

# Growth and optical properties of high-density InN nanodots

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## ABSTRACT

The alternative supply of source precursor growth (i.e. pulsed mode, PM) of InN/GaN nanodots by metal organic chemical vapor deposition (MOCVD) was investigated. The InN nanodots density of up to  $\sim 5 \times 10^{10} \text{ cm}^{-2}$  at a growth temperature of 550 °C was achieved, which is relatively higher than those ( $\sim 8.5 \times 10^9 \text{ cm}^{-2}$ ) by conventional mode (CM) method. The kinetic mechanism indicated that the diffusion activation energy at growth temperature region from 600 to 700 °C was 2.65 and 1.25 eV respectively for the PM and CM method. The high diffusion activation energy due to the high  $\text{NH}_3$  flow rate generated more reactive nitrogen adatoms on the growth surface, and is believed to be the main reason for the growth of high density InN nanodots. In addition, the PL intensity of InN nanodots that grown by PM method exhibit more intense signal than CM method. It was implied superior emission property for the PM growth of InN nanodots

**Keywords:** *InN nanodots, pulsed mode, conventional mode, diffusion activation energy, PL.*

## 1 INTRODUCTION

Since the InN band gap energy was revised to  $\sim 0.7 \text{ eV}$ , this discovery has provided new opportunities for further applications of III-nitride based optoelectronic devices. Recently there has been substantial interest in InGaN as a new thin-film solar cells material because of its wide tunable energy band gaps, which cover almost the entire solar spectrum. However, to date there are only a few reports on InGaN based solar cells due to some issues (phase separation, doping issue and poor quality material etc.) which are difficult to overcome in the commercial MOCVD system. In the past couple of years, the use of nanostructures in solar cells has offered the potential for a higher level of efficiency by using new physical concepts. For example, the benefit of multiple exciton generation (MEG) has been demonstrated in colloidal suspensions of PbSe, PbS, PbTe, CdSe, and GaAs quantum dots (QDs). A maximum theoretical efficiency of 42% has been predicted for single-junction devices employing MEG-active absorbers.

Numerous research efforts have been directed toward techniques based on the principle of self-assembly for the fabrication of nitride QDs. The growth of GaN QDs on AlN using the commonly used Stranski-Krastanow (S-K) growth mode was not reported until 1997 by Daudin et al. using MBE, and more recently by Miyamura et al. using MOVPE. Otherwise, antisuifacant method has been used to grow GaN QDs on AlGaIn ternary. Despite the numerous studies on (In)GaN QDs, the published reports on InN QDs, particularly on specific sample preparation procedure, are still quite limited.

Up to now, only a few papers have been reported about the growth of InN QDs by conventional MBE [1-2] and MOCVD [3-5]. This paper presents a feasible method for preparing high density InN nanodots on a GaN surface. Preliminary results indicate that by alternating the source precursor method, the so-called pulsed mode (PM) during the MOVPE epitaxial growth, high density InN nanodots could be achieved on a GaN epilayer. This method has been proven to be a simple yet effective way for preparing QDs structures in the InN material system and may have the potential to be used in the fabrication of infrared InN-based solar cells, light-emitting diodes, laser diodes and detector devices. In addition, result of the anomalous temperature dependence of optical emission in high density InN nanodots was of great interest and was investigated as well.

## 2 EXPERIMENT

The InN nanodots were grown on GaN/sapphire (0001) at a temperature varying between 550 to 750 °C by the PM method using trimethylgallium (TMGa), trimethylindium (TMIn) and ammonia ( $\text{NH}_3$ ) as the source materials. The gas flow sequence for the PM method, basically consists of four steps: 20-sec TMIn+ $\text{NH}_3$  growth step, 20-sec  $\text{NH}_3$  source step with 10-sec purge steps in between. During the growth step, the mole flow rates of TMIn and  $\text{NH}_3$  are  $1.53 \times 10^1$  and  $4.46 \times 10^5 \text{ } \mu\text{mole/min}$ , respectively. It is worth noting that during the 20-sec  $\text{NH}_3$  source step an amount of  $\text{NH}_3$  ( $8.04 \times 10^5 \text{ } \mu\text{mole/min}$ ) is introduced intentionally to achieve high density InN nanodots. In the present study the InN nanodots were grown by the CM method, in which the TMIn and  $\text{NH}_3$  flow rates are kept constant at  $1.53 \times 10^1$  and  $4.46 \times 10^5 \text{ } \mu\text{mole/min}$ , respectively. The total growth time

for the InN nanodots was 2 min, which is equal to the total time of six cycles of growth steps in the PM method. An NT-MDT Solver HV atomic force microscopy (AFM) system was used to perform the morphology measurement. Photoluminescence (PL) measurements were performed by using the 488-nm line of an argon-ion laser as an excitation source. The PL signals were analyzed by a 0.5-m monochromator and detected by a cooled InGaAs photodiode with a cut-off wavelength at 2.05  $\mu\text{m}$ .

### 3. RESULTS AND DISCUSSION

In order to understand the high density of InN nanodots grown by PM method, we performed a series experiment that changed the growth temperature from 550 to 750  $^{\circ}\text{C}$ . The InN nanodots density as a function of reciprocal temperature is shown in Fig. 1. As anticipated, the dots density depends greatly on the substrate temperature. There are two distinct regions in our dots density curve, divided by a temperature of  $\sim 700^{\circ}\text{C}$ . As can be seen in the Fig. 1, the dot density is reduced gradually from  $1.4 \times 10^{10}$  to  $5.1 \times 10^8 \text{ cm}^{-2}$  as the temperature is increased from 600 to 700  $^{\circ}\text{C}$ , which then tends to drop sharply with further increasing temperature and eventually become zero, i.e. no dots growth, as the substrate temperature is beyond 750  $^{\circ}\text{C}$ . For temperature higher than 700  $^{\circ}\text{C}$ , the dots density drops drastically. This dot density effect is contributed by dots coarsening, driven by the desire of the system to reduce the boundary free energy by transforming small dots into large ones. The process involves both migrations of adatoms across terraces and the evaporation of atoms from dots. It is therefore that the dots density should become a much steeper function of temperature.

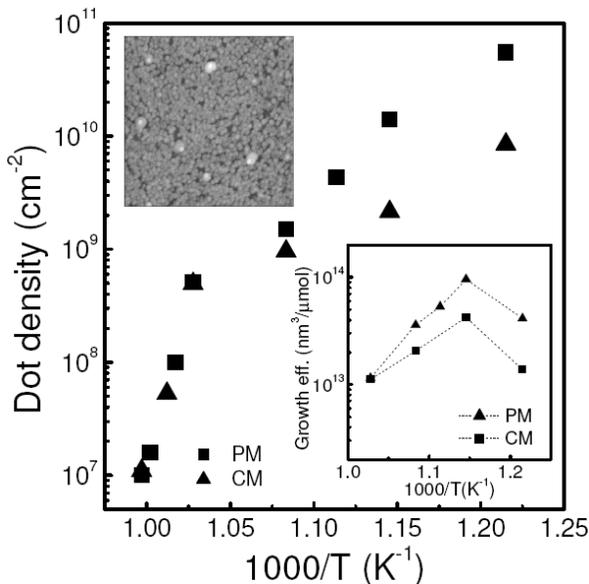


Fig. 1 The resulted Arrhenius plot of InN nanodots density as a function of reciprocal temperature. The insert shows

the growth efficiency of the InN nanodots as a function of  $1000/T$  for the CM and PM methods.

By referring to the island nucleation mechanism proposed by Robison et al., we learn that the dot density at low temperature is governed by the diffusion capability of adatom, while that at high temperatures is determined predominately by the re-evaporation rate of adatoms, hence the binding energy of adatom to the adsorbed site. The respective characteristic equations are  $N_s \propto N_{0L} \exp(E_d/3kT)$  for low temperature where  $N_s$  is dot density,  $N_{0L}$  pre-exponential parameters. The  $E_d$  activation energy of diffusing In adatom to the adsorbed sites were 2.65 eV for InN nanodots growth on GaN film by PM growth technique. The value of  $E_d$  is 1.25 eV for InN nanodots growth on GaN film by the CM method. Because of abundant supply of  $\text{NH}_3$  in  $\text{NH}_3$  step ( $8.04 \times 10^5 \mu\text{mole/min}$ ), result large density of nitrogen dangling bonds on the growing interface, and form the diffusion barrier of the In adatoms in the next growth step in pulsed mode growth scheme. This explains the high  $E_d$  diffusion activation energy of In adatom in pulsed mode as compared to conventional MOCVD method. In the high temperature region, the desorption of In adatoms from growing surface is effectively suppressed by the high  $\text{NH}_3$  supply in pulsed growth mode. For InN dot growth, O. Briot et al. [3] also conducted similar experiments in their study. They found the activation energy of diffusion In adatom  $E_d$  is  $4.19 \pm 0.53 \text{ eV}$  which is much larger than our results for InN nanodots prepared either by pulsed mode or conventional MOCVD method. Since they performed InN dot grown at V/III of  $\sim 30000$ , much higher than the V/III ratio ( $\sim 20000$ ) used in our study, this may be the reason causing the discrepancy in diffusion activation energy in the InN dot growth study.

The growth efficiency of these two kinds of growth methods is shown in the insert of Fig.2. The growth efficiency is defined by the InN nanodots volume divided by the mole flow rate of TMIn. Each InN nanodots volume was estimated by using the dome structure. The volume of the nanodots was calculated by taking the volume of a single nanodot and multiplying it by the nanodot density for a  $1 \text{ cm}^2$  area. For example, the total volume of nanodots was  $1.47 \times 10^{15} \text{ nm}^3$  and  $6.48 \times 10^{14} \text{ nm}^3$  respectively using the PM and CM method at 600  $^{\circ}\text{C}$  for a  $1 \text{ cm}^2$  area. It must be noted that the growth efficiency curves show a maximum value at the growth temperature of 600  $^{\circ}\text{C}$ . It is known that the  $\text{NH}_3$  cracking efficiency increases with the increase in growth temperature. Thus, the increase of the growth efficiency with the increase in growth temperature from 550 to 600  $^{\circ}\text{C}$  was believed to be relative to the increase in  $\text{NH}_3$  cracking efficiency. However, the growth efficiency decreased with the increase in growth temperature from 600 to 700  $^{\circ}\text{C}$ . This was evident from the increase in dissociation of the InN nanodots. In addition, the growth efficiency for the PM method was about twice as large as that of the CM method. The higher growth efficiency for

the PM method was believed to be due to the higher concentration of nitrogen atom participates into the growth of InN nanodots. Despite of the dot density, the other dots parameters that concern us are height and diameter. From AFM measurements (in Fig. 2), the InN nanodots size listed as diameter/height were 190/35 and 180/18 nm, respectively for the CM and PM technique.

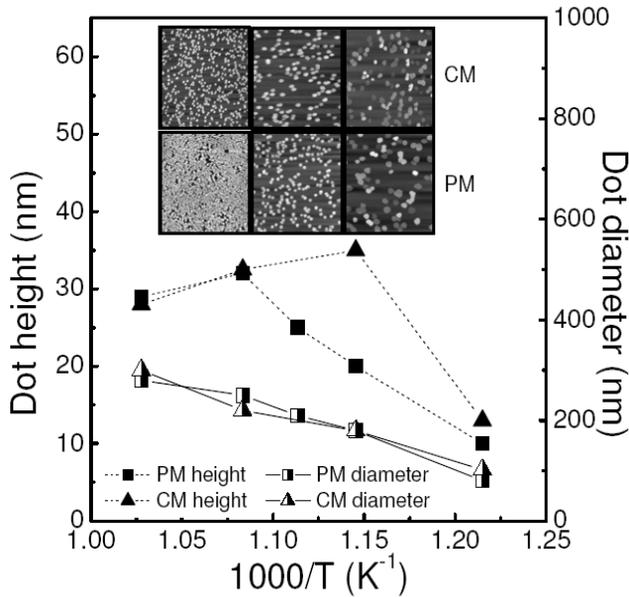


Fig. 2. Dependence of average height and average diameter of InN nanodots on growth temperature by CM and PM method. Insert shows the AFM images of CM and PM method at 600, 650 and 700°C.

The 17K PL spectra of the InN nanodots grown by the CM and PM methods are shown in Figs. 3 (a) and (b), respectively. It should be noted that these samples for PL measurement were grown at 600 °C without any GaN capping layer. The PL spectrum for the InN nanodots grown by the CM method shows a peak energy at 0.8 eV, with full width at half maximum (FWHM) of 87 meV. However, for the InN nanodots grown by the PM method, the PL peak energy was observed at 0.82 eV with FWHM of 143 meV. This emission energy of InN nanodots is higher than the reported bandgap energy of 0.69 eV [15], indicating a strong Burstein-Moss effect due to the presence of high electron concentration in the InN nanodots. Since the dot size is still too large to produce a pronounced quantum size effect, any differences in the peak energy between two samples are due mainly to variations of electron concentration in the InN nanodots. In addition, Fu et al. provides a convenient formula to determine the free-electron concentration in InN films by PL measurement [6]. The relationship between the FWHM and the free-electron concentration can be well described by the empirical formula [7-8] The free electron concentration were

estimated  $\sim 7 \times 10^{18} \text{ cm}^{-3}$  and  $\sim 2 \times 10^{19} \text{ cm}^{-3}$ , respectively for the CM and PM growth of InN nanodots.

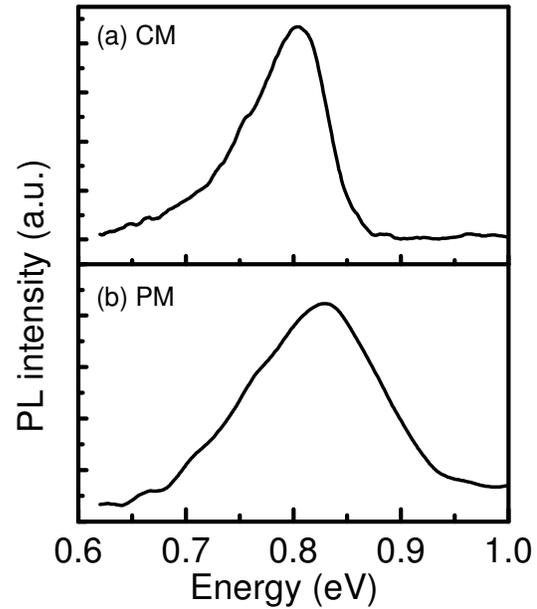


Fig. 3 The 17 K PL spectra of the InN nanodots grown by the CM and PM growth methods, respectively.

#### 4. CONCLUSION

The high density InN/GaN nanodots ( $\sim 5 \times 10^{10} \text{ cm}^{-2}$ ) were achieved by the PM MOCVD growth technique at a temperature of 550°C. The high density InN nanodots were achieved mainly as a result of the high  $\text{NH}_3$  flow rate in the  $\text{NH}_3$  source step, resulting in a high density of nitrogen adatoms on the growing surface, and forming a diffusion barrier in the next growth step of the PM growth method. The higher PL peak energy and FWHM indicate that the free carrier concentration is higher for InN nanodots grown by the PM method. It is believed that the high carrier concentration due to the high In vacancy ( $V_{\text{In}}$ ) in the InN nanodots is the main reason causing an anomalous temperature dependence of the PL peak energy for high density InN nanodots. In addition, the higher thermal activation energy of the InN nanodots indicates a stronger localization of carriers in the PM grown InN nanodots.

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