PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

Blue-light emission from GaN self-assembled quantum dots due to giant piezoelectric effect

F. Widmann, J. Simon, B. Daudin, G. Feuillet, J. L. Rouvière, and N. T. Pelekanos
Département de Recherche Fondamentale sur la Matière Condensée, CEA/Grenoble, SPMM, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*

G. Fishman
Laboratoire de Spectrométrie Physique, UMR C5588, Université Joseph Fourier, Grenoble 1, CNRS, Boîte Postale 87, 38402 St. Martin d'Hères Cedex, France

(Received 27 July 1998; revised manuscript received 25 September 1998)

It is shown that the optical properties of GaN quantum dots with the wurtzite structure result from a balance between confinement and piezoelectric effects. In ''large'' quantum dots with an average height and diameter of 4.1 and 17 nm, respectively, the photoluminescence peak is centered at 2.95 eV, nearly 0.5 eV *below* the bulk GaN band gap. We attribute this enormous redshift to a giant 5.5 MV/cm piezoelectric field present in the dots, in agreement with theoretical calculations. [S0163-1829(98)51248-9]

The current interest in low-dimensional heterostructures mainly relies on the possibility of achieving high-quality devices, due to the optical and electronic properties which are expected to result from one-dimensional (1D) (quantum wires) or 0D (quantum dots) carrier confinement. In particular, it has been theoretically predicted that the realization of light-emitting diodes (LEDs) or laser diodes (LDs) with quantum dots (QDs) in the active layer would lead to improved optical characteristics, such as low threshold current and weak temperature dependence of the threshold current.[1]

However, the practical observation of 0D confinement effects requires the use of objects with typical sizes in the 10 nm range. The first pioneering works in the field used almost exclusively lithographic patterning of QDs. Nevertheless, this approach is practically abandoned today because of the damage that lithographic processing causes on the lateral QD walls, seriously degrading the optical properties when the QD dimension becomes of the order of 10 nm. By contrast, self-organization resulting from the Stranski-Krastanov growth mode has proven to be very successful in achieving nanostructures with excellent 0D optical properties. In this growth mode, deposition of a strained 2D wetting layer is followed by elastic relaxation through 3D islanding which results in free surface formation.[2] It has been observed for various materials grown under compressive stress, such as InAs on GaAs,[3] InP on $Ga_xIn_{1-x}P$,[4] or SiGe on Si,[5] opening the way for achievement of lasers based on self-organized $In_xGa_{1-x}As$/GaAs (Refs. 6 and 7) and InAs/GaAs (Refs. 8 and 9) QDs.

Concerning III-V nitrides, the present day blue LEDs and LDs consist of stacking of 2D layers with appropriate composition.[10] Despite the successful operation of such LEDs and LDs it is still a current challenge to improve characteristics such as device life time or current threshold. In particular, the insertion of GaN QDs in the active layer appears particularly promising, following the experimental demonstration that nitrides grown under compression by molecular beam epitaxy (MBE) exhibit a Stranski-Krastanov growth mode[11] and that the size of the 3D islands is sufficiently small to allow them to behave as QDs.[12,13] Alternatively, it has also been demonstrated that 3D growth of GaN could be induced in metalorganic chemical vapor deposition (MOCVD) by using Si as an antisurfactant.[14,15]

Whatever the growth technique, i.e., MBE or MOCVD, the QDs exhibit the wurtzite structure, with the [0001] axis parallel to the growth direction. Thus, as a consequence of the noncentrosymmetry of the wurtzite structure, piezoelectric effects are expected to be present and to govern the optical properties of the dots to a certain extent, due to the huge piezoelectric constant values which are one of the most fascinating aspects of nitrides.

Actually, for fully strained GaN on AlN ($\varepsilon = 2.5\%$) piezoelectric fields as high as several MV/cm are expected.[16–18] These values are more than one order of magnitude larger than the piezoelectric fields that can be found in zincblende semiconductors for the same amount of strain.[19] Nevertheless, the role of these giant piezoelectric fields on the optical properties of nitride nanostructures has only recently started to be assessed. For example, large piezoelectric field-induced redshifts in photoluminescence (PL) spectra of $GaN/Al_xGa_{1-x}N$ quantum wells have been reported lately.[20,21]

However, the role of dislocations, interdiffusion, and residual impurities in compensating the piezoelectric field in those systems needs to be further investigated. From this point of view, GaN quantum dots are of special interest as they are fully strained in the AlN matrix and exhibit almost no interdiffusion. Although it has been observed[12] that the threading dislocations existing in the AlN buffer and originating from the sapphire/AlN interface act often as nucleation centers for the QDs, their far inferior density $\approx 10^{10}\ cm^{-2}$ compared to the QDs which are in the $10^{11}\ cm^{-2}$ range explains how the vast majority of the QDs are dislocation-free. This is further supported by the observation of intense and temperature-independent QD photoluminescence.[12]

The samples used in the present study were grown on (0001) sapphire substrate. After the nitridation step of the sapphire, a low-temperature AlN layer, about 15 nm thick, was deposited followed by the growth of a 1.5-μm-thick

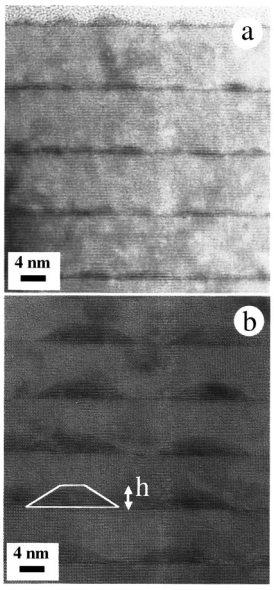

FIG. 1. HREM pictures showing a ⟨2-1-10⟩ cross section of stacked layers of GaN dots. (a) Small dots about 2.3 nm high. Unburied dots protected by the glue are visible in the sample surface. (b) Large dots about 4.1 nm high grown with a ripening step under vacuum between successive layers.

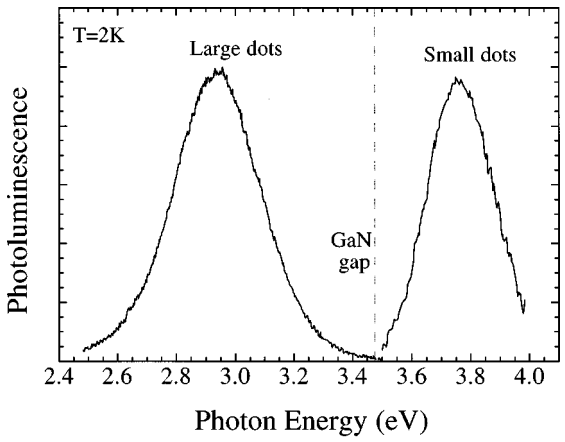

FIG. 2. Photoluminescence spectra of GaN quantum dots at $T=2$ K. Note the large redshift observed for the 4.1-nm-high dots with respect to the small ones.

AlN buffer layer. The details of the growth procedure have been published elsewhere.[22] The GaN QDs were grown by depositing the equivalent of 3 monolayers of GaN on AlN at 700 °C.[11,12] Next, they were covered by AlN in order to smooth the surface again and the operation was repeated 20 times. The size of the dots was varied, depending on whether they were allowed to evolve under vacuum or not before further covering with AlN. In this article, we discuss two different QD samples: a ''small dot'' sample where the GaN QDs are immediately covered by AlN without growth interruption and have a typical height of 2.3 ± 0.2 nm (8 nm diameter), and a ''large dot'' sample where exposure of the QDs to vacuum for about a minute increased their average height to 4.1 ± 0.4 nm (17 nm diameter) as a result of a ripening mechanism.[23] These numbers were derived from the analysis of high-resolution electron microscopy (HREM) pictures shown in Fig. 1 for the two samples, i.e., grown with and without ripening step.

In Fig. 2 we compare the $T=2$ K PL spectra for the two samples. The PL is excited by a few tens of W/cm^2 of the cw UV argon lines around 302 nm ($E_x\approx4.1$ eV) for the small dot sample and around 335 nm ($E_x\approx3.7$ eV) for the large dot sample. It should be noted that for these photon energies of excitation and considering that the band gap of AlN is at 6.2 eV, the GaN QDs are excited directly by absorption in the QD excited states, which are expected to be discrete. However, it is interesting to note that exciting discrete levels with monochromatic light does not seem to result in selective excitation of a specific family of QDs. We rather obtain broad luminescence spectra corresponding to the quasitotality of the QD size distribution. This strongly suggests the possibility that the higher QD levels are coupled, which would then allow hot carriers to diffuse and populate most of the QDs. We attribute the PL peaks to intrinsic QD emission. This is supported by PL measurements as a function of temperature, which reveal that the PL spectral shape, intensity and linewidth remain practically unaffected for both samples in the temperature range 2–300 K. This observation is consistent with intrinsic QD PL emission and excludes, for instance, the possibility that PL is due to shallow extrinsic levels in the QDs. The most striking information of Fig. 2 is the dramatic dependence of the QD PL emission energy on the QD size. For the small dot sample the PL peak is centered at 3.75 eV, nearly 0.3 eV blueshifted with respect to the GaN band gap (indicated by the dashed line). On the other hand, the large dot sample luminesces in the blue[24] at 2.95 eV, i.e., 0.5 eV *below* the bulk GaN energy gap. We attribute this striking QD size effect to the presence of a giant piezoelectric field in the QDs along the *c* axis.

In order to obtain an estimate of the piezoelectric field present in our QDs, we performed calculations of the QD ground-state transition energy as a function of the QD size for various input values of the piezoelectric field. For the zero-field case, we considered a hexagonal truncated GaN pyramidal QD embedded in AlN and we used the numerical method developed by Lanczos. The confinement energy was calculated by taking into account both the electron and the hole confinement energies, E_e and E_h, and by neglecting the variation of the exciton energy. In a further step, it has been found that for sake of simplicity, the hexagonal truncated pyramid could be approximated by a rectangular parallelepiped with a square basis. The comparison with the calculation performed using the exact shape of the pyramid of height h revealed that a very good agreement was found when choosing the height of the parallelepiped, H, equal to $0.72h$ and its volume equal to the volume of the pyramid. This approximation was found to be valid for h ranging typically from 1 to 15 nm. Then, the piezoelectric field due to the strain induced by AlN on GaN was taken into account by assuming that the pyramid could be described by a two-dimensional quantum well of equivalent width H. Finally the energy is expressed by $E=E_g+E_e+E_h-E_{\mathrm{pz}}$, where $-E_{\mathrm{pz}}$ is the decrease in energy due to the piezoelectric field. Before commenting on the results, it is worth stressing that the main source of uncertainty does not derive from the above geometrical approximations but rather from the poorly known carrier

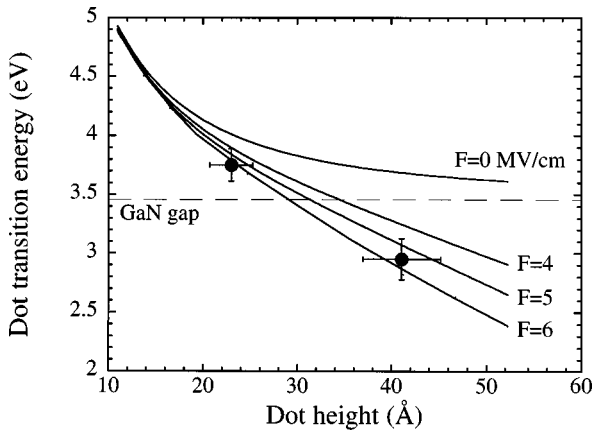

FIG. 3. Calculated transition energy as a function of the dot height for various piezoelectric field values. In the calculated curves $m_e=0.20$, $m_h=1.0$. The solid circles indicate the experimental points extracted from Figs. 1 and 2. The error bar on the dot height reflects the width of the quantum dot height distribution as deduced from the analysis of the TEM images whereas on the energy axis it is the full width at half maximum of the PL peaks. Best agreement with experimental points is obtained for a piezoelectric field of 5.5 ± 1 MV/cm.

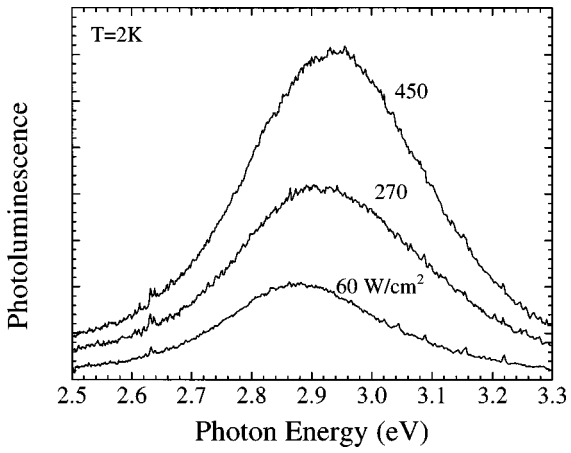

FIG. 4. Influence of the excitation density on the photoluminescence energy of large dots.

masses which are the only input parameters. Concerning the electron mass, its value ranges from 0.20 to 0.22.[25] Concerning the hole mass, an isotropic mass of 1 has been chosen, in agreement with the theoretical results of Susuki *et al.*[25] However, it is worth noting that, depending on the authors, the value of the hole mass ranges between 0.54,[26] and 2.2.[27] As a consequence, neglecting, as we did, the exciton binding energy in the calculation of the confinement energy leads to a maximum error of some tens of meV (the binding energy of the bulk exciton is 25 meV), which is negligible with respect to the error resulting from the uncertainties in the carrier mass values.

The final result is shown in Fig. 3. It exhibits a satisfactory agreement with experimental results, as a hint that the calculations described above correctly predict the general behavior of the optical properties of the GaN dots. Furthermore, it shows that a piezoelectric field value of about 5.5 MV/cm fits reasonably well the experimental data plotted as solid circles in the figure. This value is to be compared with the one of 4.7 MV/cm inferred from x-ray photoelectron spectroscopy results for GaN coherently deposited on AlN,[16] and to the one of 2.5 MV/cm deduced from Ref. 20.

The presence of a piezoelectric field in our QDs is further supported by optical power dependent PL spectra, shown in Fig. 4 for the large dot sample. Clearly, as the excitation power density increases we observe that the center of gravity of the PL peak blueshifts significantly. This behavior is typical of piezoelectric nanostructures and is due to partial screening of the piezoelectric field by the photoexcited electron-hole (e-h) pairs. Specifically, a 70 meV blueshift is observed as the power density varies from 60 to 450 W/cm^2.

In order to obtain a semiquantitative estimate of the number of e-h pairs present in the QDs under the highest excitation condition available in this experiment, we measured the absorption through the 20-period large dot sample at the photon excitation wavelength of 335 nm. We found that it was about 20%. Then, assuming that the quantum efficiency of the carrier relaxation process inside the QDs is unity (i.e., each hot e-h pair photocreated leads to an e-h pair at the QD ground state) and that the e-h pair lifetime is $\leqslant$10 nsec,[28] it was estimated that the e-h density present in a QD layer is of the order of 10^{11} cm^{-2} for an excitation density of 450 W/cm^2. Given that the $\approx10^{11}$ cm^{-2} e-h pairs are localized in a good fraction of the $\approx10^{11}$ cm^{-2} QDs, this implies that at this high excitation density there are *a few e-h pairs per single excited QD*. An order of magnitude estimate of the electric field due to a single e-h pair in a large piezoelectric dot leads to a value of about 0.2 MV/cm. It follows from Fig. 3 that an electric field value of such a magnitude may well account for the 70 meV blueshift observed in Fig. 4.

In conclusion it has been experimentally and theoretically demonstrated that the optical properties of GaN quantum dots with wurtzite structure grown on AlN by MBE of GaN are consistently explained by taking into account both confinement and piezoelectric effects. It has been found that the piezoelectric effects are dominating for QD height larger than 3 nm. This situation results from the combined effect of the QD crystallographic symmetry (wurtzite with a [0001] growth direction) and the huge piezoelectric coefficients specific to the nitride family. Finally, we suggest that a possible application of these results could be the achievement of high-efficiency blue-light-emitting devices with no In.

The authors are grateful to Dr. R. André for discussions.

*Associated with University Joseph Fourier.

[1] Y. Arakawa and H. Sakaki, Appl. Phys. Lett. **40**, 939 (1982).

[2] I. N. Stranski and V. L. Krastanov, Akad. Wiss. Lit. Mainz Abh. Math. Naturwiss. Kl. **146**, 797 (1939).

[3] S. Guha, A. Madhukar, and K. C. Rajkuma, Appl. Phys. Lett. **57**, 2110 (1990), and references therein.

[4] S. Varma, C. M. Reaves, V. Bressler-Hill, S. P. Den Baars, and W. H. Weinberg, Surf. Sci. **393**, 24 (1997).

[5] D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. **64**, 1943 (1990).

[6] K. Kamath, P. Bhattacharya, T. Sosnowski, T. Norris, and J. Phillips, Electron. Lett. **32**, 1374 (1996).

[7] R. Mirin, A. Gossard, and J. Bowers, Electron. Lett. **32**, 1732 (1996).

[8] D. Bimberg, N. N. Ledentsov, M. Grundmann, N. Kirstaedter, O. G. Schmidt, M. H. Mao, V. M. Ustinov, A. Yu Egorov, A. E. Zhukov, P. S. Kopev, Zh. I. Alferov, S. S. Ruvimov, U. Gösele, and J. Heydenreich, Jpn. J. Appl. Phys., Part 1 **35**, 1311 (1996).

[9] Q. Xie, A. Kalburge, P. Chen, and A. Madhukar, IEEE Photonics Technol. Lett. **8**, 965 (1996).

[10] For a recent review, see S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer-Verlag, Heidelberg, 1997).

[11] B. Daudin, F. Widmann, G. Feuillet, Y. Samson, M. Arlery, and J. L. Rouvière, Phys. Rev. B **56**, R7069 (1997).

[12] F. Widmann, B. Daudin, G. Feuillet, Y. Samson, J. L. Rouvière, and N. Pelekanos, J. Appl. Phys. **83**, 7618 (1998).

[13] B. Daudin, G. Feuillet, F. Widmann, Y. Samson, J. L. Rouvière, N. Pelekanos, and G. Fishman, in *Nitride Semiconductors*, edited by F. A. Ponce, S. P. DenBaars, B. K. Meyer, S. Nakamura, and S. Strite, MRS Symposia Proceedings No. 482 (Materials Research Society, Pittsburgh, 1998), p. 205.

[14] Satoru Tanaka, Sohachi Iwai, and Yoshinobu Aoyagi, Appl. Phys. Lett. **69**, 4096 (1996).

[15] Satoru Tanaka, Hideki Hirayama, Yoshinobu Aoyagi, Yukio Narukawa, Yoichi Kawakami, Shizuo Fujita, and Shigeo Fujita, Appl. Phys. Lett. **71**, 1299 (1997).

[16] G. Martin, A. Botchkarev, A. Rockett, and H. Morkoç, Appl. Phys. Lett. **68**, 2541 (1996).

[17] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. Lett. **79**, 3958 (1997).

[18] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B **56**, R10 024 (1997).

[19] See, for instance, R. Andre, J. Cibert, Le Si Dang, J. Zeman, and M. Zigone, Phys. Rev. B **53**, 6951 (1996), and references therein.

[20] Jin Seo Im, H. Kollmer, J. Off, A. Sohmer, F. Scholz, and A. Hangleiter, Phys. Rev. B **57**, R9435 (1998).

[21] R. Langer, J. Simon, O. Konovalov, N. Pelekanos, A. Barski, and M. Leszczynski, MRS Internet J. Nitride Semicond. Res. **3**, 46 (1998).

[22] G. Feuillet, F. Widmann, B. Daudin, J. Schuler, M. Arlery, J. L. Rouvière, N. Pelekanos, and O. Briot, Mater. Sci. Eng., B **50**, 233 (1997).

[23] B. Daudin, F. Widmann, G. Feuillet, Y. Samson, J. L. Rouvière, and N. Pelekanos, Mater. Sci. Eng., B (unpublished).

[24] It is worthwhile to mention that the sample is blue to the naked eye and remains so even at room temperature.

[25] M. Susuki, T. Uenoyama, and A. Yanase, Phys. Rev. B **52**, 8132 (1995).

[26] C. Merz, M. Kunzer, and U. Kaufmann, Semicond. Sci. Technol. **11**, 712 (1996).

[27] J. S. Im, A. Moritz, F. Steuber, V. Härle, F. Scholz, and A. Hangleiter, Appl. Phys. Lett. **70**, 631 (1997).

[28] S. Hess (private communication).