

Growth of indium gallium nitride nanorod arrays by HVPE using indium metal

Hwa-Mok Kim^{a,*}, Tae Won Kang^a and Kwan Soo Chung^b

^aQuantum-functional Semiconductor Research Center, Dongguk University, Seoul 100-715, Korea

^bSchool of Electronics & Informations, Kyunghee University, Yongin 449-701, Korea

This work demonstrates the properties of InGa_xN nanorod arrays with various In mole fractions by modified hydride vapor phase epitaxy (HVPE) method using In metal at a low growth temperature. The nanorods grown on (0001) sapphire substrates are preferentially oriented in the c-axis direction. We found that the In mole fractions in the nanorods linearly increased at $x \leq 0.1$. However, In mole fractions slightly increased at $x > 0.1$ and then gradually saturated at $x = 0.2$. Cathodoluminescence (CL) spectra show strong blue emissions from 428 nm ($x = 0.1$, 2.89 eV) to 470 nm ($x = 0.2$, 2.64 eV) at room temperature. From this result, we found the fact that increasing the In mole fraction in the InGa_xN nanorod shifts the peak position of the CL spectrum emitted from InGa_xN nanorods to the low energy region.

Key words: InGa_xN, nanorods, arrays, modified HVPE, In mole fractions, blue emission.

Introduction

Recent results have challenged the long-standing band gap value for indium nitride (InN) (~2 eV) and asserted 0.9 eV as the true band gap for high quality InN films.¹ This alone makes indium gallium nitride (InGa_xN) a promising material for blue/violet emission (and even a candidate for deep ultraviolet (UV) and infrared (IR) emission). If InGa_xNs indium (In) mole fraction can be successfully tuned from 0 to 1, InGa_xN represents a ternary alloy capable of emitting photons from 0.9 eV to 3.4 eV – that is, from GaN's UV emission (~365 nm) to InN's emission (~1380 nm). The most common method to achieve white light emission is to combine a phosphor wavelength down-converter with a blue InGa_xN/GaN light emitting diode (LED). A blue LED is typically placed in a parabolic mirror and subsequently coated with a phosphor-containing epoxy.² The LED emits blue light which is absorbed by the phosphor and re-emitted as a longer-wavelength phosphorescence. This occurs via a process known as down-conversion. These two wavelength (generally blue and yellow) combine to form white light.³ Unfortunately, many threading dislocations (TDs) are produced in the InGa_xN/GaN layer, used for blue light source, due to lattice mismatch with the substrate and a difference of thermal expansion coefficient with the substrate, and thus they affect significantly the device performance in terms of non-radiative recombination centers.⁴ On the other hand, the growth mechanism for nanorods is

completely different, and threading dislocations can be all but non-existent in nanorods. Therefore, the nanorods have the potential for negligible non-radiative recombination loss, and thus the efficiency of down-conversion is much higher than for bulk InGa_xN/GaN. However, no one has successfully grown InGa_xN and InGa_xN/GaN nanorods to date. Here, we demonstrate the optical properties of InGa_xN nanorod arrays on (0001) sapphire substrates by a modified hydride vapor phase epitaxy (HVPE) method with various In mole fractions. Ga and In metals were used as Ga and In precursors (group III), respectively. NH₃ was used as N precursor (group V). InGa_xN nanorods in this study were characterized by scanning electron microscopy (SEM), energy dispersive x-ray spectrometry (EDS), wavelength dispersive x-ray spectrometry (WDS), transmission electron microscopy (TEM) and cathodoluminescence (CL).

Experimental Procedures

The InGa_xN nanorods were grown by a modified HVPE method similar to that used in our previous work.⁵ Sapphire (0001) wafer was used as a substrate. The substrate was cleaned by an HCl solution and rinsed with deionized water before use. The Ga and In precursors were synthesized via a reaction of HCl gas (5N) (in a N₂ diluent gas) with Ga (7N) and In (6N) metal at 600 °C. These precursors were then transported to the substrate area where they were mixed with NH₃ (6N4) to form InGa_xN ternary nanorods at 510 °C. In this process, the HCl flow rate for the Ga precursor was in the range of 100-300 sccm and for the In precursor was in the range of 5-100 sccm. The NH₃ flow rate was 4000-5000 sccm and growth time was 1

*Corresponding author:
Tel : +82-2-2260-3952
Fax: +82-2-2260-3945
E-mail: hmkim@dongguk.edu

hour. InGaN nanorods were grown directly on (0001) sapphire substrates. After the furnace was cooled to room temperature, a light yellow layer was found on the surface of the substrate. The morphologies of the resulting materials were characterized using a field emission (FE) gun SEM (FEI, SIRION). Structural and elemental analyses of a single nanorod were performed using TEM (JEOL, JEM_2010 at 200 kV), selective area electron diffraction patterns (SAEP), EDS (EDAX, NEW XL-30) and WDS (EDAX, LambdaSpec). For the optical characterization of InGaN nanorods with various In mole fractions, CL spectroscopy was carried out using a FESEM (FEI, XL 30 SFEG) with a CL system (Gatan, MONOCL2).

Results and Discussion

Figure 1(a) and (b) show the InGaN nanorod arrays grown on (0001) sapphire substrate by using the modified HVPE system. The growth temperature for growing InGaN nanorods was about 510 °C compared to the growth temperature of GaN nanorods.⁶ The average diameter and length were 70 nm and 2 μm, respectively. The control of the InGaN nanorods diameter and length were achieved by adjusting the growth temperature and growth time, respectively. Figure 1(c) shows the EDS spectrum from a single InGaN nanorod. From this spectrum, we could observe an InL line from a

single nanorod. Figure 1(d) shows a TEM image of a single InGaN nanorod. In this image, the [0001] direction was parallel to the long axis of rod, indicating that the [0001] direction is a common growth direction in an InGaN nanorod. SAEP of the same nanorod from the $[2\bar{1}10]$ direction confirmed that it was a single crystal, and that the electron diffraction pattern could be indexed to the reflections of hexagonal InGaN crystal.

For investigating In mole fractions in the InGaN nanorods, we measured the WDS spectra of our InGaN

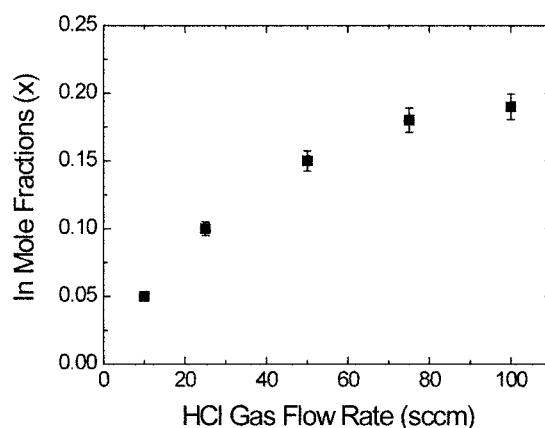


Fig. 2. Variation of In mole fractions (x) in the InGaN nanorods with various HCl reactant gas flow rates by WDS measurements.

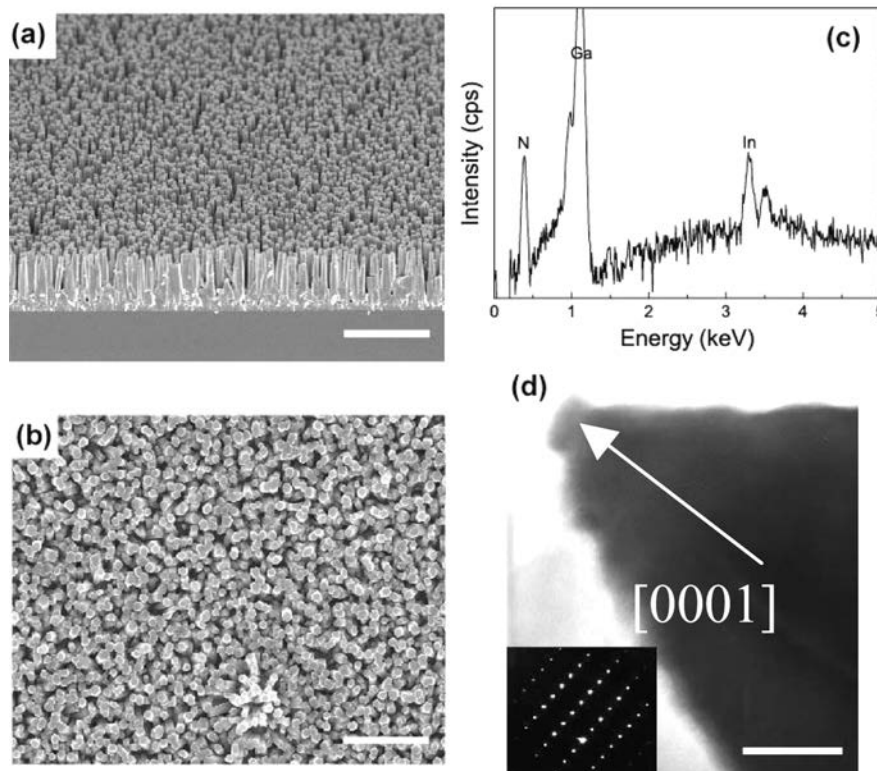


Fig. 1. SEM, EDS and TEM characterizations of straight InGaN nanorods on (0001) sapphire substrate grown by HVPE at 510 °C. (a) 30° tilted view, scale bar, 2 μm. (b) plan view SEM image, scale bar, 1 μm. (c) EDS spectrum of a single crystalline InGaN nanorod and (d) TEM image of the InGaN nanorod and corresponding electron diffraction pattern (inset). Scale bar is 8 nm.

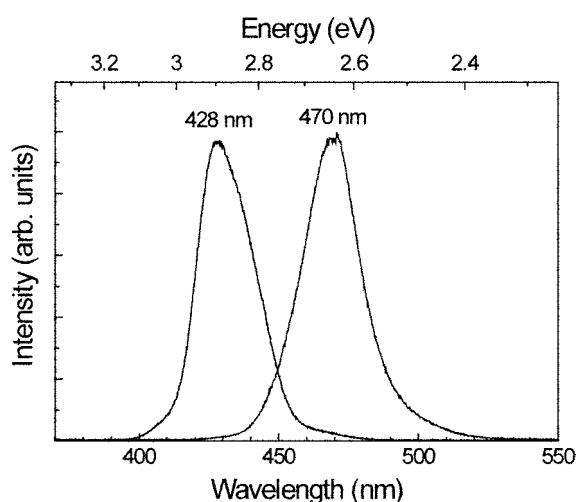
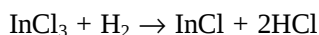
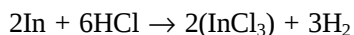


Fig. 3. Optical properties of two individual InGaN nanorods with In mole fractions of $x = 0.1$, and 0.2 by CL measurement at 300 K , respectively.

nanorods samples as shown in Fig. 2. Increasing the HCl gas flow rate for reacting In metal, that is In precursor, from 10 sccm to 100 sccm , In mole fractions (x) were increased from 0.04 to 0.20 in the nanorods. In this case, NH_3 , the main carrier of N_2 and HCl carrier N_2 gas flow rates were kept 4000 sccm , 5000 sccm and 2000 sccm , respectively. The growth temperature was 510°C . When the HCl reactant gas flow rate was small ($\leq 25\text{ sccm}$), In mole fraction linearly increased with HCl gas flow rate. As HCl reactant gas flow rate was increased, however, In mole fractions in the InGaN nanorods were slightly increased and then these saturated. One of the reasons for saturation of the In mole fraction is thought to be the consumption of InCl_3 in the reactor by hydrogen reduction, because the hydrogen partial pressure in the reactor increases with the decomposition of HCl due to the increasing HCl gas flow rate. With an increase of the hydrogen partial pressure, the following reaction of InCl_3 consumption proceeds to the right-hand side.



Since the InCl produced does not react effectively for the deposition of InN ,⁷ it is thought that the consumption of InCl_3 by the above reaction leads to the saturation of the In mole fraction in the InGaN nanorods as seen in the In-HCl- NH_3 system.

To investigate the optical properties of two individual InGaN nanorods with In mole fractions of $x = 0.1$ and 0.2 , respectively, we carried out CL experiments at 300 K . Figure 3 shows the CL spectra of two individual InGaN nanorods with In mole fractions of $x = 0.1$ and 0.2 . The CL peak positions of 428 nm (2.89 eV) and 470 nm (2.64 eV) were observed for the InGaN

nanorods with In mole fractions (x) of 0.1 and 0.2 , respectively. These values are very close to that observed from the optical properties of InGaN alloys.⁸ From the CL spectra, we found that, if we make p-n junctions in the InGaN nanorods, we can fabricate a nanoscale blue LED based on the InGaN nanorod. If it is possible, we will fabricate high-efficiency white emitting luminescence conversion (LUCO) LEDs.

Conclusions

This work demonstrates the optical properties of InGaN nanorod arrays with various In mole fractions by a modified HVPE technique at a low growth temperature. The nanorods grown on (0001) sapphire substrates are preferentially oriented in the c-axis direction. We found that the In mole fractions in the nanorods linearly increased at $x \leq 0.1$. However, In mole fractions slightly increased at $x > 0.1$ and then gradually saturated at $x = 0.2$. CL spectra show strong blue emissions peaking at around 428 nm (2.89 eV) and 470 nm (2.64 eV) at room temperature, with In mole fractions of 0.1 and 0.2 respectively. We believe the approach presented is a simple one for practical application to nanoscale white light devices. In the near future, we will accurately control the In mole fraction in the InGaN nanorods and fabricate blue LEDs by using p-n junction in InGaN nanorods based on our previous work.⁹

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