 W cm^{-2}.

behaviors (inset of Fig. 4(a)). They may thus be associated to the excitonic and biexcitonic recombinations of the same QD. Polarization measurements of X and XX do not reveal any fine-structure splitting that would allow us to unambiguously attribute such peaks to neutral exciton and biexciton peaks. However, X and XX are linearly copolarized, as expected for exciton and biexciton peaks (Fig. 4(b)). Although we expect the radiative lifetimes of X and XX to be respectively τ_X and $\tau_{XX} = \tau_X/2$, measured lifetimes with no deconvolution give $\tau_X = 270 \pm 11$ ps and $\tau_{XX} = 215 \pm 4$ ps. This is due to the vicinity of the 200 ps time-resolution limit. Attributing X and XX peaks to neutral exciton and biexciton recombinations translates into a large negative biexciton binding energy $E_{XX}^B = -47$ meV. This is typically the kind of energy found in large wurtzite GaN QDs[1,9,10] where the giant built-in electric field separates the hole and electron wavefunctions, leading to an attractive electron-hole Coulomb interaction C_{eh} that is smaller than the hole-hole C_{hh} and electron-electron C_{ee} repulsive interactions. However, in the studied non-polar ZB GaN QDs, the reduced piezoelectric potential demonstrated by the short radiative lifetimes allows for a good overlap between the electron and hole wavefunctions,[11] and one would not expect such a large negative biexciton binding energy. However, negative biexciton energies can still be found in non-polar QDs in the case of a small binding contribution of correlation and exchange, as observed, e.g., in small InAs/GaAs QDs.[12] It should also be noted that a similar negative biexciton binding energy ($E_{XX}^B = -36$ meV) has been recently found in non-polar wurtzite-phase InGaN QDs despite a good electron and hole wavefunction overlap.[13] Alternatively, we might be here dealing with charged excitons and biexcitons: although the sample is not intentionally doped, residual O contamination form the nitrogen plasma source and the vicinity of the SiC heterosubstrate interface leads to the presence of O, Si, and C impurities that would favor the formation of charged excitonic complexes.

To estimate the typical binding biexciton energy of DE QDs, we perform 8-band k.p calculations of the electron and hole ground state wavefunctions $|\psi_h(r)\rangle$ and $|\psi_e(r)\rangle$ and use the simple model $E_{XX}^B = 2C_{eh} - C_{ee} - C_{hh}$, where $C_{ij} = \langle\psi_i(r_i)\psi_j(r_j)|C|\psi_i(r_i)\psi_j(r_j)\rangle$ and $C = \pm[4\pi\varepsilon_0\varepsilon_r|r_i - r_j|]^{-1}$. The QDs are modelled as lens-shaped ZB GaN/AlN QDs with an aspect ratio varying between 0.05 and 0.5 and heights varying between 0.75 nm and 3.5 nm. The effect of strain and piezoelectricity are included in the calculations and the band structure parameters are extracted from Ref. 14. According to calculated data, large negative biexciton binding energies (up to $E_{XX}^B = -36$ meV) can only be obtained for the smallest QDs emitting beyond 4 eV. Similar calculations including the p shell QD energy levels allow us to estimate the energy separation between charged exciton and biexciton complexes. The positively or negatively charged exciton and biexciton complexes can be separated by negative energies close to our experimental value of -47 meV, but again such values are only obtained for small QDs emitting beyond 4 eV. This is at odds with our experimental results and shows that more advanced measurements such as magnetophotoluminescence spectroscopy[15] or a more accurate model using, e.g., configuration interaction[16] would be needed to get further insight into that matter and determine whether we are here dealing with neutral or charged exciton and biexciton complexes.

In summary, we have shown that DE ZB GaN QDs are very similar to their SK counterparts with fast radiative recombination lifetimes and narrow spectral linewidths down to 0.6 ± 0.07 meV. They even show better prospects for high-temperature single photon emission as single QD microphotoluminescence has been observed up to room-temperature and the low QD density limits the background contamination that hinders the performance of their SK counterparts.[5] Although further theoretical investigations need to be carried out on ZB GaN QD biexcitons, if confirmed, the large biexciton binding energy measured in this letter would also be a significant advantage for single photon emission: it would limit the contamination from the biexciton peak that has been shown to limit high-temperature $g^2(0)$ values, e.g., in self-assembled wurtzite GaN QDs.[1]

This work was supported by the Project for Developing Innovation Systems of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), by Japan Society for the Promotion of Science (JSPS) through its Funding Program for world-leading Innovation R&D on Science and Technology (FIRST Program), by the DFG graduate program GRK 1464 "Micro- and Nanostructures in Optoelectronics and Photonics" and via Sonderforschungsbereich TRR 142.

[1]S. Kako, C. Santori, K. Hoshino, S. Gotzinger, Y. Yamamoto, and Y. Arakawa, Nature Mater. **5**, 887 (2006).
[2]M. J. Holmes, K. Choi, S. Kako, M. Arita, and Y. Arakawa, Nano Lett. **14**, 982 (2014).
[3]J. P. Garayt, J. M. Gérard, F. Enjalbert, L. Ferlazzo, S. Founta, E. Martinez-Guerrero, F. Rol, D. Araujo, R. Cox, B. Daudin, B. Gayral, L. S. Dang, and H. Mariette, Physica E **26**, 203 (2005).
[4]S. Sergent, S. Kako, M. Bürger, D. J. As, and Y. Arakawa, Appl. Phys. Lett. **103**, 151109 (2013).
[5]S. Kako, M. Holmes, S. Sergent, M. Bürger, D. J. As, and Y. Arakawa, Appl. Phys. Lett. **104**, 011101 (2014).
[6]J. Simon, N. Pelekanos, C. Adelmann, E. Martinez-Guerrero, R. André, B. Daudin, L. S. Dang, and H. Mariette, Phys. Rev. B **68**, 035312 (2003).
[7]E. Martinez-Guerrero, C. Adelmann, F. Chabuel, J. Simon, N. T. Pelekanos, G. Mula, B. Daudin, G. Feuillet, and H. Mariette, Appl. Phys. Lett. **77**, 809 (2000).
[8]T. Schupp, T. Meisch, B. Neuschl, M. Feneberg, K. Thonke, K. Lischka, and D. J. As, J. Cryst. Growth **312**, 3235 (2010).
[9]S. Kako, K. Hoshino, S. Iwamoto, S. Ishida, and Y. Arakawa, Appl. Phys. Lett. **85**, 64 (2004).
[10]C. Kindel, S. Kako, T. Kawano, H. Oishi, Y. Arakawa, G. Hönig, M. Winkelnkemper, A. Schliwa, A. Hoffmann, and D. Bimberg, Phys. Rev. B **81**, 241309(R) (2010).
[11]V. A. Fonoberov and A. A. Balandin, J. Appl. Phys. **94**, 7178 (2003).
[12]S. Rodt, R. Heitz, A. Schliwa, R. L. Sellin, F. Guffarth, and D. Bimberg, Phys. Rev. B **68**, 035331 (2003).
[13]B. P. L. Reid, T. Zhu, C. C. S. Chan, C. Kocher, F. Oehler, R. Emery, M. J. Kappers, R. A. Oliver, and R. A. Taylor, Phys. Status Solidi C **11**, 702 (2014).
[14]I. Vurgaftman and J. R. Meyer, J. Appl. Phys. **94**, 3675 (2003).
[15]M. Bayer, G. Ortner, O. Stern, A. Kuther, A. A. Gorbunov, A. Forchel, P. Hawrylak, S. Fafard, K. Hinzer, T. L. Reinecke, S. N. Walck, J. P. Reithmaier, F. Klopf, and F. Schafer, Phys. Rev. B **65**, 195315 (2002).
[16]S. Rodt, A. Schliwa, K. Pötschke, F. Guffarth, and D. Bimberg, Phys. Rev. B **71**, 155325 (2005).