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**MOVPE** Growth of Wurtzite InN and its Characteristics

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## 1. Introduction

Since we proposed the InGaAlN system with a wurtzite structure [1], InGaN has become the leading material for the active layer of light emitting devices (LEDs). This alloy has been used for commercially available LEDs in the visible region such as blue and green color. At the same time as we proposed the InGaAlN system, we reported, based on a series of absorption experiments on high-quality In<sub>x</sub>Ga<sub>1-x</sub>N films, that the fundamental band-gap energy Eg decreased monotonically from 3.4 (x=0) to 2.1 eV (x=0.42). We also pointed out that InN single crystals would have a much smaller Eg than the commonly believed value, which was measured using poly-crystals [2,3]. Thus, InN remains the most mysterious material. Eg of InN has very recently been investigated using metalorganic vapor phase epitaxy (MOVPE) [4,5,6] and molecular beam epitaxy (MBE) [7,8]. The Eg of single-crystal InN has been measured to be generally to be less than 1 eV. In this paper, the optical characteristics of InN grown by MOVPE are reported in relation to Eg. How the characteristics depend on the growth conditions is also described.

# 2. Experiments

The samples were grown by a two-step MOVPE at ambient pressure. The structure is InN (0.1-0.2  $\mu$ m thick)/GaN (1.6  $\mu$ m thick)/sapphire (0001). InN was also directly grown on sapphire. The growth temperature was 1010°C for GaN and 500 to 600°C for InN. Trimethylindium (TMI), trimethylgallium (TMG) and ammonia were the source gases. The flow rate of TMI was 1.07 to 4.68  $\mu$ mol/min under the constant ammonia flow rate of 15 standard liter/minute. At this growth temperature, ammonia decomposes by less than 0.1%. As a carrier gas, nitrogen was used instead of hydrogen to promote ammonia decomposition. The reactor pressure was 650 Torr. Single-crystal growth of a (0001)-oriented hexagonal InN layer was confirmed after growth by transmission electron diffraction and  $\omega$ -2 $\theta$  scan of x-ray diffraction (XRD). A confocal Raman microprobe was employed to observe the crystallinity of the InN layer. Photoluminescence (PL) and absorption experiments were carried out to examine the fundamental band gap.

## 3. Results and Discussion

The sample showed smooth surface morphology without In droplets. In X-ray diffraction, metal indium was not observed. From Raman scattering spectra, lowand high-carrier-density regions were commonly observed as well as high-quality InN epitaxial layers, which remains a kind of mystery [9]. The typical carrier density and Hall mobility of InN grown at 500°C was 10<sup>18</sup> to 10<sup>19</sup>/cm<sup>3</sup> and 100-200 cm<sup>2</sup>/Vs. As an optical characteristic of InN directly grown on sapphire, Fig.1 shows the relationship between squared absorbance and photon energy, which was

measured at room temperature. This sample was grown at 500°C with a TMI flow of 1.07 rate µmol/min. Α linear relation in the region with large absorption was clearly observed. indicating that InN has a direct optical transition



function of photon energy.

characteristic like AlN and GaN. By drawing the tangential line in Fig.1, Eg can be determined. However, the unique tangential line could not be drawn because the film was not homogeneous as shown by the Raman

scattering measurements. Therefore, two lines having the maximum and minimum gradient were drawn instead. From Fig.1, Eg is 0.8 to 1.0 eV. PL was also observed at room temperature. The origin of the PL was not donor-acceptor pairs, but near band-edge emission, because the emission intensity increased linearly to the excitation power [5]. The peak wavelength did not depend on the TMI flow rate in the experiments. Instead, as shown in Fig.2, it depended on the growth temperature, though in the longer wavelength region each spectrum includes a weak shoulder, which seems to be some kind of deep emission. Thus, Eg could not be uniquely determined, as was also the case in the absorption experiments. Considering the above results,

the relationship Eg between and the lattice constant along the aaxis in the InGaAlN system can be replotted as shown in Fig.3. The band bowing of InGaN in this work becomes smaller than that in the previous work. peculiar А characteristic of InN, the dependence of PL on measurement temperature, is show in Fig.4. The shift of the wavelength with increasing temperature is very small. This



Fig. 2 Dependence of PL on growth temperature. Excitation power density and wavelength is 8W/cm<sup>2</sup> and 514.5 nm.



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wavelength stability is far superior to usual III-V materials, such as InP and GaAs [10]. This characteristic suggests that InN is a promising material for the laser diodes of the next generation of optical communications system because an uncooled laser diode is desired for reducting system cost and introducing dense wavelength-division-multiplexing.

## 4.Conclusions

Eg of single crystalline InN was described on the basis



of optical absorption and PL. Eg could not be determined uniquely because of the soft absorption characteristic, PL including emission from some deep level, growth temperature dependency, and high carrier density; however, Eg was near 0.8 eV. In order to uniquely determine Eg, homogeneous high-quality InN with low carrier density is necessary. The discrepancy of Eg between this work and the previous data measured using poly-crystals is thought to arise from a Burnstein-Moss shift due to the high carrier density of  $10^{20}$ /cm<sup>3</sup>, indium oxide with large Eg due to oxidization, and quantum effects originating from the small grain size.

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