Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Crystal Growth 249 (2003) 144–148
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Growth of nanoscale InGaN self-assembled quantum dots

L.W. Ji[a], Y.K. Su[a], S.J. Chang[a,*], L.W. Wu[a,b], T.H. Fang[c], J.F. Chen[a], T.Y. Tsai[a], Q.K. Xue[d], S.C. Chen[e]

[a] *Department of Electrical Engineering, Institute of Microelectronics, National Cheng Kung University, No. 1 Ta Hseuh Road, Tainan, Taiwan 70101, ROC*
[b] *South Epitaxy Corporation, Hsin-Shi, Taiwan 744, ROC*
[c] *Department of Mechanical Engineering, Southern Taiwan University of Technology, Yong-Kan, Taiwan 710, ROC*
[d] *Institute of Physics, Chinese Academy of Science, Beijing 100080, People's Republic of China*
[e] *Department of Eletronic Engineering, National Yunlin University of Science and Technology, Touliu, Taiwan 640, ROC*

Received 13 October 2002; accepted 23 October 2002
Communicated by M. Schieber

Abstract

It has been demonstrated that we can use interrupted growth mode in metalorganic chemical vapor deposition (MOCVD) to fabricate nanoscale InGaN self-assembed quantum dots (QDs). With a 12-s growth interruption, we successfully formed InGaN QDs with a typical lateral size of 25 nm and an average height of 4.1 nm. The QDs density is about $2\times10^{10}\,cm^{-2}$. In contrast, much larger InGaN QDs were obtained without growth interruption. Compared with samples prepared without growth interrupt, a much larger photoluminescence (PL) intensity and a large 67 meV PL blue shift was observed from samples prepared with growth interrupt. These results suggest such a growth interrupt method is potentially useful in nitride-based optoelectronic devices grown by MOCVD.
© 2002 Elsevier Science B.V. All rights reserved.

PACS: 68.66.Hb; 78.67.Hc; 81.16.Dn; 82.33.Ya; 68.37.Ps

Keywords: A1. Atomic force microscopy; A1. Photoluminescence; A3. Metalorganic chemical vapor deposition; A3. Quantum dots; B1. InGaN

1. Introduction

III–V nitride semiconductor materials have a wurtzite crystal structure and a direct energy band gap. At room temperature, the band gap energy of AlInGaN varies from 1.95 to 6.2 eV and depends on its composition. Therefore, III–V nitride semiconductors are particularly useful for light-emitting devices in the short wavelength region [1–3]. Indeed, III–V nitride-based blue and green high-brightness light-emitting diodes (LEDs) made from InGaN/GaN quantum wells structures are now commercially available with output power larger than 2.5 mW at 20 mA, i.e. external quantum efficiency $>10\%$. Such a performance is quite amazing considering the high 10^{8}–$10^{12}\,cm^{-2}$

*Corresponding author. Tel.: +886-6275757; fax: +886-62761854.
E-mail address: changsj@mail.ncku.edu.tw (S.J. Chang).

0022-0248/03/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-0248(02)02130-9

dislocation density in these LEDs [4]. There is strong evidence to support that InGaN alloy inhomogeneities play a key role in the high efficiency of nitride-based LEDs grown on sapphire [5–7]. It has been proposed that nanoscale indium composition fluctuation due to InGaN phase separation results in the formation of indium-rich clusters, which acts as quantum dots (QDs) [5–7]. Hence, InGaN system acts as an extremely sophisticated quantum capture system, and in QDs, the charge carriers are deeply localized so as to hinder their migration toward nonradiative defects (dislocations) [7,8]. Therefore, high-luminescence efficiency could be expected if the density of QDs is much higher than that of dislocations.

Low-dimensional carrier confinement nanostructures such as quantum wires and dots (or islands) are quite attractive for application to high-performance electronic and optical devices. It has been shown that nitride QDs can be self-organized using the strain-induced Stranski–Krastanov (S–K) growth mode [8–10]. Another way to form nitride QDs is to take advantage of surfactants or antisurfactants, which are often used to change the surface free energy of epilayers [11–14]. It had been reported that nitride-based QDs could be formed by using Si as the antisurfactant [11–13]. Self-assembled nitride QDs had already been fabricated by molecular-beam epitaxy [8,10] using S–K growth mode. Recently, Tachibana et al. reported the growth of InGaN/GaN QDs by metalorganic chemical vapor deposition (MOCVD) without using any surfactant [9]. However, it remains uncertain if the formation of QDs was due to strain-induced mode or phase separation since small three-dimensional InGaN islands were found after the deposition of up to 20 monolayers (MLs) of InGaN [10].

In this paper, we report an approach to grow InGaN QDs using a novel method in a commercial MOCVD reactor. An interrupted growth mode was proposed to grow self-assembled InGaN QDs without the use of surfactants or antisurfactants. Atomic force microscopic (AFM) images reveal that InGaN self-assembled QDs were successfully obtained by using the interrupted growth mode, and their dimensions were small enough to expect zero-dimensional quantum effects. In contrast, much larger InGaN dots, probably without the zero-dimensional quantum effects, were formed when no growth interrupt was introduced. The optical properties of the InGaN QDs grown with and without growth interrupts were studied by room temperature photoluminescence (PL) measurements. The physical properties of these QDs will also be discussed.

2. Experimental procedure

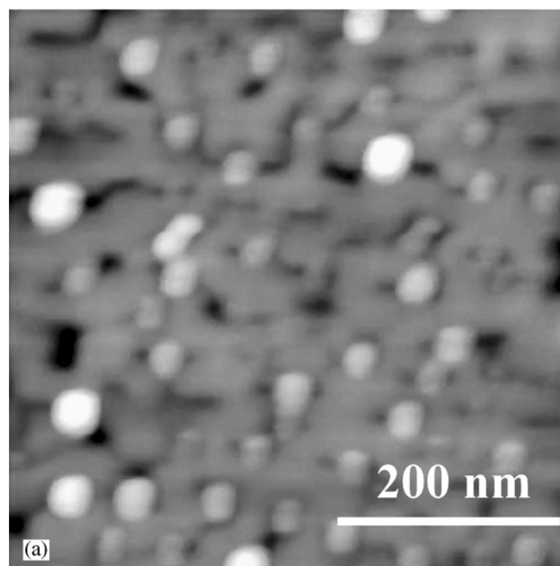
All InGaN QDs samples used in this study were grown on (0 0 0 1)-oriented sapphire (Al_2O_3) substrates in a vertical low-pressure MOCVD reactor (EMCORE D180) with a high-speed rotation disk. The gallium, indium and nitrogen sources were trimethylgallium (TMGa), trimethylindium (TMIn), and ammonia (NH_3), respectively. After a 30-nm-thick low-temperature GaN nucleation layer was deposited onto the sapphire substrate at 500°C, the temperature was raised to 1000°C to grow a 2 μm-thick undoped GaN buffer layer with a growth rate of 2 μm/h. During the growth of GaN buffer layer, the flow rate of TMGa was kept at 88 μmol/min while the flow rate of H_2 carrier gas was kept at 10 l/min. The growth temperature was then reduced to 730°C to grow InGaN QDs. During the growth of InGaN QDs, the flow rates of TMGa and TMIn were kept at 10 and 35 μmol/min, respectively. The carrier gas was switched to N_2 and we fixed the N_2 carrier gas flow rate at 20 l/min. According to our calibration, the average indium composition in the $In_xGa_{1-x}N$ layer should be around $x = 0.3$. Knowing the lattice mismatch between GaN and InN equals 11%, the mismatch between $In_{0.3}Ga_{0.7}N$ and the underneath GaN buffer should be around 3.3% ($\Delta a/a = 11\% \times 0.3 = 3.3\%$). In our experiment, the growth rate of InGaN layer is estimated to be 0.04 nm/s and two samples with the same nominal InGaN thickness were prepared under the same growth conditions except the mode of growth interruption. In other words, during the deposition of InGaN, an interrupted growth method was employed in preparing sample 1. We first deposited a thin 4.5 MLs InGaN on top of the

GaN buffer, then stopped the growth for 12 s. After growth stop, another 4.5 MLs of InGaN were again deposited so as to achieve an InGaN layer with a total thickness of about 9.0 MLs. Without using the interrupted growth method, as the same growth condition as sample 1, sample 2 was prepared by directly depositing 9 MLs InGaN for comparision.

The surface morphologies of these samples were then characterized ex situ by an AFM system (Shimmadzu SPM-9500JZ) with a sharpened Si_3N_4 tip at room temperature. PL was also used to study the optical properties of these samples. During PL measurement, a He–Cd laser with 325 nm wavelength was used as the excitation source. The collected luminescence signal was dispersed by a monochromator, and detected by a GaAs photomultiplier tube.

3. Results and discussions

Figs. 1(a) and (b) show $500 \times 500\,nm^2$ and $1 \times 1\,\mu m^2$ AFM images of sample 1, respectively. As shown in the surface morphology of these figures, it can be seen that small circular InGaN QDs were formed by the interrupted growth mode during MOCVD growth. From these AFM pictures, it was found that the diameter of these circular QDs was in the range of 20–38 nm, with an average height of 4 nm. On the other hand, the density of these circular QDs was estimated to be around $2 \times 10^{10}\,cm^{-2}$. In addition, we also observed some dark spots, which appeared on the sample surface [15–18]. We believe these dark spots originated from the threading dislocations (TDs) in our samples [15–18]. From Fig. 1(b), we found that the TDs density was about $4.8 \times 10^9\,cm^{-2}$. Fig. 2 shows the AFM image of sample 2. In contrast to the small circular QDs observed from sample 1, big oval InGaN QDs were found in sample 2 without growth interruption during MOCVD growth. It was found that the longer width of these oval QDs was around 140 nm while the shorter width of these oval QDs was about 70 nm, with an average height of 1.7 nm. We also found that the density of these big oval QDs was about $5.6 \times 10^9\,cm^{-2}$. From these AFM pictures shown in Figs. 1(a), (b) and 2, it can be seen clearly that by introducing the interrupted growth method, we could significantly change the surface morphology of the MOCVD grown InGaN samples. It should be noted that the size of the QDs observed from sample 1 was much



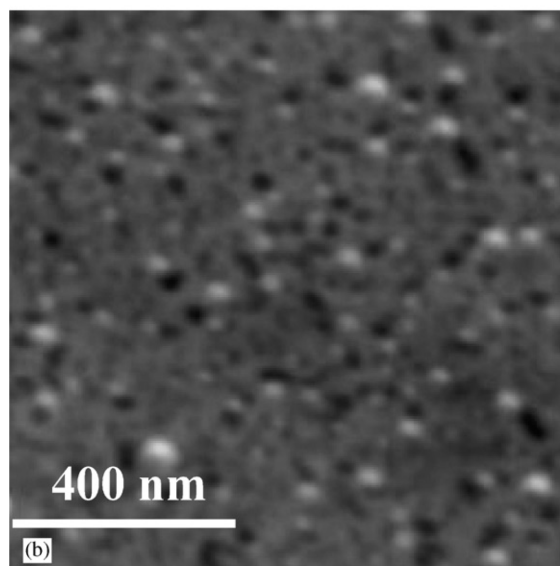


Fig. 1. (a) $500 \times 500\,nm^2$ and (b) $1 \times 1\,\mu m^2$ AFM images of sample 1 (with the smaller InGaN QDs, grown by the use of interrupted growth mode in MOCVD).

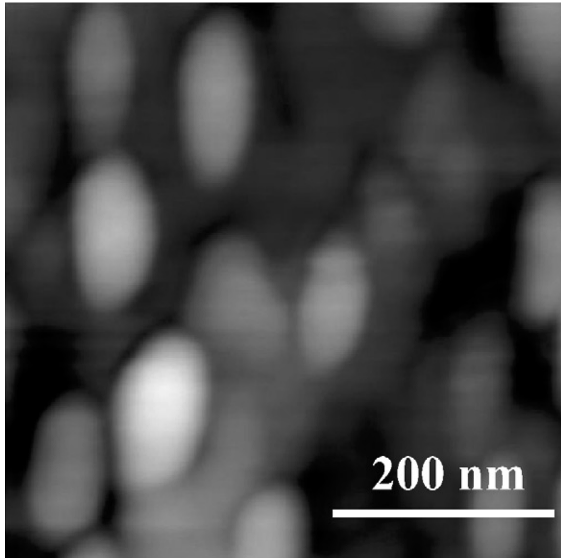


Fig. 2. $500 \times 500\,nm^2$ AFM image of sample 2 (with the larger InGaN QDs, grown without using the interrupted growth mode in MOCVD).

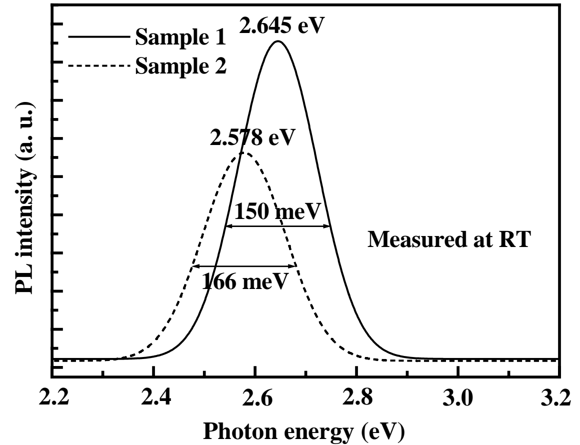


Fig. 3. Gaussian curve-fitting PL and original PL spectra (on top of right side in the figure) of the InGaN QDs samples measured at room temperature, where sample 1 was prepared by interrupted growth mode, sample 2 was prepared without using interrupted growth mode.

smaller than that observed from sample 2. Thus, we should be able to significantly enhance the zero-dimensional quantum effects by the introduction of growth interrupt.

Fig. 3 shows the room temperature PL spectra of these two samples. It can be seen from Fig. 3 that the PL peak position of sample 1 is located at 2.645 eV with full-width at half-maximum (FWHM) of 150 meV, while the PL peak position of sample 2 is located at 2.578 eV with FWHM of 166 meV. It was also found that the PL intensity observed from sample 1 was 50% larger than that observed from sample 2. In other words, the PL peak position blue shifted by 67 meV when the growth interrupted was introduced. It should be noted that although we introduced growth interrupt during the growth of sample 1, the total thickness of InGaN epilayer of these two samples was the same (i.e. 9 MLs). Thus, we believe the huge PL blue shift in PL spectra was attributed to the size effect of QDs. For the QDs, it is well known that the sub-band energies will become larger when the size of QD becomes smaller. Thus, although the total thickness of InGaN epilayer was the same for these two samples, we could observe a larger PL transition energy from the sample prepared with growth interrupt (i.e. sample 1), since growth interrupt will result in a smaller QD size. Furthermore, it was found that the FWHM of sample 1 (i.e. 150 meV) was smaller than that of sample 2 (i.e. 166 meV). One possible reason for such a difference is again due to the different QD size in these two samples. Since the QDs observed from sample 2 were large (i.e. $70\,nm \times 140\,nm$) with a high density (i.e. $5.6 \times 10^9\,cm^{-2}$), it is extremely possible that some of those dots were located on the InGaN defects. Thus, we would observe a broader PL spectrum. This could also be used to explain the weaker PL intensity from sample 2 since nonradiative recombination might also occur easily in this sample. The other possible explanation for the different FWHM in these two samples is the different degrees of fluctuations in dot size and indium composition. However, it has already been shown that we should be able to neglect the fluctuation effect of dot size for nitride-based QDs, since the effective mass in InGaN system is large [9,19–20]. Hence, we suspect that the smaller PL FHWM might be due to the more uniform indium composition in sample 1. A more detailed study on the indium composition distribution within these QDs should be performed. Compared with the PL FWHM reported by Tachibana et al. (i.e. 390 meV)

[9] who prepared the InGaN QDs by MOCVD without growth interrupt, it was found that the PL FWHM of sample 1 (i.e. 150 meV) was much smaller. We believe such a smaller FWHM we observed from sample 1 could be attributed to the more uniform indium composition of InGaN epilayer (includes QDs and wetting layer) by using the interrupted growth method in MOCVD. It should be noted that the growth interrupt method reported in this paper is not optimalized. With the optimization of QD formation by such a growth interrupt method, we should be able to further improve the optical properties of InGaN QDs, and such a growth interrupt method is potentially useful in nitride-based optoelectronic devices grown by MOCVD.

4. Conclusion

In conclusion, it has been demonstrated that we can use interrupted growth mode in MOCVD to fabricate nanoscale InGaN self-assembed QDs. With a 12-s growth interruption, we successfully formed InGaN QDs with a typical lateral size of 25 nm and an average height of 4.1 nm. The QDs density is about $2 \times 10^{10}\,\mathrm{cm}^{-2}$. In contrast, much larger InGaN QDs were obtained without growth interruption. Compared with samples prepared without growth interrupt, a much larger PL intensity and a large 67 meV PL blue shift was observed from samples prepared with growth interrupt. These results suggest such a growth interrupt method is potentially useful in nitride-based optoelectronic devices grown by MOCVD.

Acknowledgements

This work was financially supported by the National Science Council of Taiwan (Project No. NSC 90-2215-E-006-024).

References

[1] S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, Jpn. J. Appl. Phys. 34 (1995) L797.
[2] I. Akasaki, H. Amano, Jpn. J. Appl. Phys. 36 (1997) 5393.
[3] W.C. Lai, S.J. Chang, M. Yokoyama, J.K. Sheu, J.F. Chen, IEEE Photon. Technol. Lett. 13 (2001) 559.
[4] S. Nakamura, Science 281 (1998) 956.
[5] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, S. Nakamura, Appl. Phys. Lett. 70 (1997) 981.
[6] S.F. Chichibu, A.C. Abare, M.S. Minsky, S. Keller, S.B. Fleischer, J.E. Bowers, E. Hu, U.K. Mishra, L.A. Coldren, S.P. DenBaars, S. Sota, Appl. Phys. Lett. 73 (1998) 2006.
[7] K.P. O'Donnell, R.W. Martin, P.G. Middleton, Phys. Rev. Lett. 82 (1999) 237.
[8] B. Damilano, N. Grandjean, S. Dalmasso, J. Massies, Appl. Phys. Lett. 75 (1999) 3751.
[9] K. Tachibana, T. Someya, Y. Arakawa, Appl. Phys. Lett. 74 (1999) 383.
[10] C. Adelmann, J. Simon, G. Feuillet, N.T. Pelekanos, B. Daudin, Appl. Phys. Lett. 76 (2000) 1570.
[11] S. Tanaka, S. Iwai, Y. Aoyagi, Appl. Phys. Lett. 69 (1996) 4096.
[12] X.Q. Shen, S. Tanaka, S. Iwai, Y. Aoyagi, Appl. Phys. Lett. 72 (1998) 344.
[13] H. Hirayama, S. Tanaka, P. Ramvall, S. Keller, Y. Aoyagi, Appl. Phys. Lett. 72 (1998) 1736.
[14] J. Zhang, M. Hao, P. Li, J. Chua, Appl. Phys. Lett. 80 (2002) 485.
[15] X.H. Wu, L.M. Brown, D. Kapolnek, S. Keller, S.P. DenBaars, J.S. Speck, J. Appl. Phys. 80 (1996) 3228.
[16] T. Sugahara, M. Hao, T. Wang, D. Nakagawa, Y. Naoi, K. Nishino, S. Sakai, Jpn. J. Appl. Phys. 37 (1998) L1195.
[17] K. Uchida, J. Gotoh, S. Goto, T. Yang, A. Niwa, J. Kasai, T. Mishima, Jpn. J. Appl. Phys. 39 (2000) 1635.
[18] H.K. Yuh, E. Yoon, S.K. Shee, J.B. Lam, C.K. Choi, G.H. Gainer, G.H. Park, S.J. Hwang, J.J. Song, J. Appl. Phys. 91 (2002) 3483.
[19] Y.C. Yeo, T.C. Chong, M.F. Li, J. Appl. Phys. 83 (1998) 1429.
[20] E.W.S. Caetano, et al., Physica E 13 (2002) 1106.