

InGaN quantum dots grown by metalorganic vapor phase epitaxy employing a post-growth nitrogen anneal

Rachel A. Oliver^{a)} and G. Andrew D. Briggs

Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH United Kingdom

Menno J. Kappers and Colin J. Humphreys

Department of Materials, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ United Kingdom

Shazia Yasin

Microelectronics Research Centre, Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE United Kingdom

James H. Rice,^{b)} Jonathon D Smith, and Robert A. Taylor

Department of Physics, University of Oxford, Parks Road, Oxford, OX1 3PU United Kingdom

(Received 25 February 2003; accepted 27 May 2003)

We describe the growth of InGaN quantum dots (QDs) by metalorganic vapor phase epitaxy. A thin InGaN epilayer is grown on a GaN buffer layer and then annealed at the growth temperature in molecular nitrogen inducing quantum dot formation. Microphotoluminescence studies of these QDs reveal sharp peaks with typical linewidths of $\sim 700 \mu\text{eV}$ at 4.2 K, the linewidth being limited by the spectral resolution. Time-resolved photoluminescence suggests that the excitons in these structures have lifetimes in excess of 2 ns at 4.2 K. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1595716]

The growth of self-assembled nanostructures during semiconductor heteroepitaxy is an exciting route to the exploration and exploitation of carrier confinement in quantum dots (QDs). In particular, the performance of InGaN laser diodes could potentially be enormously improved by introducing self-assembled InGaN QDs into device active layers. Higher brightnesses, lower threshold currents,¹ and better temperature stability² should result. Both molecular beam epitaxy^{3,4} (MBE) and metalorganic vapor phase epitaxy⁵ (MOVPE) have been employed in the growth of InGaN nanostructures, and (for growth by MOVPE) the confinement of excitons within the quantum dot has been confirmed via the observation of discrete, narrow lines in spatially resolved photoluminescence (PL) spectra.⁶

In this letter, we report the growth of nanostructures by MOVPE, by employing a short post-growth anneal in molecular nitrogen at the InGaN growth temperature to induce nanostructure formation. Development of a variety of growth methodologies enables greater flexibility in the design of quantum dot arrays. We demonstrate the quantum dot nature of our nanostructures by performing microphotoluminescence (μPL) at 4.2 K. We observed very sharp peaks in the luminescence spectra, with linewidths at the limit of the resolution of the optical system. Furthermore, we have used time-resolved single photon counting to estimate the lifetimes of excitons confined in QDs.

The samples were grown by MOVPE in a Thomas Swan close-coupled showerhead reactor on sapphire (0001) substrates. The trimethyl compounds of In, and Ga, and ammonia were used as precursors. About 10 ML of InGaN were grown on 2.8- μm -thick GaN templates at a temperature of 700 °C, with a growth rate of 4.8 ML/min and a V:III ratio of

17 100. The uncapped samples were examined by atomic force microscopy (AFM). Samples for photoluminescence measurements were capped with 7 nm of GaN grown at 700 °C, after which a 100-nm-thick Al layer was evaporated onto the sample surface and a mask pattern fabricated by electron-beam lithography. Square apertures were produced by reactive ion etching using SiCl_4 with side length varying from 2 μm to 100 nm; in addition, markers were fabricated to indicate their position and size.

For μPL measurements, the sample was mounted in a cold-finger cryostat that could be cooled to 4.2 K. A HeCd laser operating at 325 nm was focused through a microscope objective lens, to a spot size of $\sim 2 \mu\text{m}$, which was aligned with an aperture on the sample surface using a charge coupled device (CCD) camera. The signal was collected by the microscope objective lens, and monitored using a CCD detector, through a 25 cm monochromator, with a 2400 grooves/mm grating, giving a spectral resolution of $\sim 700 \mu\text{eV}$.

Time-resolved PL measurements were performed at 4.2 K using a time-correlated single photon counting method. Laser excitation from a frequency-tripled Ti-sapphire laser at 266 nm was employed with the photon density below one photon per QD. Further experimental details will be published elsewhere.⁷

Figure 1 shows two InGaN epilayers which have been grown under identical conditions, and then annealed at 700 °C for 30 s in (a) NH_3 as a control, and (b) N_2 . The NH_3 annealed sample shows a surface covered in flat platelets, aligned along the step edges of the GaN template. The indium content of this sample has been estimated as 20%–25%. The N_2 anneal changes the surface morphology significantly. Small nanostructures with a density of $1 \times 10^{10} \text{ cm}^{-2}$, and an average height of $0.93 \pm 0.1 \text{ nm}$ have formed, along with many small pits in the wetting layer.

^{a)}Electronic mail: rachel.oliver@materials.ox.ac.uk

^{b)}Electronic mail: jrice1@physics.ox.ac.uk

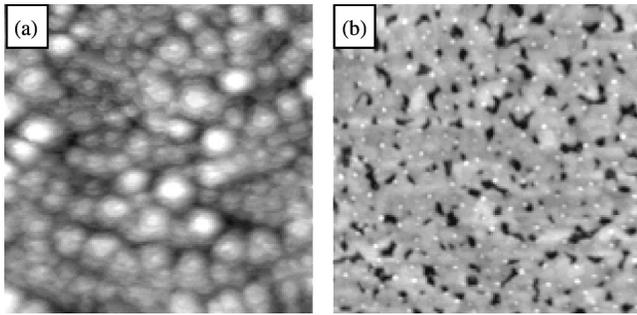


FIG. 1. $1.8\ \mu\text{m} \times 1.8\ \mu\text{m}$ contact mode AFM scans of InGaN epilayers on GaN. (a) Epilayer annealed in NH_3 for 30 s after growth. Image height = 1.72 nm. (b) Epilayer annealed in N_2 for 30 s after growth. Image height = 5.82 nm.

We suggest that pits are created by the decomposition of indium-rich regions in the InGaN film (formed by spinodal decomposition), which appear to be unstable in a nitrogen atmosphere. Furthermore, when we examined the effects of etching the as-grown nanostructures in $\text{HCl}/\text{H}_2\text{O}$ (1:3) we saw a significant reduction in the nanostructure density. Hence, we suggest that the nanostructures observed by AFM may be very small indium droplets, also formed due to this decomposition, since InGaN nanostructures would not be removed by the etch process. These droplets will then rereact with ammonia, before or during the growth of the capping layer, and this—coupled possibly with some interdiffusion with the GaN capping layer—results in the formation of InGaN quantum dots.

The macroscopic PL spectrum for the capped sample shows a GaN peak at 3.48 eV, and two broad overlapping peaks, centred at approximately 2.85 and 2.53 eV. The higher energy peak corresponds to luminescence from quantum dots, whereas the lower energy peak is attributed to luminescence from the wetting layer.

Figure 2(a) shows a μPL spectrum from an unmasked sample excited with a $2\ \mu\text{m}$ spot size. A section of the broad QD band is shown with minima at 2.87, 2.96, and 3.09 eV due to Fabry–Pérot interference effects. Figure 2(b), shows a μPL spectrum taken through a 500 nm aperture to limit the area illuminated. The spectrum consists of a number of sharp peaks indicating the presence of excitons strongly confined

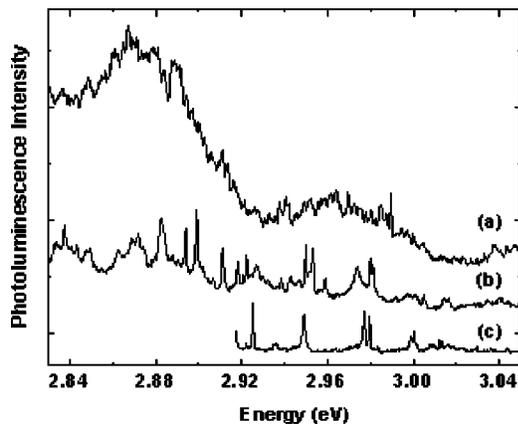


FIG. 2. (a) Macroscopic PL spectrum from InGaN quantum dot sample. (b) μPL spectrum from masked QD sample employing a 500 nm aperture. (c) μPL spectrum from masked QD sample employing a 200 nm aperture. All spectra were recorded at 4.2 K.

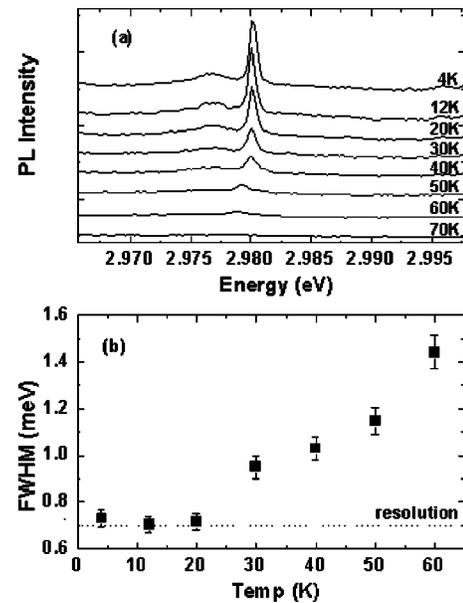


FIG. 3. (a) μPL spectrum of the luminescence from a single dot at various temperatures. (b) Temperature dependence of the linewidth.

in QDs. A μPL spectrum taken through a 200 nm aperture [Fig. 2(c)] shows fewer peaks and the background almost entirely eliminated. The narrowest lines have a full width at half maximum (FWHM) of $\sim 700\ \mu\text{eV}$, a value which is limited by the spectral resolution of the monochromator.

The temperature dependence of the sharp emission peaks was then examined over a temperature range from 4.2 to 70 K. Figure 3(a) shows the changes in a single peak as the temperature is increased, and Fig. 3(b) shows the temperature dependence of the peak width. Below 20 K the FWHM is limited by the spectral resolution, but above 20 K we see significant broadening, at a rate much lower than the thermal energy dispersion. This type of broadening has previously been observed in both InGaN⁶ and InAs⁸ and is characteristic of QD structures.

Time-correlated single photon counting was then employed to estimate the lifetime of excitons in our quantum dots. Figure 4 shows a typical PL intensity decay spectrum for luminescence emitted at 2.82 eV. Morel *et al.*⁹ have recorded similar spectra for InGaN quantum dots grown by MBE. They observed a multiexponential decay with the decay rate typified by a time, τ_e , (the time in which the starting

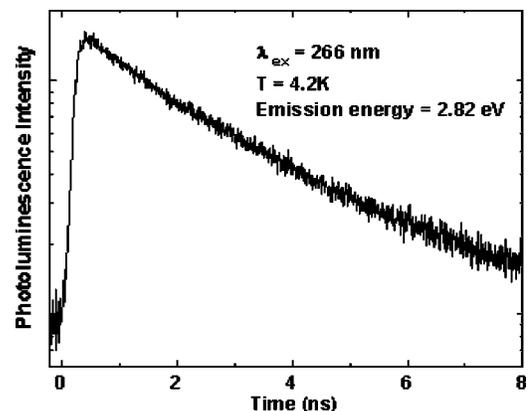


FIG. 4. PL intensity decay spectrum for InGaN QDs recorded at 4.2 K.

intensity is divided by a factor of e) ranging from 2.7 to 27.4 ns. Here we observe a similar multiexponential decay with $\tau_e = 2.7$ ns, consistent with their observations for dots of comparable size. Further analysis of this and similar data will be published elsewhere.⁷

In summary, we have demonstrated a method for the growth of InGaN nanostructures by MOVPE and have established the quantum dot nature of these structures by the observation of very sharp PL peaks with linewidths as narrow as 700 μeV at 4.2 K. This indicates that the excitons are strongly confined in the InGaN QD structure. We have observed long lifetimes for excitons localized in our quantum dots.

This work was supported in part by a Foresight LINK Award “Nanoelectronics at the Quantum Edge”, by the EPSRC, and by Hewlett-Packard Labs.

- ¹M. Asada, Y. Miyamoto, and Y. Suematsu, *IEEE J. Quantum Electron.* **22**, 1915 (1986).
- ²Y. Arakawa and H. Sakaki, *Appl. Phys. Lett.* **40**, 939 (1982).
- ³B. Daudin, G. Feuillet, G. Mula, H. Marriette, J. L. Rouviere, N. Pelekanos, G. Fishman, C. Adelmann, and J. Simon, *Phys. Status Solidi A* **176**, 621 (1999).
- ⁴B. Damilano, N. Grandjean, F. Semond, J. Massies, and M. Leroux, *Appl. Phys. Lett.* **75**, 962 (1999).
- ⁵K. Tachibana, T. Someya, and Y. Arakawa, *Appl. Phys. Lett.* **74**, 383 (1999).
- ⁶O. Moriwaki, T. Someya, K. Tachibana, S. Ishida, and Y. Arakawa, *Appl. Phys. Lett.* **76**, 2361 (2000).
- ⁷J. H. Rice, J. W. Robinson, A. Jarjour, J. D. Smith, R. A. Taylor, R. A. Oliver, G. A. D. Briggs, M. J. Kappers, C. J. Humphreys, and Y. Arakawa (unpublished).
- ⁸K. Asoaka, Y. Ohno, S. Kishimoto, and T. Mizutani, *Jpn. J. Appl. Phys., Part 1* **38**, 546 (1999).
- ⁹A. Morel, M. Gallart, T. Taliercio, P. Lefebvre, B. Gil, J. Allegre, H. Mathieu, N. Grandjean, and J. Massies, *Phys. Status Solidi A* **180**, 375 (2000).