 Optical properties of InGaN Quantum Dots


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Abstract

This study provides a novel technique in MOVPE for growing nanometer scale InGaN QDs. Growth interruption method had been introduced into epitaxial processes of InGaN layers, and we successfully formed InGaN SAQDs with a typical lateral size of 25 nm and an average height of 4.1 nm. The QDs density is about 2×10^{10} cm^{-2}. Micro-Raman measurement reveals that samples with the nanoscale InGaN QD structures of high strain shows a strong biaxial compressive stress in InGaN layer. Furthermore, the introduction of growth interruption would result in a PL blueshift as large as 72 meV at 17K.

I. INTRODUCTION

In the last several years, low-dimensional carrier confinement nanostructures such as quantum wires and dots (or islands) have been quite attractive for application to high performance electronic and optical devices. Many research groups have been devoted to the study of III-V semiconductor nanostructures such as In(Ga)As/GaAs QDs and related optoelectronic devices in the past decade. Regarding the research and development of III-nitride QDs, there are three main kinds of formation mechanism for the growth of InGaN SAQDs. First, it has been proposed that nanoscale indium composition fluctuation due to InGaN phase separation or indium segregation results in the formation of indium-rich clusters, which acts as QDs (QDs-like) [1-3]. Hence, QDs-like 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) [1, 4]. Therefore, high luminescence efficiency could be expected if the density of QDs is much higher than that of dislocations. Second, it has been shown that nitride QDs can be self-organized using the strain-induced Stranski-Krastanov (S-K) growth mode [4-6]. Third, another way to form nitride QDs is to take advantage of surfactants or antisolvents, which are often used to change the surface free energy of heterostructure interface [7-10]. So far, that the self-assembled nitride QDs can be fabricated by molecular-beam epitaxy (MBE) has been reported [4, 6]. Recently, Tachibana et al. reported the growth of InGaN/GaN QDs by metalorganic chemical vapor deposition (MOCVD) without using any antisurfactants [5]. However, it is still uncertain whether the formation of QDs was due to strain-induced S-K growth mode or phase separation since small three-dimensional (3D) InGaN islands were found after the deposition of up to 20 monolayer (ML) of InGaN [6].

In this work, we report an approach to grow InGaN nanostructures in a MOCVD reactor. An interrupted growth mode was proposed to grow nanoscale InGaN SAQDs without the use of 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 were studied by photoluminescence (PL) and Raman spectroscopy. The physical properties of these QDs will also be discussed.

II. EXPERIMENTS

All samples used in this study were grown on (0001)-oriented sapphire (Al_{2}O_{3}) substrates in a vertical low-pressure MOVPE reactor (EMCORE D180). During the MOVPE growth, trimethylgallium (TMG), trimethylindium (TMI), and ammonia (NH_{3}) were used as aluminum, gallium, indium, and nitrogen sources, 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 TMG was kept at 88 µmol/min while the flow rate of H_{2} carrier gas was kept at 10 l/min. NH_{3} was used as a group V source with a flow rate of 4 l/min, which corresponds to a V/III ratio of about 2000. The growth temperature was then reduced to 730°C to grow InGaN layer. During the growth of InGaN layer, the flow rates of TMG and TMI 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. The flow rate of NH_{3} was 10 l/min. It should be noted that we needn’t shut down NH_{3} flow (group V source) during growth interruption. If we did that, nitrogen atoms could be insufficient at such a temperature (GaN or InGaN films will be decomposed). According to our calibration, the average indium composition in the In,Ga,N layer should be around x=0.3. Knowing the lattice mismatch between InN and GaN equals 11%, the mismatch between
In_{0.3}Ga_{0.7}N and the underneath GaN buffer should be around 3.3% ($\Delta a/a=11.6\%\times0.3=3.3\%$). In our experiment, the growth rate of InGaN layer is estimated to be 0.04 nm/s, 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 A. That is, we deposited a 1.2-nm-thick InGaN layer on top of the undoped GaN buffer layer, stopped the growth for 12 s, and then deposited another 1.2-nm-thick InGaN layer so as to achieve a total InGaN layer thickness of 2.4 nm, as shown in Fig. 3.7. For comparison, sample B was prepared by directly depositing a 2.4-nm-thick InGaN layer on top of the GaN buffer layer, as also shown in Fig. 1. In addition, a sample C with 1.2-nm-thick InGaN was also prepared in the same growth condition as sample B. Furthermore, sample D without the nanostructures was also prepared by depositing a 100-nm-thick InGaN layer on top of the undoped GaN buffer layer.

Photoluminescence (PL) was used to study the optical properties of these samples under RT and different temperatures ranging from 17 K to 300 K. During PL measurements, a 325 nm He-Cd laser was used as the excitation source. The collected luminescence signal was dispersed by a monochromator and detected by a photomultiplier tube (PMT).

Micro-Raman measurements were performed in a Raman spectrometer (LabRam-010), an argon ion ($Ar^+$) laser with 514.53 nm line was used as a source of excitation. Raman spectra were measured in the backscattering geometry at temperatures from 100 K to 298 K. The direction of incident laser beam was along the c-axis of the wurtzite structure (z-direction) as shown in Fig. 2.

![Figure 1](image1.png)

**Figure 1.** Scheme showing the two growth methods for InGaN nanostructure samples.

![Figure 2](image2.png)

**Figure 2.** Schematic for Raman measurements. Raman spectra were measured in the backscattering geometry at temperatures from 100 K to 298 K. The direction of incident laser beam was along the c-axis of the wurtzite structure (z-direction).

### III. Results and Discussion

Figs. 3(a) and (b) show the 3D AFM images of samples A an B, respectively. As shown in Fig. 3(a), small circular InGaN nanostructures were formed by the interrupted growth mode. From these AFM images, it was found that the diameters of these circular nanostructures were in the range of 20-38 nm, with an average height of 4.1 nm. On the other hand, the density of these circular nanostructures was estimated to be approximately $2\times10^{10}$ cm$^{-2}$. We can see that it has a uniform distribution of QD structure in sample A. In contrast to the small circular nanostructures observed from sample A, large oval InGaN 3D islands were found in sample B as shown in Fig. 3(b). It was found that the larger width of these oval 3D islands was approximately 140 nm while the smaller width of these oval 3D islands was approximately 70 nm, with an average height of 1.7 nm. We also found that the density of these large oval 3D islands was approximately $3.5\times10^8$ cm$^{-2}$. Furthermore, it can be seen that it is not uniform in QD distribution. From the AFM images shown in Fig. 3, 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 nanostructures observed from sample A were much smaller than those observed from sample B. Thus, we should be able to observe a more significant quantum confinement effect from sample A.

![Figure 3](image3.png)

**Figure 3.** (a) 3D $2\times2$ $\mu$m$^2$ AFM images of sample A (with InGaN QD structures, using growth interruption in MOVPE). (b) 3D $4\times4$ $\mu$m$^2$ AFM images of sample B (with larger InGaN 3D islands, grown without using the interrupted growth mode in MOVPE).

Fig. 4 shows the measured RT PL spectra for samples A, B and D. It can be seen that the PL peak position of sample A is located at 2.645 eV while the PL peak position of sample B is located at 2.578 eV. It was also found that the normalized PL intensity observed from
sample A was 50% larger than that observed from sample B. In other words, the introduction of growth interruption would result in a PL blue shift as large as 67 meV. It should be noted that the nominal thickness of InGaN epilayer of these two samples were the same (i.e. 2.4 nm), i.e. they had the same InGaN coverage. The possible reason for huge PL blueshift will be discussed in detail later. Thus, although the InGaN coverage was the same for samples A and B, we could observed a larger PL transition energy from sample A prepared with growth interrupt, since growth interrupt will result in a smaller nanostructure size. Furthermore, we can see that the sample A is about 180 times the normalized PL intensity of sample D, it is possible that sample D have no quantum structures like quantum wells or dots can confine the excitons which will be trapped by defects (e.g. threading dislocations) results in the low probability of radiation recombination. Hence sample D showed the weak PL intensity.

\[ \text{Figure 4. Room temperature PL spectra for samples A (interrupted growth, 2.4-nm-thick InGaN), B (direct growth, 2.4-nm-thick InGaN) and D (100-nm-thick InGaN).} \]

Fig. 5 shows the PL full widths at half maximum (FWHMs) of samples A and B at different temperatures. It can be seen that the FWHM of sample A (i.e. 118 meV at 17 K) was much smaller than that of sample B (i.e., 150 meV at 17 K). As a result, the InN molar fraction \( x \) of the structures in sample A could be smaller than that in sample B. The reduction in InN molar fraction in sample A might be due to re-evaporation of In or InN during the long growth interruption. It should be noted that sample A with smaller InN molar fraction has a wider energy band-gap; in other words, sample A has a higher transition energy than sample B. Fig. 6 shows the measured PL peak energies as functions of temperature for samples A and B. It can be seen that the PL peak energy of sample A is always larger than that of sample B. For example, the PL peak energies measured at 17 K were 2.702 eV and 2.630 eV for samples A and B, respectively. That is, the introduction of growth interruption would result in a PL blueshift as large as 72 meV. Due to the well-known polarization-field-induced quantum-confined Stark effect (QCSE) in nitride-based quantum heterostructures [11, 12], the separation of electron-hole pairs to opposite interfaces of the well as well as the redshift of the luminescence peak occur. Hence, the transition energy of the 4.1-nm-thick sample (sample A) should generally be more redshifted compared to the 1.7-nm-thick one (sample B), but the results show otherwise. On the other hand, since sample A has a smaller InN molar fraction and a smaller lateral size of nanostructures than sample B, the two factors will increase PL transition energy, i.e., they reveal that the PL peak energy of sample A should be blueshifted in relation to sample B. In this study, the above-mentioned three reasons (QCSE, In composition and size effect of QDs) will affect PL peak energy; hence a more detailed research should be undertaken.

\[ \text{Figure 5. PL FWHMs of samples A and B measured from 17 K to 300 K.} \]

\[ \text{Figure 6. PL peak energy of samples A and B measured from 17 K to 300 K.} \]

Fig. 7 shows a typical RT Raman spectrum of 2-µm-thick GaN on sapphire, it can be seen that the peak of \( E_2^{\text{H}} \) phonon mode is located on 569.4 cm\(^{-1}\); the substrate (sapphire) signal and the peak of \( A_1(LO) \) mode are also observed at 419.5 cm\(^{-1}\) and 736.4 cm\(^{-1}\), respectively. As shown in Fig. 8, the \( E_2^{\text{H}} \) and \( A_1(LO) \) peaks of sample B (2.4-mm thick InGaN with big 3D islands/GaN/sapphire) were measured at 571.1 cm\(^{-1}\) and 738 cm\(^{-1}\) respectively. The Raman spectra of sample A (2.4-mm thick InGaN with SAQDs/GaN/sapphire) and sample D (100-nm- nGaN/GaN/sapphire) at temperature from 100 K to 298 K are shown in Figs.9 and 10. At RT (298 K), Fig. 3.21 shows \( E_2^{\text{H}} \) and \( A_1(LO) \) peaks are at 572.4 cm\(^{-1}\) and 738 cm\(^{-1}\) respectively. Similarly, Fig. 3.22 shows these of sample D are observed at 571 cm\(^{-1}\) and 736.4 cm\(^{-1}\) respectively. As shown in Fig. 11, it can be seen that the energy peaks of \( E_2^{\text{H}} \) modes blueshift while temperatures decrease.
Figure 7. The room-temperature Raman spectra measured from 2-µm thick GaN/sapphire sample.

Figure 8. The Raman spectra measured from sample B (2.4-nm thick InGaN/GaN/sapphire) at temperature 298 K.

Figure 9. The Raman spectra measured from sample A (2.4-nm thick InGaN with SAQDs/GaN/sapphire) at temperatures from 100 K to 298 K.

Figure 10. The Raman spectra measured from sample D (100-nm thick InGaN/GaN/sapphire) at temperatures from 100 K to 298 K.

Figure 11. Measured Raman shifts of the $E_2^{11}$ of sample A and D in dependence on the temperatures.

It should be noted that $E_2^{11}$ modes in the Raman spectra are used this purpose because it has been proven particularly sensitive to biaxial stress in GaN epifilms [13]. The Raman spectra observed from the samples A, B, D, and GaN/sapphire sample, revealed that a compressive stress existed in InGaN epilayer since their $E_2^{11}$ peaks exhibited a blueshift of 3, 1.7 and 1.6 cm$^{-1}$, respectively. As a result, sample A with the InGaN QD structures of high strain shows a strong compressive stress in InGaN epilayer. On the contrary, the smaller $E_2^{11}$ peaks blueshift were observed from samples B and D due to their InGaN epilayers could relax partially biaxial strain. A. Link et al. have reported that the temperature dependences can be described by a model which takes into account the anharmonicity of crystal lattice potential and the thermal mismatch between the sapphire substrate and the layers [14].

IV. CONCLUSION

We provides a novel technique in MOVPE for growing nanometer scale InGaN QDs. Growth interruption method had been introduced into epitaxial processes of InGaN layers, i.e. with 12-s growth interruption time, we successfully formed InGaN SAQDs with a typical lateral size of 25 nm and an average height of 4.1 nm. The QDs density is about $2 \times 10^{10}$ cm$^{-2}$. In contrast, much larger InGaN 3D islands were obtained without growth interruption procedure. AFM results revealed that the surface morphology of the 1.2-nm thick InGaN film could become smoother by introducing 12-s growth interruption time into MOVPE growth; and it will easily form discrete and small self-organized QDs after the other 1.2-nm-thick InGaN epilayer was deposited. On the contrary, the direct growth of InGaN epilayer will result in the larger 3D islands. By means of Raman spectroscopy, the smaller $E_2^{11}$ peaks blueshift were observed from samples B and D due to their InGaN epilayers could relax partially biaxial strain. On the contrary, sample A with the InGaN QD structures of high strain shows a strong compressive stress in InGaN layer. Furthermore, the introduction of growth interruption would result in a PL blueshift as large as 72 meV at 17K. Here QCSE, In composition and size effect of SAQDs can affect PL peak energy and FWHM; hence a more detailed research should be undertaken.
REFERENCES


