Ga
N quantum dots: from basic understanding to unique applications (invited)

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Abstract. The GaN self-assembled quantum dots constitute a very special and intriguing type of semiconductor nanostructure, mainly because they carry in their structure a giant internal electric field that can reach a value up to 7MV/cm. In this report, we review the most important structural and optical properties of GaN quantum dots, and we discuss their advantages and limitations for blue-UV optoelectronic applications.

1. Introduction
Gallium nitride (GaN) quantum dots (QDs) have recently received considerable attention, because they combine all the particularities of a hexagonal (WZ) wide band-gap semiconductor with large exciton binding energy [1], oscillator strength [2], and intrinsic polarization fields [3], with the discrete energy spectrum, strong localization, and few-carrier effects of zero-dimensional structures [4]. A great variety of methods have been reported in the literature for the fabrication of GaN QDs, and it is worthwhile to give here a representative short list. Early on, the formation of GaN islands was achieved epitaxially using Si as anti-surfactant, both by metal-organic chemical vapor deposition (MOCVD) [5] and molecular beam epitaxy (MBE) [6]. This method resulted to rather large QDs with diameters of 50-150nm, with no clear sign of internal fields most likely due to severe n-type doping by the Si atoms. Subsequently, self-organized GaN [7] and InGaN [8] QDs were demonstrated by using the Stranski-Krastanow (SK) growth mode in MBE. The SK QDs have typically much smaller diameters in the 10-20nm range and exhibit very strong internal fields [9,10]. Further refinements in the SK growth of GaN QDs enabled enhanced QD size and density control [11,12]. The above works referred exclusively to WZ QDs. However, cubic (ZB) GaN SK QDs have been also demonstrated [13]. Besides epitaxy, GaN nanocrystals have been synthesized by several methods, such as inorganic chemical reactions [14], the vapor-liquid-solid mechanism [15], ion implantation in dielectrics [16], annealing of MBE-grown Ga droplets in the presence of N2 [17], and electron nanolithography of gallium azide [18].
In this paper, we review the basic properties of self-assembled GaN QDs grown in the SK mode, and we discuss their potential for optoelectronic applications. In section 2, the structural properties of WZ and ZB GaN QDs are described, based on AFM and TEM images’ analysis. In section 3 we demonstrate the existence of a strong internal field in the WZ QDs by presenting a dramatic size dependence of the photoluminescence (PL) emission wavelength and the radiative lifetime. In section 4, possible optoelectronic applications of GaN QDs are discussed in some detail, before we conclude in section 5.

2. Structural properties
The WZ QD samples were grown by MBE on (0001) sapphire substrates. After the nitridation of the substrate by exposure to N₂-plasma, a typical growth procedure involved the growth of a 30nm AlN buffer layer at 550°C and of a 0.5μm AlN film at 730°C [7,19]. Subsequently, the GaN QD layers were grown at temperatures between 680°C and 730°C, by depositing the equivalent of 3 mono-layers (MLs) of GaN on the smooth AlN surface. The GaN layer undergoes a SK transition in order to release the built-up lattice mismatch strain. In the given temperature range, strain relaxation occurs through 3D GaN island formation on top a 2ML-thick wetting layer (WL). RHEED studies indicate the growth of pyramidal QDs with hexagonal base and well-defined facets with an angle of 30° relative to the surface [19]. The diameter of the pyramids was found correlated to their height, with a diameter/height aspect ratio close to five. This value is larger than that estimated for full pyramids, suggesting the growth of truncated pyramids [19]. Each GaN QD layer was typically capped with AlN of sufficient thickness (>5nm) to recover a smooth surface, on which it was possible to grow the next QD layer. By repeating this procedure several times, one could obtain a QD superlattice.

For the ZB QD samples, we used cubic 3C-SiC (001) templates grown by CVD on Si(001) substrates. After the MBE deposition of a relatively thick AlN buffer layer at 720°C, the QD layer was subsequently formed by the deposition of a few MLs of GaN on the AlN bare surface, leading to the SK formation of GaN tetragonal pyramids with (111) facets, on top of a 2ML-thick WL [13]. A typical ZB QD layer has dot density of 1.3×10¹¹cm⁻², QD height of 2.5±0.5nm, and a diameter/height aspect ratio close to 8. The latter is much larger than the theoretical value of \( \sqrt{2} \) for full pyramids, suggesting also in the cubic phase the formation of truncated pyramid-shaped QDs.

3. Manifestation of giant internal field in hexagonal dots
It is well known that hexagonal nitrides carry, due to their crystal symmetry, important macroscopic polarizations which can be written in the form \( P_{tot} = P_{PZ} + P_{SP} \), where \( P_{PZ} \) is the piezoelectric (PZ) polarization which is proportional to the strain applied to the layer, and \( P_{SP} \) is the material built-in spontaneous (SP) polarization whose value depends only on the material composition. As a consequence, in most nitride heterostructures (including QD ones) there is a non-zero polarization difference \( \Delta P_{tot} \) at every hetero-interface, generating giant internal electric fields of the order of MV/cm.

A clear manifestation of the internal field present in WZ GaN/AlN QDs is found in Figure1, where we compare the \( T=2K \) PL spectra of two 20-period QD samples consisting of large and small WZ dots. For the small dot sample with QD height \( h=2.2 \) nm, the PL peak is centered at 3.75eV, almost
0.3eV blueshifted with respect to the bulk GaN bandgap $E_g$. In contrast, the large dot sample ($h=4.1\,\text{nm}$) exhibits strongly redshifted PL emission energy, almost 0.5eV below $E_g$. The only way to explain this dramatic size dependence is to assume the existence of a strong internal field $F$ along the c-axis, inside the WZ QDs. The QD $e_1h_1$ transition can then be expressed as:

$$e_1h_1 = E_g(S) + E_C(F) + E_V(F) - E_\beta(F) - e \cdot F \cdot h$$

(1)

where $E_g(S)$ is the strained GaN bandgap, $E_C(F)$ and $E_V(F)$ are the electron and hole confinement energies respectively, and $E_\beta(F)$ is the exciton binding energy. In the small dot limit, the last term remains small and the confinement terms dominate, resulting in transition energies higher than $E_g$, while for sufficiently large QDs, the field term prevails and hence QD transition energies below $E_g$ are possible. Obviously, in cases such as the ZB GaN QDs where $F=0$, the QD transition energies are always higher than $E_g(S)$ regardless of the QD size.

| QD Height (Å) | Hexagonal GaN/AlN QDs | Cubic GaN/AlN QDs |
|---------------|------------------------|-------------------|
| $F=0$         | $E_{PL}-E_{gap}$ (meV) |                   |
| $F=6$         | $E_{PL}-E_{gap}$ (meV) |                   |
| $F=7$         | $E_{PL}-E_{gap}$ (meV) |                   |
| $F=8$         | $E_{PL}-E_{gap}$ (meV) |                   |

The results of the calculations are depicted in Figure 2, where the calculated QD transition energies as a function of QD height for various values of $F$ are plotted with respect to the strained GaN bandgap, and are compared to experimentally measured PL emission energies of different WZ and ZB QD samples. In order to determine the amplitude of $F$ in the WZ GaN QDs, calculations of the fundamental transition energy as a function of the QD size have been performed for various $F$ values, according to the following approximation scheme. First, the confinement energies have been calculated for $F=0$, within the effective mass approximation, using the Lanczos numerical method and taking into account the full 3D hexagonal truncated pyramidal shape of GaN QDs embedded in AlN [9]. To reduce the calculation time, it was found that identical confinement energies could be obtained if the truncated pyramid was replaced by a parallelepiped of equal volume and width equal to $0.72\cdot h$. To include then the effect of the internal field on the QD transitions, it was assumed that the truncated pyramid could be described by a 2D quantum well (QW) of width $0.72\cdot h$, on which an internal field $F$ is applied. The dependence of $E_\beta$ on $F$ and $h$ has been neglected, and uniform strain has been assumed throughout the QD volume.
samples. As can be seen, the experimental data points for WZ QDs can be well accounted for, if an internal field of 7MV/cm is assumed to be present in the QDs. On the other hand, the zero-field curve fits very well the experimental points for ZB QDs, confirming the theoretically expected absence of internal field. It should be mentioned that, in spite of the simplifying assumptions of the model, the above results are in good agreement with more complete models for GaN QDs [20,21].

Additional evidence of the strong internal field in WZ QDs can be found in the field-induced modification of the carrier radiative lifetimes $\tau_R$ in GaN QDs. In order to investigate this modification, time-resolved PL (TRPL) experiments have been performed and the PL decay time $\tau_D$ has been measured as a function of QD height, for both WZ and ZB GaN QD samples [10]. To extract $\tau_R$ from the measured $\tau_D$, we took notice of the fact that $\tau_D$ remained constant for $h>35\text{Å}$, indicating predominance of non-radiative (NR) channels for large WZ QDs. Analysis of this observation led us to a unique assumption for the NR times [10], which allowed us to extract the $\tau_R$ values plotted in Figure 3 for both WZ and ZB QDs as a function of $h$. The experimental $\tau_R$ points are compared with theoretical $\alpha/f$ curves estimated for various electric fields, where $f$ is the oscillator strength and $\alpha$ is the proportionality factor determined from the assumption for the NR times. By inspection of Figure 3, it is clear that the WZ QDs exhibit one order of magnitude longer $\tau_R$ compared to ZB QDs of the same height. This is attributed to the field-induced carrier separation in the WZ case, resulting to decreased oscillator strength and increased $\tau_R$. For the same reason, we observe a strong size dependence of $\tau_R$ for the WZ QDs, while in the ZB case $\tau_R$ remains basically independent of $h$.

![Figure 3](image.png)

**Figure 3.** Comparison between experimentally obtained radiative times and theoretically calculated inverse oscillator strengths $\alpha/f$ curves for various internal field values as a function of QD height, for both hexagonal (triangles), and cubic (squares) GaN/AlN QDs. The coefficient $\alpha$ is extracted based on a unique assumption on the non-radiative times for the WZ QDs

As mentioned above, the 7MV/cm internal field in the WZ GaN/AlN QDs stems from the polarization difference $\Delta P$ between GaN and AlN. Assuming zero average field across the QD heterostructure, $\Delta P$ can be deduced based on the relationship:

$$ F = \frac{\Delta P}{\varepsilon \varepsilon_0} \frac{L_B}{L_B + L_W} $$

(2)

where $L_B$ and $L_W$ are the widths of the barrier and QD layers, respectively, and $\varepsilon$ is the static dielectric constant of GaN. For Eq.2, $\varepsilon_{\text{GaN}}=\varepsilon_{\text{AlN}}$ has been assumed. In order to estimate the relative importance of SP and PZ polarizations in $\Delta P$, we have calculated the piezoelectric contribution $\Delta P_{\text{PZ}}$ assuming that
the GaN QDs are coherently strained on AlN according to: $\Delta P_{PZ} = 2d_{33} [c_{11} + c_{12} - 2c_{13} \cdot c_{33}] e_{xx}$, where $d_{33}$ is the relevant PZ coefficient, $c_{ij}$ are the elastic constants, and $e_{xx}$ is the biaxial in-plane strain of the GaN QD layer. For the calculation of $\Delta P_{PZ}$, we have used the $d_{33}$ values of $-2.4 \cdot 10^{-10}$ cm/V for AlN and $-1.4 \cdot 10^{-10}$ cm/V for GaN, based on ab initio calculations [22]. In Figure 4, we plot as a function of aluminum mole fraction the $\Delta P/\Delta P_{PZ}$ ratios extracted not only for the multiple-period GaN/AlN QD samples of Figure 1, but also for the GaN/Al$_x$Ga$_{1-x}$N QWs of ref. [23]. Clearly, the experimental $\Delta P/\Delta P_{PZ}$ points seem to aggregate around the value of 2, suggesting that in the GaN/AlGaN system the SP and PZ contributions to $\Delta P$ are almost equal. The dashed lines in Figure 4 represent the theoretical $\Delta P/\Delta P_{PZ}$ ratios, estimated with the PZ and SP coefficients of Bernardini et al. [22]. The fact that the majority of experimental data stand below the theoretically calculated curves, can be attributed either to overestimated polarization coefficients or to secondary effects such as residual doping, which could reduce the experimental $\Delta P$ values.

4. Optoelectronic applications

The presence of the large internal field in WZ GaN QDs influences strongly their optical and optoelectronic properties. As discussed in Section 3, the main consequence of the internal field is the strong size-dependence of the PL emission energy and radiative lifetime due to field-induced carrier separation inside the QD. In Figure 5, we plot for WZ GaN/AlN QDs the calculated electron-hole wavefunction overlap and corresponding transition wavelength as a function of $h$. In this estimate, as well as in the rest of the paper, $F$ has been taken 7MV/cm, and the GaN QD of height $h$ has been approximated by a QW of width $W=0.72\cdot h$ and the same field value. As illustrated in Figure 5, by varying $h$ merely in the range of 28 to 55Å, the QD transition energy spans essentially the whole visible spectrum. This broadly tunable emission over a wide range of wavelengths for relatively small variations of the QD size, that can be easily attained by adjusting the growth conditions [19], allows for the fabrication of GaN QD-based light emitting diodes (LEDs) emitting all the way from the near-UV to the red spectral range. Alternatively, it has been shown, by incorporating in a single LED GaN QD layers emitting at selected complementary wavelengths, that it is possible to obtain single-chip white LED emission [24]. Evidently, however, there is a price to pay for this large wavelength tunability of GaN QDs. As shown in Figure 5, in the QD height range from 28 to 55Å there is a variation of the wavefunction overlap of nearly four orders of magnitude. Regarding QD LEDs, this implies a dramatic QD size dependence of switching times, due to the field-induced increase of the radiative lifetime.

![Figure 5. Fundamental eigenfunctions overlap (solid squares) and transition energy (solid circles) versus GaN/AlN QD height, at T=300K. The open circles indicate the simulated $e_1 h_1$ lasing wavelengths of a laser structure with a single GaN/AlN QD layer as the active medium and cavity losses of 2000 cm$^{-1}$.](image)

Hence, the “red” QD emitters are expected to exhibit very long switching times of the order of msec, whereas their “blue” counterparts can switch in a fraction of a µsec, compromising thus the fast operation of GaN QD LEDs.
The strong decrease in oscillator strength with increasing QD height, shown in Figure 5, is expected to affect critically the lasing properties of GaN QD-based laser diodes (LDs). In order to draw the main characteristics of this important device, we have employed modeling of a laser structure containing a single GaN/AlN QD layer, using the QW-approximation described above. In addition, we have neglected inhomogeneous broadening effects, and we have taken into account only the highest heavy hole-like valence band. The latter is fully justified by the large 2.4% compressive strain in the GaN layer separating far apart the hole bands. The model, presented in detail elsewhere [25], involves a self-consistent Schroedinger-Poisson solution incorporating strain and carrier screening effects, based on which we have calculated gain and spontaneous emission spectra for various injected carrier densities. For the gain estimates, we have assumed $T=300K$ and a carrier scattering time of $50fs$. Assuming next cavity losses of $2000cm^{-1}$, which is a reasonable value for state of the art nitride LDs, we can define the $e_1 h_1$ lasing wavelength as the wavelength for which the maximum of the $e_1 h_1$ gain peak matches the assumed cavity losses. These values are plotted in Figure 5 as open circles for various QD heights. With increasing QD height, we observe an increasing deviation of the lasing wavelength from the calculated $e_1 h_1$ transition wavelength, as a consequence of screening of the internal field by the carriers needed to induce lasing. Hence, the advantage of large tunability of GaN/AlN QDs does not hold for LDs, since due to screening the lasing wavelength is not expected to exceed $400nm$. In fact, the situation is even more complex for large QDs ($h>45\AA$), where gain peaks from higher transitions surpass the $e_1 h_1$ gain peak, implying that lasing would occur at even shorter wavelengths.

Based on the calculated gain spectra, and assuming that carriers at threshold are lost only through radiative recombination, we can estimate for a given value of cavity losses the corresponding threshold current density $J_{th}$ [25]. In Figure 6, we plot the estimated $J_{th}$ of a single GaN/AlN QD LD as a function of $h$, assuming cavity losses of $2000cm^{-1}$.

![Figure 6](image1.png) **Figure 6.** Simulated threshold current density $J_{th}$ versus QD height for a laser structure with a single GaN/AlN QD layer as the active medium and cavity losses of $2000cm^{-1}$.

![Figure 7](image2.png) **Figure 7.** Effect of the internal field on the threshold current density of a laser structure with a single GaN/AlN QD layer with cavity losses of $2000cm^{-1}$ and a QD height of $4nm$.

Somewhat surprisingly, we observe that $J_{th}$ follows a non-monotonic behavior, showing a clear minimum for $h=4.2nm$. This behavior can be understood by the fact that the enhanced carrier separation in large QDs has two opposing effects. First, it reduces the gain coefficient, forcing the lasing to occur at higher carrier densities, which in turn tend to increase $J_{th}$. Simultaneously, however, the field reduces the spontaneous emission rate, which brings in lower carrier loss rate and reduced $J_{th}$. According to our calculations, as we increase $h$ from 2 to 4.2 nm, the carrier loss rate by spontaneous
emission more than compensates the gain reduction leading to lower $J_{th}$ values. On the other hand, for $h$ > 4.2 nm the gain reduction mechanism dominates, leading to increased $J_{th}$.

We would like now to examine the effect of the internal field’s amplitude on $J_{th}$. In Figure 7, we plot the estimated $J_{th}$ as a function of $F$, assuming a single layer of 4 nm-high GaN/AlN QDs and cavity losses of 2000 cm⁻¹. As depicted in Figure 7, the existence of the 7 MV/cm internal field in WZ GaN/AlN QDs increases $J_{th}$ by at least a factor of 5 over the zero-field value. On the other hand, it is interesting to note the distinct minimum observed for $J_{th}$ at $\approx 1.5$ MV/cm, implying that the optimum operating condition in terms of threshold current for the GaN/AlN QD laser is not the zero-field one. The mechanism behind this minimum is identical to that employed in explaining the minimum of Figure 6.

5. Conclusions

In this report, we have reviewed the main properties of hexagonal GaN/AlN QDs, grown by MBE in the Stranski-Krastanow mode. We have shown that they contain a large internal field of 7 MV/cm, dominating their optical properties. Furthermore, we have examined the impact of the internal field in light emitting applications of these QDs. We have found that while the field brings in some distinct advantages, such as for instance wavelength tunability of LEDs and threshold current reduction in LDs for some field values, overall the role of the field is considered negative and should be avoided if possible.

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7. References

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