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Optical properties of high density InGaN QDs grown by MOCVD

C.K. Lee [a,*], J.H. Hsu [b], D.C. Wang [c], Y.H. Chang [c], H.C. Kuo [c], S.C. Wang [c]

[a] Institute of Electro-Optical Engineering, National Sun Yat Sen University, 70, Lien-Hei Rd., Kaohsiung, 804 Taiwan, ROC
[b] Department of Materials and Optoelectronic Engineering, National Sun Yat Sen University, Taiwan, ROC
[c] Institute of Electro-Optical Engineering, National Chiao Tung University, Taiwan, ROC

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Abstract

In this article, we investigate the relaxation time constant and optical properties of InGaN QDs following different durations of SiN_x treatment. We find that the smaller size QDs have smaller red shift as temperature increasing, only about 10 meV. Time-resolved PL at various emitting wavelength of the three samples is also investigated. Decreasing time constant as increasing QDs size is observed. Besides, we also find the decreasing time constant with shorter wavelength. Meanwhile, decreasing time constant as increasing emitting wavelength is characterized and attributed as an increasing confinement of excitons in QDs with higher localization energy and thus with a higher electron-hole overlap.
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1. Introduction

GaN and related materials are currently the subjects of intense research due to their applications in laser diodes (LDs) and light-emitting diodes (LEDs) that operate between the ultraviolet and the visible regions. InGaN/GaN quantum wells (QWs) structures have successfully been used as the active layers in LEDs and LDs [1]. However, the threshold current density is high for LDs with InGaN QWs structures. Having quantum dots (QDs) instead of QWs as the active layer is expected to improve the performance of LDs. LDs with QDs structures in the active layer have been theoretically predicted to have superior characteristics, including lower threshold currents and narrow spectra [2]. Moreover, because of the localization of carriers trapped at dislocations, QDs structures have been expected to increase the efficiency of the luminescence of LDs [3]. To ensure suitability for QDs laser applications, QDs layers with high spatial density and of uniform size must be grown [4]. Several approaches have been investigated for fabricating InGaN QDs, including the Stranski–Krastanow growth mode [5,6] and growth using anti-surfactant [7,8]. The deposition of silicon anti-surfactant or a SiN_x nano-mask alters the morphology of the AlGaN films from that of step flow to that of a three-dimensional island, facilitating the formation of GaN [7] QDs and InGaN QDs [8] on the AlGaN.

This study investigates the optical properties, the surface morphology and the density of InGaN QDs following different durations of SiN_x treatment on the underlying GaN layer before the InGaN layers were deposited. Using time correlated single-photon counting technique, time-resolved PL at various emitting wavelength of the samples is investigated.

2. Growth procedure

InGaN QD samples that had undergone different durations of SiN_x treatment of the underlying GaN layer before the InGaN layer was deposited were grown on c-face sapphire substrates by metalorganic vapor phase epitaxy (MOVPE) [9–11]. A 30 nm thick low-temperature GaN nucleation layer was first grown at 550 °C. Then, the reactor temperature was increased to 1000 °C to grow a 2 μm thick underlying Si-doped GaN underlying layer, providing a step flow grown surface as confirmed by atomic force microscopy (AFM). Then, a rough SiN_x layer with different durations of SiN_x treatment was grown on the n-type GaN underlying layer. During the treatment of the SiN_x layer, the flow rates of NH_3 and the diluted Si_2H_6 were 5 slm and 50 sccm, respectively. The

* Corresponding author. Tel.: +886 7 5252000x4474; fax: +886 7 5254499.
E-mail address: chuckcklee@yahoo.com (C.K. Lee).

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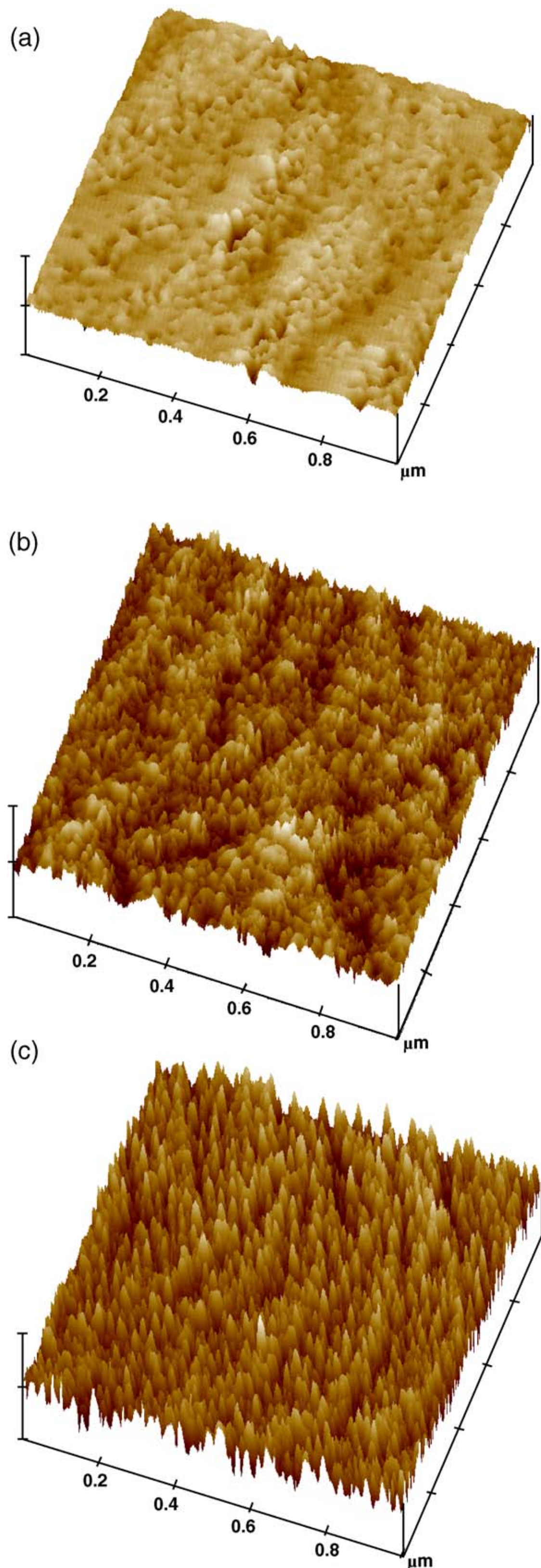

Fig. 1. AFM images of InGaN layers with (a) 120 s, (b) 160 s, (c) 195 s of SiN_x treatment on the underlying GaN layers.

temperature was then ramped down to 800 C to grow the $In_xGa_{1-x}N$ layers. As soon as the InGaN layers deposition was complete, the growth temperature was reduced to room temperature. During the growth of the InGaN layers, the vapor phase ratio TMIn/(TMIn+TEGa) was fixed at 0.35. Additional eight InGaN layers capped with a 10 nm undoped GaN layer were grown to investigate the optical property of the InGaN layers.

The surface morphology of all samples grown was characterized by AFM. Scans were performed over a surface area of 1 µm. In Fig. 1, AFM images of uncapped samples are showed. The average lateral size and thickness of the smallest QD-200 with 120 s of SiN_x treatment, as determined by averaging ten scans, are 33.2 nm and 0.64 nm. As increasing the duration of treatment, the QD sizes are larger, 0.79 nm height and 35.2 nm width for QD-240 sample with 160 s of SiN_x treatment. For QD-315 sample with 195 s of SiN_x treatment, the average height is up to 2.46 nm and the lateral size is almost the same as former. In addition, the morphology of the QD-315 surface forms a shape QDs according to AFM data. The densities of different size QDs were estimated to increase approximately from 2.1×10^{11} cm^{-2} to 2.9×10^{11} cm^{-2}. The ultrahigh density is much larger than the dislocation density. This means that the main parts of the QDs are free of defects. This is useful for achieving high efficiency room-temperature (RT) emission and related optical characterizations.

3. Optical characterization

We have reported that intense luminescence of the InGaN QDs samples were obtained at room temperature [12]. The optical characteristics were first evaluated using temperature dependent PL with a 20 mW HeCd laser operated at 325 nm increasing the temperature from 10 K to 300 K. The luminescence was analyzed by a 320 mm grating monochromator and detected by CCD. Fig. 2 demonstrates the PL peak wavelength at 10 K of the InGaN QDs samples is red shifted as the duration of SiN_x treatment increases. The red shift as the duration of the SiN_x treatment increases could be attributed to the increasing height of the QDs due to quantum effects caused by the vertical component of the internal piezoelectric field

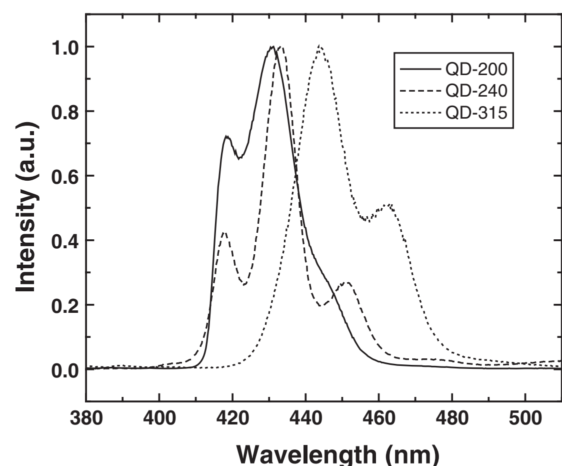

Fig. 2. The PL spectra at 10 K of the InGaN QDs samples with the different duration of SiN_x treatment.

induced in the QDs; i.e. the quantum-confined Stark effect (QCSE) [13]. To explore the emission mechanism, the PL peak position versus temperature was plotted for QDs with different size. Fig. 3 revealed the PL peak positions for several QD sizes at different temperature. The peaks of all samples at 10 K were normalized to zero. The PL positions, before normalization peak positions were 2.897, 2.869, and 2.754 meV for heights of about 0.64, 0.79, and 2.46 nm, respectively. According to the figure, we find that the smaller size QDs (QD-200 and QD-240) have smaller red shift of only ~10 meV as temperature increase. When the lattice temperature of the QD-315 was increased from 10 K, a gradual shift of the PL peak to lower energy occurred. A total shift of 40 meV was observed in the temperature range of 10–300 K. This shift is obviously lower than that of bulk GaN (80 meV) [14] and InGaN/GaN MQW (54 meV) [15,16]. However, by increasing the duration of treatment time, the peak energy behavior of the larger InGaN QDs is more similar to the presentation of InGaN MQW.

It is well known that the red shift of the band-gap energy originates from the interaction with phonon. The smaller red shift observed for QD structures can be explained by partial decoupling of the phonon–exciton interaction of the QDs [17,18]. The phonon coupling clearly decreases with QD size decreasing. Therefore, a direct consequence of the decreased phonon coupling is the smaller red shift of the PL peak with increasing temperature [14]. Besides, the smaller size of two QD samples showed clearly the “S-shaped” emission shift behavior with increasing temperature. This situation is explained by a carrier localization effect at low temperature. The blue shift results from the confinement-induced shift of the electronic levels, whereas the red shift results from the increased Coulomb energy induced by a compression of the exciton Bohr radius. In alloy inhomogeneity and/or In phase separation have been proposed as the origin of the localized states [19]. It reveals different potential fluctuations within these two samples compared with a larger size of high-density QD.

To further understand recombination dynamic, time-resolved PL at various emitting wavelength of the three samples was investigated using typical time correlated single-photon counting (TCSPC) technique. A frequency-doubled mode-locked Ti:sapphire laser with duration of 100 fs is used as excitation light source. The pumping wavelength of SHG from laser is around 360 nm. A double monochromator is used to spectrally select wavelength of fluorescence under excitation. Temporal resolution of 30 ps could be obtained by high-speed micro-channel plate photo-multiplier tube (MCP PMT). The time constants were fitted as exponential decay format. Fig. 4 shows the spectral dependence of time constants of the InGaN QDs samples with the different duration of SiN_x treatment. As shown in the plot, decreasing time constant as increasing QDs size was observed. For example, time constant at 450 nm was 0.56 ns, 0.51 ns and 0.27 ns for QD-200, QD-240, and QD-315, respectively. In addition, we also find the time constant was decreasing with shorter wavelength and is similar to the result reported [20]. It indicates the rising contribution of nonradiative recombination of localized excitons. Meanwhile, decreasing time constant as increasing emitting wavelength was characterized and attributed as an increasing confinement of excitons in QDs with higher localization energy and thus with a higher electron-hole overlap.

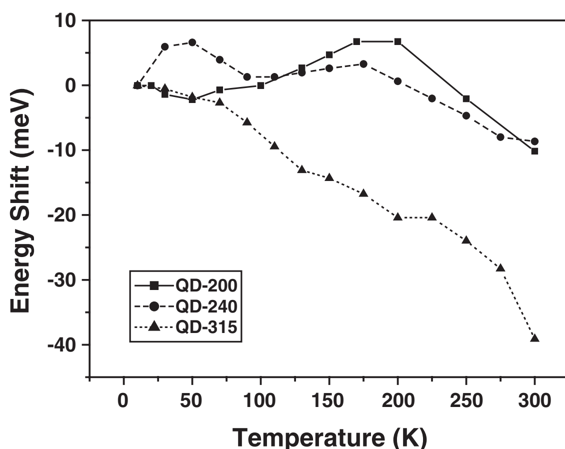

Fig. 3. The energy shift, related to the peak energy of PL spectra at 10 K, at different temperature from 10 K to 300 K of the QDs samples with the different duration of SiN_x treatment.

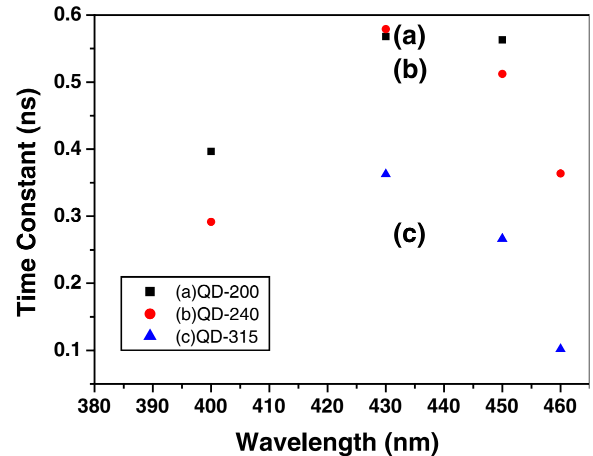

Fig. 4. Spectral dependence of time constants of the InGaN QDs samples with the different duration of SiN_x treatment.

4. Conclusions

In summary, this study investigates the relaxation time constant and optical properties of InGaN QDs following different durations of SiN_x treatment. The PL peak positions for several QD sizes at different temperature are demonstrated. We find the smaller size QDs have smaller red shift as temperature increasing, only about 10 meV. Furthermore, with increasing the duration of treatment time, the peak energy behavior of the larger InGaN QDs is more similar as the presentation of film, the shift as well as 40 meV. The smaller red shift observed for QD structures can be explained by partial decoupling of the phonon–exciton interaction of the QDs. Time-resolved PL at various emitting wavelength of the three samples is also investigated. Decreasing time constant as increasing QDs size is observed. Besides, we also find the decreasing time constant with shorter wavelength. It indicates

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References

[1] S. Nakamura, G. Fasol, The Blue Laser Diode, Springer, Heidelberg, 1997.
[2] C. Adelmann, J. Simon, G. Feuillet, N.T. Pelekanos, G. Fishman, Appl. Phys. Lett. 76 (2000) 1570.
[3] B. Damilano, N. Grandjean, S. Dalmasso, J. Masies, Appl. Phys. Lett. 75 (1999) 3751.
[4] D. Bimberg, M. Grundmann, N.N. Ledentsov, Quantum Dot Heterostructures, Wiley, England, 1999.
[5] K. Tachibana, T. Someya, Y. Arakawa, Appl. Phys. Lett. 74 (1999) 383.
[6] B. Daudin, F. Widmann, G. Feuillet, Y. Samson, M. Arlery, J.L. Rouvière, Phys. Rev., B 56 (1997) R7069.
[7] S. Tanaka, S. Iwai, Y. Aoyagi, Appl. Phys. Lett. 69 (1996) 4096.
[8] H. Hirayama, S. Tanaka, P. Ramvall, Y. Aoyagi, Appl. Phys. Lett. 72 (1998) 1736.
[9] R.C. Tu, C.J. Tun, J.K. Sheu, W.H. Kuo, T.C. Wang, C.E. Tsai, J.T. Hsu, J. Chi, G.C. Chi, IEEE Electron Device Lett. 24 (2003) 206.
[10] R.C. Tu, C.J. Tun, S.M. Pan, C.C. Chuo, J.K. Sheu, C.E. Tsai, T.C. Wang, G.C. Chi, IEEE Photonics Technol. Lett. 15 (2003) 1342.
[11] R.C. Tu, C.J. Tun, S.M. Pan, H.P. Liu, C.E. Tsai, J.K. Sheu, C.C. Chuo, T.C. Wang, G.C. Chi, I.G. Chen, IEEE Photonics Technol. Lett. 15 (2003) 1050.
[12] R.C. Tu, C.J. Tun, C.C. Chuo, B.C. Lee, C.E. Tsai, T.C. Wang, J. Chi, C.P. Lee, G.C. Chi, Jpn. J. Appl. Phys. 43 (2B) (2004) L264.
[13] T. Saito, Y. Arakawa, J. Cryst. Growth 237–239 (2002) 1172.
[14] P. Ramvall, P. Riblet, S. Nomura, Y. Aoyagi, J. Appl. Phys. 87 (2000) 3883.
[15] J.-L. Reverchon, F. Huet, M.-A. Poisson, J.-Y. Duboz, B. Damilano, N. Granjean, J. Massies, Mater. Sci. Eng., B 82 (2001) 197.
[16] B. Damilano, N. Grandjean, J. Massies, F. Semond, Appl. Surf. Sci. 164 (2000) 241.
[17] S. Chichibu, T. Azuhata, T. Sota, S. Nakamura, Appl. Phys. Lett. 70 (1997) 2822.
[18] M. Grundmann, J. Christen, N.N. Ledentsov, J. Bohrer, D. Bimberg, S.S. Ruvimov, P. Werner, U. Richter, U. Gosele, J. Heydenreich, V.M. Ustinov, A.Y. Egorov, A.E. Zhukov, Z.I. Alferov, Phys. Rev. Lett. 74 (1995) 4043.
[19] Y. Narukawa, Y. Kawakami, S. Fujita, S. Fujita, S. Nakamura, Phys. Rev., B 55 (1997) R1938.
[20] T. Bartel, M. Dworzak, M. Starssburg, A. Hoffmann, A. Strittmatter, B. Bimberg, Appl. Phys. Lett. 85 (2004) 1946.