Complex behavior of biexcitons in GaN quantum dots due to a giant built-in polarization field

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In-depth optical spectroscopic studies of single polar GaN/AlN quantum dots (QDs) grown by molecular beam epitaxy are carried out by means of low-temperature microphotoluminescence. Luminescence linewidths as low as 700 μeV are obtained allowing thorough characterization of the QD electronic properties. Biexciton emission is observed for a wide range of dot size. It is shown that the binding energy (E_{XX}^b) exhibits two regimes. The main one is governed by the dot height through the quantum confined Stark effect leading to a variation of E_{XX}^b from +3 meV for the smallest dots to −11 meV for the largest ones. A secondary variation of opposite sign is demonstrated for dots having the same height but different lateral size.

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I. INTRODUCTION

Over the past decade, III-V nitride heterostructures have attracted much attention for the realization of short-wavelength optoelectronic devices.[1] In particular, self-assembled GaN quantum dots (QDs) have been considered for UV-visible light emitters.[2–5] Indeed, they could open brand new photonic applications as true quantum effects are still present at high temperature in such a system. This is exemplified by the recent report of single-photon emission up to 200 K.[6] In fact, GaN QDs are of special interest because of their large exciton binding energy and oscillator strength. Another interesting property of such nanostructures, when grown along the (0001) polar axis, is the presence of a huge built-in electric field (F) of several MV/cm, which originates from both spontaneous and piezoelectric polarizations.[7] As a consequence, a giant quantum confined Stark effect (QCSE) takes place, which induces a large dipole due to electron and hole spatial separation.[8] In this respect, note that it could be used as a basis for quantum information processing operations.[9] In addition, a long spin decoherence time is predicted for nitride-based semiconductors making them suitable for spin-based information processing.[10] Therefore, a comprehensive understanding of electron-hole interactions forming excitons and biexcitons in single GaN dots would be extremely valuable.

Presently, the excitonic properties of nitride QDs have been scarcely studied,[11–18] if one compares to their InAs dot counterparts.[19–21] Spectroscopy of III-nitride single dots using standard techniques such as microphotoluminescence (μPL) is usually made difficult by the very high dot density ($>10^{11}$ cm^{-2}),[2,3] which is typically 1 order of magnitude larger than the values currently reported in the InAs/GaAs system. Research efforts were thus aimed at decreasing the dot density, but at the expense of an increase of the dot size, a typical feature for Stranski-Krastanov QDs.[4,22] However, large dots are not well suited for single dot spectroscopy purposes because of the presence of the aforementioned giant QCSE.[23] This effect makes the dots very sensitive to surrounding charge fluctuations, due, e.g., to impurities, because of the built-in dipole.[16] As a result, both fast and slow spectral diffusion effects have been observed,[16] which broaden the emission linewidth. For example, a spectral linewidth of 6 meV has been measured for QDs emitting at 3.2 eV.[14]

These intrinsic difficulties have likely hindered detailed studies of excitons and biexcitons in GaN single dots, except the major contributions by Kako *et al.* [6,14] These authors reported an exceptionally large negative biexciton binding energy (E_{XX}^b) of −30 meV in large GaN QDs. To explain this unusual value, they proposed a model linking E_{XX}^b to F and the increased repulsive interaction occurring between charges trapped in the dots.[6] However, no experimental confirmation regarding the evolution of E_{XX}^b for small dot sizes has been given yet leaving the discussion widely open.

In this paper, we report a thorough study of excitons and biexcitons in single wurtzite GaN/AlN QDs. Observation of sub-meV broad luminescence peaks ascribed to single dot emission was made possible using a sample genuinely designed to reduce the dot density. This allows measuring E_{XX}^b for a wide range of emission energies, i.e., dot sizes. A twofold behavior is observed, related to the separate influence of the vertical and lateral exciton confinements. A large antibinding energy of −11 meV, as well as a transition between binding and antibinding regimes, exemplify the important role of the QCSE on the excitonic properties of polar QDs.

II. SAMPLE AND EXPERIMENT

The QD sample is grown by molecular beam epitaxy (MBE) using ammonia as a nitrogen source. A relaxed 100 nm thick AlN layer is first deposited on a 2 μm thick c-plane GaN template. Then, 5 monolayers (ML) of GaN (1 ML=0.26 nm) are deposited at T_g=830 °C. The growth is further interrupted, while the V/III ratio is strongly reduced in order to allow GaN epilayer islanding.[3] Though this procedure is usual to form GaN QDs in ammonia-MBE, it generally leads to a very high density of islands.[3] Here, a temperature higher than usual (830 °C vs 800 °C) is used to promote Ga adatom diffusion at the surface. Multiatomic step edges, typical of MBE grown AlN layers,[24] act as preferential island nucleation sites reducing thereby their density on the terraces. An atomic force microscopy (AFM) image of an uncapped sample is presented in Fig. 1. It can be seen that the step edges are fully decorated with large islands. Their average height is ~4.5 nm. On the other hand, small islands are present on the terraces with an average height of ~1 nm

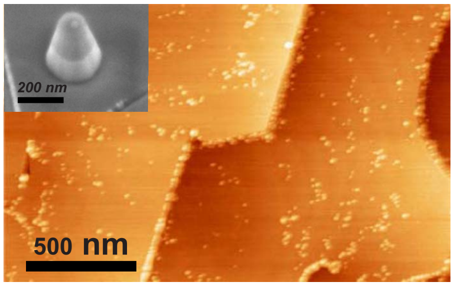

FIG. 1. (Color online) AFM image of an uncapped QD sample. Inset: scanning electron microscopy image of a 200 nm wide mesa.

and an aspect ratio ~0.15.[25] The average local island density can be as low as 10^9 cm^{-2}, which is suitable to perform single dot spectroscopy. Furthermore, the island height exhibits a large dispersion that will reduce *de facto* the QD spectral density once capped with a 15 nm thick AlN layer. A standard low-temperature (LT) UV-μPL setup, having spatial and spectral resolutions of 250 and 0.012 nm, respectively, is used for the measurements. Typical integration times are in the range of several tens of minutes under continuous wave excitation at 244 nm (5 eV, $P_0 \sim 1$ W/cm^2) in the wetting layer (WL) continuum.[3]

III. RESULTS AND DISCUSSION

A typical LT μPL spectrum of the QD ensemble is displayed in Fig. 2(a). A set of luminescence peaks is observed above the emission of the GaN template at 3.48 eV. This picture completely differs from previously reported standard QD PL spectra that exhibit a single broad band.[2–4] Temperature dependent measurements (not shown) clearly demonstrate that the peak maxima follow a semiempirical Varshni law and thus they cannot be attributed to Fabry-Perot interference. In addition, the energy separation between each PL peak decreases with the photon energy. This series of luminescence lines corresponds to the emission of dots of different heights, in a sequence following integer number of MLs. The large energy separation may appear surprising although it is intrinsic to the GaN/AlN QD system. First, the quantum confinement energies of carriers (electrons and holes) are very sensitive to the QD height variations. For instance, theoretical calculations, without considering the internal electric field, predict that in small dots, the transition energy does change by more than 100 meV for a height variation of only 1 ML.[26] Second, the giant internal electric field induces severe redshifts through the QCSE. If one considers a built-in electric field of ~5 MV/cm, then a 1 ML increase of the dot height may redshift the transition energy by more than 125 meV.[3] In Fig. 2(a), the typical energy separation between two adjacent PL peaks is larger than 200 meV, which can therefore be well accounted for by a 1 ML variation of the dot height. Finally, the observation of well resolved peaks is the consequence of the low dispersion of the dot diameters and to the fact that the dependence of the transition energy on the dot diameter is much less than that on the dot height. This means that for a set of QDs having a given height, the inhomogeneous broadening is smaller than the transition energy difference induced by a ±1 ML variation of the dot height. Thus, each of the observed broad peaks consists of the luminescence of an ensemble of QDs with the same height, the energy variations coming mainly from the fluctuations of the dot diameter, strain state, and possible Ga-Al intermixing at the interface. The observation of a clear PL signature for each subset of dots having the same height enables discriminating their optical properties as a function of their height and diameter. PL data have then been compared to calculated transition energies considering built-in electric fields of 3.8 or 8.2 MV/cm.[26] A dot height ranging between 5 and 9 ML and an electric field of ~5.5 MV/cm [Fig. 2(b)] have been deduced.

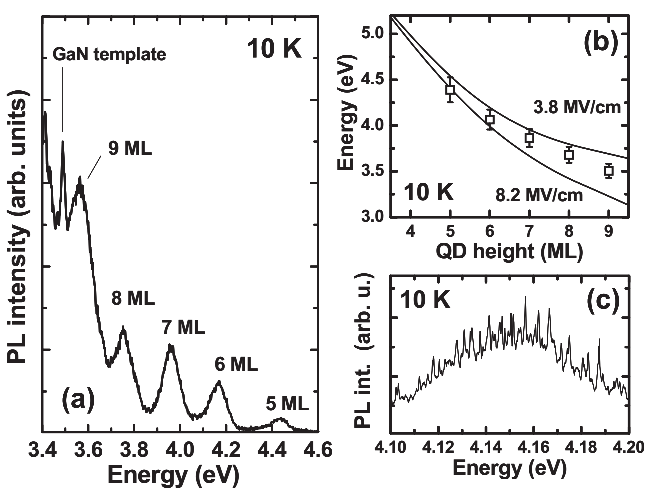

FIG. 2. (a) LT μPL spectrum of the QD ensemble. (b) QD height dependence of the μPL emission energy and simulated dependences for F=3.8 or 8.2 MV/cm (Ref. 26). Error bars correspond to the full spectral width of each dot subset. (c) High spectral resolution spectrum of the peak ascribed to 6 ML high dots.

High spectral resolution LT μPL measurements carried out on the unprocessed sample reveal that each peak of Fig. 2(a) is actually composed of several tens of narrow peaks [Fig. 2(c)]. The underlying broad feature stems from superposition of the peak tails, and has been previously observed in other QD systems.[12,19] Each individual peak is thus ascribed to single dot emission, and the observation is made possible owing to the low dot density. The typical linewidth being measured is about 1 meV. Such a value is still larger than the homogeneous broadening expected from the intrinsic radiative lifetime and phonon scattering.[14] This is likely due to the rather long acquisition times that result in a jittering averaging. Nevertheless, the present PL linewidths are sharper than previously reported data for polar GaN/AlN QDs, and long time scale spectral diffusion is not observed.[6,16] These improved optical properties are ascribed to the reduction of the QCSE, thanks to the small size of the dots.[27] This is a key result that allows performing a detailed spectroscopic investigation of these nanostructures.

Mesas with a diameter of 200 nm were then fabricated by reactive ion etching (inset of Fig. 1) to probe single dot emission properties. According to the dot density estimated from AFM images, there should be no more than a few small ones

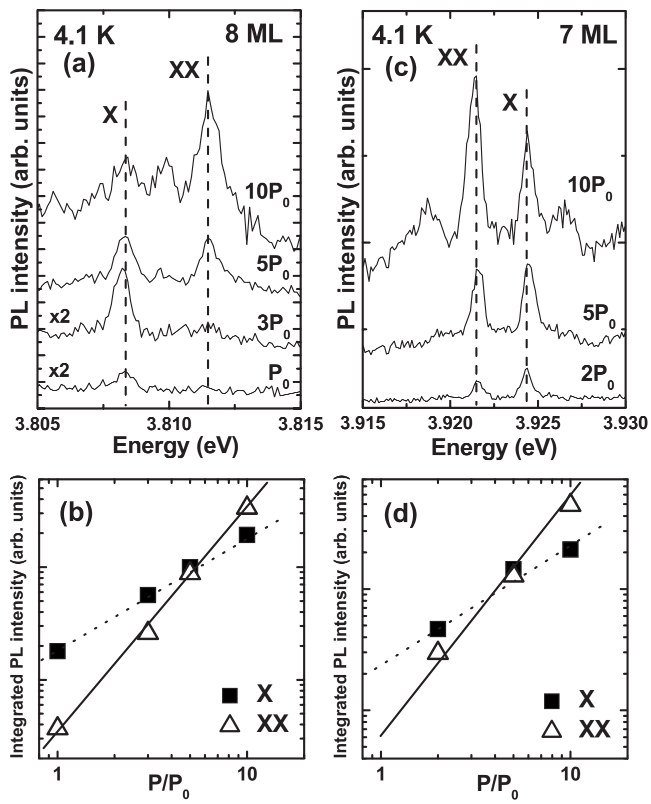

FIG. 3. (a) LT μPL spectra, shifted for clarity, of a single 8 ML high dot presenting a negative E^b_{XX} measured at various power densities ($P_0 \sim 1$ W/cm^2). Exciton (X) and biexciton (XX) emission lines are labeled. (b) Power dependence of the integrated μPL intensity for the exciton and biexciton emission lines of a single 8 ML high dot on a logarithmic scale. The dashed and the full lines indicate a slope of 1 and 2, respectively. (c) Same as (a) for a single 7 ML high dot presenting a positive E^b_{XX}. (d) Same as (b) for a single 7 ML high dot.

in each mesa. Furthermore, due to their large size distribution, the probability of finding several dots with the same height within a mesa is very low. This is confirmed by the fact that most of the mesas present only one sharp PL peak under low power excitation or even no signal. PL linewidths as narrow as 700 μeV have been measured,[28] which compares favorably with those reported for nonpolar GaN/AlN QDs.[15]

Single dots with heights of 7, 8, and 9 ML have been investigated [cf. Fig. 2(b)]. A typical feature observed in the μPL spectra when pumping at high power densities is a doublet [Figs. 3(a) and 3(c)]. When performing power dependent measurements, one of the peaks exhibits a quadratic dependence of its integrated intensity with increasing pumping power, as shown in Figs. 3(b) and 3(d). This behavior is typical of biexcitonic complexes and the energy difference E^b_{XX} between the exciton and biexciton emission lines characterizes the exciton-exciton interactions in the dots. Binding energies of +3 or −3 meV are measured for dot heights of 7 and 8 ML, respectively. The ratio between E^b_{XX} and the emission linewidth is generally larger than that previously reported for GaN dots and reaches 10 for dots with a height of 9 ML.[6] This could be of interest for the realization of single-photon emitters operating at high temperature. Another intriguing feature is the change of the sign of E^b_{XX} when varying the dot height. For bulk or weakly confined systems, the biexciton is a stable complex made of two bound excitons, meaning that E^b_{XX} is always positive. For QDs, the situation can be quite different as two excitons can coexist in an antibinding state due to the three-dimensional spatial confinement, i.e., negative E^b_{XX} may occur. Such a situation was theoretically predicted and observed in small InAs/GaAs QDs.[30] In this latter system, E^b_{XX} is positive for large QDs, then gets smaller when decreasing the dot size, and eventually becomes negative for very small dots.

The evolution of E^b_{XX} as a function of the exciton emission energy is reported in Fig. 4. The corresponding QD heights labeled in Fig. 4(a) are deduced from Fig. 2(b). The salient features are a clear decrease of E^b_{XX} with increasing dot height and a change of E^b_{XX} from positive to large negative values (−11 meV for a 9 ML dot height). When the dependence of E^b_{XX} on the exciton energy is extrapolated to lower energies, a good agreement is found with previous experimental data.[6,14] This confirms that biexcitons can experience large antibinding energies in large GaN QDs.[29] Such a behavior is in contrast with that observed in InAs/GaAs QDs.[30] This is explained by the presence of a giant built-in polarization field in polar GaN/AlN QDs. The related QCSE leads to a separation of the carriers, where electrons are strongly localized at the dot apex while holes are located in the WL.[31] This feature is true for excitons and remains unchanged for biexcitons as the screening induced by the additional electron-hole pair is negligible compared to the huge built-in

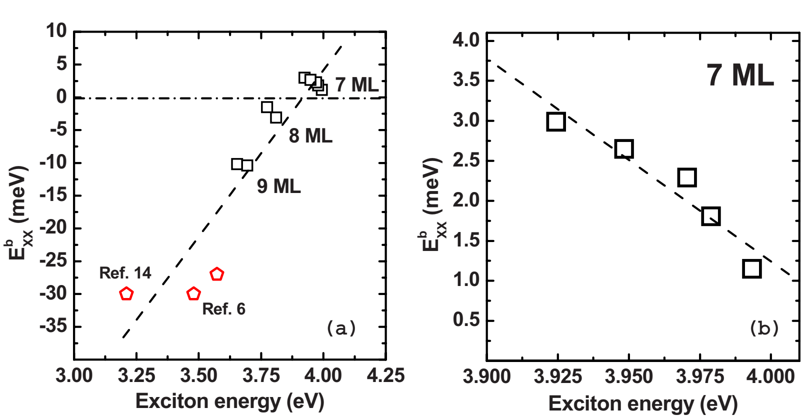

FIG. 4. (Color online) (a) Dependence of E^b_{XX} on the exciton emission energy for QDs of different vertical sizes. (b) Dependence of E^b_{XX} on the exciton emission energy for QDs with the same vertical size (7 ML). Dashed lines are linear fits used as a guide for the eyes.

electric field.[26] The resultant increase of the spatial separation between opposite charges with increasing dot heights leads to a significant reduction of the attractive Coulomb term. As a consequence, electron-electron and hole-hole repulsive interactions dominate inside the dot leading to a reduction of E_{XX}^b. As the electron-hole separation is given by the dot size along the polar axis, the evolution of the attractive interactions will be essentially governed by the dot height. Consequently, E_{XX}^b will decrease with the dot height increase, which will eventually lead to large negative E_{XX}^b values for the largest dots. Such negative values have been simulated for GaN dots using a Hartree approximation.[6] However, it does not account for the positive E_{XX}^b values observed for the smallest dots. Therefore, more advanced theoretical models taking fully into account the specificities of nitride dots are required.

Let us now discuss the evolution of E_{XX}^b for a given dot height. Notice that we succeeded in extracting a set of reliable data for a dot height of 7 ML, for which the QCSE is less pronounced, leading to a positive E_{XX}^b value. Figure 4(b) displays E_{XX}^b as a function of the exciton luminescence energy for such QDs. We observe a negative slope when the PL energy increases, i.e., when the confining potential increases. As the dot height is constant, the electron-hole charge separation is fixed by the QCSE and the effect of small lateral confining potential changes mainly affects the electron-electron and hole-hole repulsive interactions. Thus, an increased lateral confinement of the carriers will induce a reduction of E_{XX}^b. This is the usual dependence reported for InAs/GaAs QDs,[30] which is not surprising as the QCSE can be ignored in small GaN/AlN QDs.

Finally, one may discuss the general trend seen in Fig. 4(a), namely, an overall decrease of E_{XX}^b when decreasing the PL energy. This might be surprising at first sight as an increase of the dot height is likely accompanied by a simultaneous increase of the dot diameter due to the conservation of the aspect ratio. This, in turn, may reduce the lateral confinement and therefore produce an increase of E_{XX}^b, as seen in Fig. 4(b). However, electrons (and holes to a lower extent) in polar GaN/AlN dots are strongly localized laterally inside the dot due to the electric field,[31] which significantly reduces the influence of any lateral dot size changes on the charge separation. As a consequence, E_{XX}^b will decrease when the dot height increases [Fig. 4(a)]. Meanwhile, for a fixed dot height, the lateral confinement changes will induce a classical E_{XX}^b variation [Fig. 4(b)]. Such a twofold behavior is a peculiar feature for semiconductor QDs. Eventually, one can see that the complex behavior of E_{XX}^b in small single GaN dots can be qualitatively accounted for on the grounds of electrostatic interactions only, i.e., without considering exchange interaction and correlation effects which may have a minor impact in such dots as already pointed out in small InAs dots due to the large energy splitting between exciton states.[30]

IV. CONCLUSION

In conclusion, technological issues usually encountered when aiming at performing in-depth spectroscopic studies on polar GaN/AlN QDs have been circumvented. This allows us to observe narrow emission lines attributed to single dots. The large dispersion of the dot size combined to the giant QCSE leads to the observation of luminescence peaks ascribed to an ensemble of QDs having a given height but different diameters. Then, biexciton emission has been evidenced. The biexciton binding energy exhibits a twofold behavior depending on the dot height and lateral size variations. For small dots, the situation is similar to that reported for the prototypical InAs/GaAs system. In contrast, the increase of the dot height reveals an unexpected behavior, namely, a steep decrease of E_{XX}^b leading to large negative values (−11 meV). This latter effect is attributed to the QCSE present in polar nitride QDs. Therefore, we demonstrate that the internal electric field leads to a peculiar twofold behavior for the biexcitonic interactions in polar GaN/AlN QDs.

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