Magnesium Doping of In-rich InGaN

Chin-An CHANG, Tzu-Yu TANG, Pen-Hsiu CHANG*, Nie-Chuan CHEN, and Chi-Te LIANG¹

Department of Electronic Engineering, Chang Gung University, Tao-Yuan, Taiwan, Republic of China

¹*Department of Physics, National Taiwan University, Taipei, Taiwan, Republic of China*

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InN and In-rich InGaN were grown by metal organic vapor phase epitaxy with magnesium doping. A set of samples were grown at 550 °C, whereas a second set of samples were grown at increasing temperature with Ga content. Upon annealing, p-InGaN was obtained from the second set up to an In content above 50%, with an acceptor concentration of $\sim 1 \times 10^{19} \text{ cm}^{-3}$ and a mobility of $1\text{--}2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. None of the samples grown at a constant temperature of 550 °C showed a p-behavior after heat treatment. The electrical, optical, structural and morphological characteristics of the films grown were analyzed, and the leveling off of hole concentration beyond an In content of 30% was consistent with the reported decreasing activation energy of Mg with increasing In content. [DOI: 10.1143/JJAP.46.2840]

KEYWORDS: InN, In-rich InGaN, metal organic vapor phase epitaxy, magnesium doping, p-InGaN

1. Introduction

Research on InN and In-rich InGaN has been intensive in recent years owing to the narrow band gap of InN.^{1–3)} The possible realization of nitride optoelectronic devices up to a wavelength of 1.6 μm has prompted a wide interest in such materials. However, the technical challenges is the growth of p-InGaN with high In content. Kumakura *et al.* reported a correlation between the activation energy of Mg and the measured hole concentrations in the InGaN films up to an In content of 13%.⁴⁾ An increase in In content was accompanied by both an increase in hole concentration and a decrease in the activation energy of magnesium. A recent report has extended the Mg-doping to InGaN with an In content of 40%.⁵⁾ In this paper we report the growth of Mg-doped InGaN with different In contents using both fixed and varying growth temperatures. The samples grown at elevated temperatures showed a p-behavior upon annealing up to an In content above 50%, likely the highest value being reported.

2. Experimental Procedure

InGaN films with different In contents were grown on (0001) sapphire substrates by metal organic vapor phase epitaxy (MOVPE) in an Aixtron 200/4 RF-S reactor. A 20 nm GaN nucleation layer was first deposited at 500 °C, followed by a 2 μm GaN layer grown at 1000 °C. Thereafter, a 200–300 nm Mg-doped InGaN layer was grown by one of the following two methods. A constant growth temperature of 550 °C was used for the first set of samples, and elevated temperatures were used for the second set of samples, as shown in Table I. The compositions indicated were for the intended growth based on the growth rates of InN and GaN. A comparison with the actual compositions shown later helped evaluate the effect of the preferential evaporation of InN at different temperatures. The purpose of designing two sets of growth conditions was to prevent the preferential evaporation of InN during the growth of an alloy of InN and GaN at elevated temperatures. It also allowed a correlation between the film properties and growth temperatures for the individual compositions. The metalorganic precursors used were triethylgallium (TEG) for Ga, trimethylindium (TMI)

Table I. In contents of samples grown at different temperatures.

x of $\text{In}_x\text{Ga}_{1-x}\text{N}$	1	0.8	0.6	0.4	0.2	0
Sample number	A	B	C	D	E	—
Growth temp. (°C)	550	550	550	550	550	—
Sample number	—	b	c	d	e	f
Growth temp. (°C)	—	600	650	700	750	900

for In, and NH_3 for nitrogen, all with nitrogen carrier gases. Biscyclopentadienyl magnesium (Cp^*Mg) was used for Mg doping. The typical flow rates used were 400 sccm for TMI, varying rates for TEG, 18,000 sccm for NH_3 , and 8×10^{-7} mole/min for Cp^*Mg . Both sets of InGaN layers were annealed at 600, 650 and 700 °C in a nitrogen ambient to activate the doped magnesium. The films were analyzed by Hall measurement, photoluminescence (PL), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

3. Results and Discussion

As shown by electrical measurement later, p-InGaN was achieved only for the second set of samples grown at elevated temperatures. Therefore, we concentrate on the characterization of this set of samples and compare this set with the first set when needed. A detailed comparison between the two sets of samples will be reported at a later date. The compositions of the InGaN films were determined by X-ray diffraction analysis, as shown in Fig. 1. Using Vegard's law, the determined compositions were labeled in the insets in the figures. Except for the samples intended for an In content of 80%, all the InGaN samples grown at temperatures higher than 550 °C showed a lower In content than those grown at 550 °C. This is attributed to the high evaporation rate of InN at elevated temperatures. Similar results were reported by Yoshimoto *et al.*⁶⁾ As shown below for both sets of InGaN, the deviation between the intended and actual compositions correlated with both the growth temperatures and contents of In and Ga in the InGaN grown. The deviation was small toward the In-rich end; however, it was large toward the Ga-rich end. In addition, all the InGaN layers grown at 550 °C showed a narrower full-width at half-maximum (FWHM) than those grown at temperatures higher than 550 °C. The most possible reason will be discussed

*E-mail address: phchang@mail.cgu.edu.tw

Fig. 1. X-ray diffraction patterns of second set (II) of InGaN grown at different temperatures. The growth temperatures used were 550, 600, 650, 700, 750, and 900 °C for the samples A, b, c, d, e, and f, respectively.

later. Within each set of InGaN samples, the FWHM increased toward the $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ region. The FWHM values measured were 118, 258, 540, 252, and 160 arcsec for the samples grown at 550 °C with the In contents of 100, 79, 57, 36, and 19%, respectively. For the samples grown at elevated temperatures, the FWHM values were 538, 1014, 756, 154, and 15 arcsec for the InGaN films with the In contents of 82, 56, 32, 13, and 0%, respectively. This is consistent with the pattern of non uniformity in the alloy growth.

The PL measurement of the InGaN films showed the progressive shifts of emission wavelength from about 1.7 μm to 361 nm for both sets of samples. The PL spectra measured at 10 K are shown in Fig. 2 for the second set of samples. The long-wavelength emission of InN reported by many groups⁷⁻¹³⁾ was again confirmed here. The FWHM varied from sample to sample and was also affected by the growth temperatures used. The AFM analysis of the surface morphology indicated a progressively smoother surface toward the Ga-rich end of the InGaN films grown. This was observed for both sets of samples.

Fig. 2. PL spectra of second set (II) of InGaN grown at different temperatures. The growth temperatures were 600, 650, 700, 750, and 900 °C for the samples b, c, d, e, and f, respectively.

Fig. 3. Electrical measurement of two sets of InGaN grown at different temperatures and annealed. Upper: carrier concentration as function of In content of InGaN films. Lower: carrier mobility as function of In content of InGaN films.

The electric measurement showed an interesting result for the samples grown at different temperatures. Each set went through the same annealing. Annealing was performed at 600, 650, 700 °C for 30 min in N_2 atmosphere. All the samples grown at 550 °C were n-type before and after annealing. Using elevated growth temperatures, p-type InGaN was achieved after annealing up to an In content of 56%. This was likely the highest In content reported for p-InGaN. The measured carrier concentration and mobility are summarized in Fig. 3 for both sets of samples. The hole concentrations were in the range of $(5-10) \times 10^{18} \text{ cm}^{-3}$, with a hole mobility of $1-2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In addition, as previously mentioned, Fig. 3 clearly shows a correlation of the deviation between the intended and actual compositions with the growth temperatures and In contents used. The increasing deviation noted for the second set of samples toward the Ga-rich end was consistent with the preferential evaporation of InN at high temperatures. The annealing at increasing temperatures caused a large reduction in both the electron concentration and mobility for both InN and In-rich InGaN films. This is related to the accompanied changes in film thickness at elevated temperatures. One example is shown in Fig. 4 for sample d. The thickness of

Fig. 4. Cross-sectional scanning electron micrographs of sample d annealed at (a) 650 and (b) 700 °C, showing reduced thickness for (b).

the $\text{In}_{0.32}\text{Ga}_{0.68}\text{N}$ layer changed from 188 to 147 nm after annealing at 650 and 700 °C.

The hole concentrations of both $\text{In}_{0.32}\text{Ga}_{0.68}\text{N}$ and $\text{In}_{0.56}\text{Ga}_{0.44}\text{N}$ were much higher than that of $3 \times 10^{17} \text{ cm}^{-3}$ for the Mg-doped GaN. The flow rates used for the various precursors of Mg, In, and Ga, as previously described, indicated a $\text{Cp}_2\text{Mg}/\text{III}$ ratio of $\sim (1-4) \times 10^{-3}$, which corresponds to a Mg incorporation of about 10^{19} cm^{-3} . By the Hall measurement of the p-InGaN grown, an activation rate of about 10% was estimated for Mg in these InGaN films. This is consistent with the analysis of Kumakura, Makimoto, and Kobayashi (KMK)⁴⁾ These authors showed that the activation energy of Mg in InGaN decreases with increasing In content up to 13%, with a simultaneous increase in measured acceptor concentration. Figure 5 shows our data on the hole concentration as a function of the In content of the InGaN grown. Also added in the figure are the results of KMK that correlate well with the current results. The concentration seemed to level off at an In content above 30%. An interesting correlation might exist between such an observation and the reducing activation energy of Mg as reported by KMK. The extrapolation of the latter work

seemed to indicate a decrease in the activation energy of Mg at an In content of around 30%. This would be favorable to the growth of high-concentration, p-type In-rich InGaN for both contact and device applications. Whether the analogy described is a mere coincidence is worthy of further investigation.

The growth of magnesium-doped, p-type In-rich InGaN faced the challenge of compensating a high background donor concentration. Our study has shown a clear role of the growth temperatures of InGaN. None of the samples grown at 550 °C showed a p-InGaN after annealing. Only those grown at elevated temperatures showed p-behavior after annealing up to an In content above 50%. Apparently, the growth at a higher temperature benefited the incorporation of Mg into a favorable site for the subsequent activation to occur. Such growth should also improve the quality of InGaN that, in turn, contributes to the activation process considered. One puzzling fact is the FWHM values of the samples grown at increasing temperatures are larger than those of the samples grown at 550 °C. Whether the larger FWHM values of the former are partly due to the presence of phase separation requires the detailed analysis of the PL spectra. Our earlier study on the In-rich InGaN showed a phase separation at an In content of around 80%.¹⁰⁾ A low growth temperature would normally hinder the migration of the adsorbed In and Ga, preventing the best lattice arrangement required for the phase separation to grown at a constant temperature of 550 °C. In addition, the growth at such a temperature would also generate films with an inferior quality, which is unfavorable to the activation of Mg. In this regard, annealing at temperatures higher than those reported here might shed light to this issue provided that the thermal decomposition of InGaN could be avoided.

4. Conclusions

In summary, Mg-doped InGaN films with different compositions were grown at both constant and elevated temperatures. The effects of growth temperatures on the actual compositions obtained were correlated with the preferential evaporation of InN, which became increasingly larger toward the Ga-rich end. P-type InGaN with an In content higher than 50% was achieved at elevated growth

Fig. 5. Hole concentration of InGaN films as function of In content. Also included are the hole concentration reported by KMK and the activation energy of the Mg acceptor in InGaN (ref. 3).

temperatures. The leveling off of the hole concentrations beyond an In content of 30% was correlated with the likely vanishing activation energy of Mg in InGaN at such a composition.

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