Achieving p-$In_xGa_{1-x}N$ alloys with high In contents

B. N. Pantha, A. Sedhain, J. Li, J. Y. Lin, and H. X. Jiang

Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, Texas 79409, USA

ABSTRACT

Mg-doped $In_xGa_{1-x}N$ alloys were grown by metal organic chemical vapor deposition (MOCVD) on semi-insulating c-GaN/sapphire templates. Hall effect measurements showed that Mg-doped $In_xGa_{1-x}N$ epilayers are p-type for x up to 0.35. Mg-acceptor levels (E_A) as a function of x, (x up to 0.35), were experimentally evaluated from the temperature dependent hole concentration. The observed E_A in Mg-doped $In_{0.35}Ga_{0.65}N$ alloys was about 43 meV, which is roughly 4 times smaller than that of Mg doped GaN. A room temperature resistivity as low as 0.4 Ωcm (with a hole concentration ~5×10^{18} cm^{-3} and hole mobility ~3 cm^2/Vs) was obtained in Mg-doped $In_{0.22}Ga_{0.78}N$. It was observed that the photoluminescence (PL) intensity associated with the Mg related emission line decreases exponentially with x. The Mg energy levels in InGaN alloys obtained from PL measurements are consistent with those obtained from Hall-effect measurements.

Keywords: InGaN, p-type doping, acceptor energy level, MOCVD, Hall Effect measurement, PL

1. INTRODUCTION

Achieving highly conductive p-type GaN and AlGaN is very difficult due to the high activation energies (E_A) of the Mg-acceptor, which is a universally accepted p-type dopant for GaN and related alloys [1-3]. Since E_A decreases with a decrease in band gap energy [3], Mg-doped InGaN (InGaN:Mg) is expected to have a higher hole concentration (p) than Mg-doped GaN. Additionally, p-type InGaN is synthesized at a much lower temperature than p-type GaN. Thus, the use of p-type InGaN instead of p-type GaN in device structures is beneficial, particularly in devices such as green laser diodes, long wavelength emitters, and solar cells where the active region has to be grown at temperatures much lower than that of the top p-type GaN layer. Low etching damage and low contact resistance are other superior characteristics of p-type InGaN over p-type GaN [1]. Improvements in the performance of GaN based devices using p-type InGaN either as a contact layer or as the p-layer itself has already been demonstrated [4-6]. In recent years, applications of InGaN alloys have expanded into areas such as optoelectronics/photonics, solar cells, photoelectrochemical cells for hydrogen generation, and thermoelectric materials for converting heat to electricity [7-12]. For all these applications, high optical and electrical quality p-type InGaN is highly sought after. For hydrogen generation, p-type InGaN alloys are expected to be more stable in aqueous solutions than n-type materials.

P-type doping in relatively high In content InGaN alloys is highly challenging due to the presence of high background electron concentrations, which is believed to originate from defects such as oxygen and hydrogen impurities or nitrogen vacancies [13,14]. Nitrogen vacancies could be the consequence of an insufficiency of nitrogen atoms which results from the low decomposition rate of ammonia, as high In-content InGaN has to be grown at temperatures lower than 800 °C (while the growth temperature of GaN is generally > 1000 °C). Although the synthesis of p-type InGaN has been reported as early as 1995 [15], there are only a few reports on the properties of p-type InGaN [1,16-21]. However, the use of high In-content p-InGaN is inevitable in the near future as nitride based devices are rapidly expanding towards longer wavelength emitters [7].

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2. EXPERIMENTAL

Mg-doped p-type $In_xGa_{1-x}N$ alloys ($0 \leq x \leq 0.35$) were grown on semi-insulating c-GaN (SI-GaN)/sapphire templates by MOCVD. We have chosen SI-GaN templates to minimize electrical measurement errors of top InGaN:Mg alloys. Since the p-type $In_xGa_{1-x}N$ layer is relatively thin (~200 nm), resistivity of the layer underneath has to be high in order to assure accuracy in the measurement results. Ammonia (NH_3), trimethylgallium (TMGa), trimethylindium (TMIn), and biscyclopentadienyl-magnesium (Cp_2Mg) were used as N, Ga, In, and Mg sources, respectively. N_2 gas was used as a carrier gas. Growth temperatures were varied from 1050 to 740 °C to increase x from 0 to 0.35. Variable temperature Hall-effect measurements were performed to determine the hole concentration (p), hole mobility (μ_h), and resistivity (ρ) of the samples. Photoluminescence (PL) spectra were measured using a Ti-sapphire laser spectroscopy system coupled with a tripler. This system gives an average output power of about 40 mW at 4.7 eV and a spectral resolution of about 0.2 meV [21]. Indium contents were determined from the peak angles of (002) ω-2θ x-ray diffraction (XRD) curves and using Vegard law.

3. RESULTS

Since highly conductive p-type III-nitrides are extremely difficult to achieve, one has to systematically optimize the process parameters such as growth temperature, pressure, growth rate, and doping concentrations, etc. Figure 1 (a) and 1(b), for example, shows the p-type resistivity of $In_{0.15}Ga_{0.85}N$ as functions of a ratio of CP_2Mg/group III and growth pressure. We increased or decreased this ratio by increasing or decreasing the Cp_2Mg flow rate. The optimum ratio for this In content was found to be $4x10^{-3}$ while optimized growth pressure was found to be 250 torr.

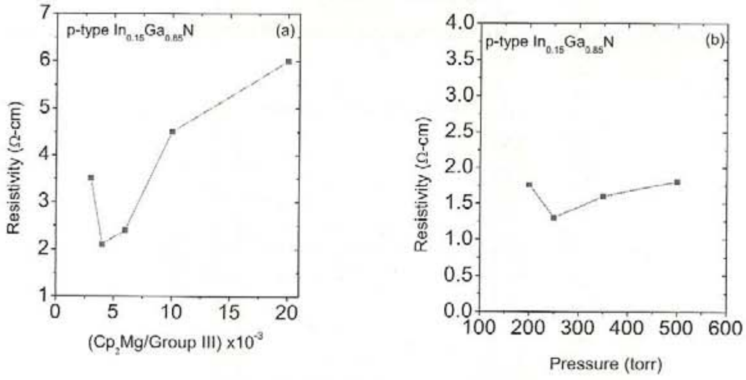

Figure 1. Resistivity of p-type $In_{0.15}Ga_{0.85}N$ as functions of (a) a ratio of Cp_2Mg/group III flow and (b) growth pressure

Figure 2 shows the (002) ω-2θ XRD curves of p-type $In_xGa_{1-x}N$ alloys. The In content corresponding to each curve is indicated. No phase separation was observed even at higher In content; however, intensity and line-width were inferior to low In content p-type InGaN alloys.

The room temperature electrical properties of p-type $In_xGa_{1-x}N$:Mg alloys as a function of x are plotted in Fig. 3. It was found that p continuously increases from $2x10^{17}$ for $x = 0$ (GaN) to $5x10^{18}$ cm^{-3} when $x = 0.22$. μ_h was found to decrease from 15 to 1.8 cm^2/Vs as x increases from 0 to 0.35. The variation in ρ with x shows that ρ decreases as x increases and reaches a minimum value of 0.4 Ωcm at $x = 0.22$ ($In_{0.22}Ga_{0.78}N$). This value of ρ is among the lowest reported for p-type InGaN. Though an even higher p value has been reported for similar In-content InGaN:Mg [18] and GaN:Mg grown by molecular beam epitaxy [23], the μ_h values of our samples are higher, which results in lower ρ values. Higher μ_h values are a result of enhanced material quality, while reduced ρ values will significantly improve device performance for many practical applications. The reduction in p values observed in p-type In_xGa_{1-}

$_x$N with $x > 0.22$ was due to the effects of hole compensation by background electrons. The presence of high background electron concentrations is the main hindrance for obtaining p-type conductivity and p-type In$_x$Ga$_{1-x}$N alloys with In content $x > 0.35$.

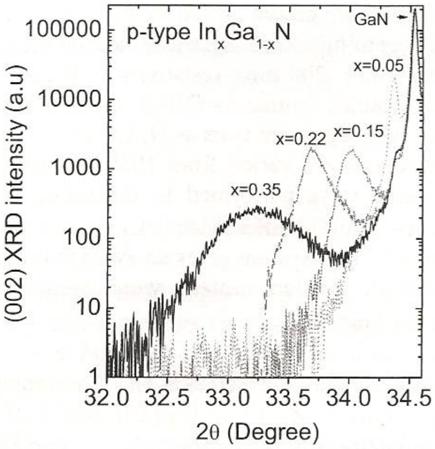

Figure 2. XRD ω-2θ curves of (002) planes of p-type In$_x$Ga$_{1-x}$N grown on semi-insulating GaN/Al$_2$O$_3$ templates

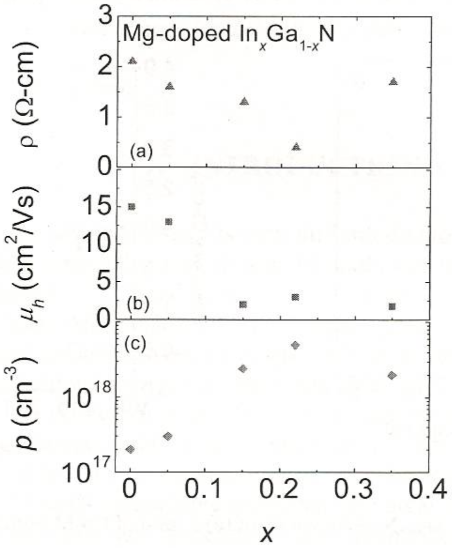

Figure 3. Room temperature (a) resistivity ρ, (b) hole mobility μ_h, and (c) hole concentration p as functions of In content (x) in Mg doped In$_x$Ga$_{1-x}$N alloys.

Temperature dependent p of p-type In$_x$Ga$_{1-x}$N alloys was also measured. Figure 4 shows the Arrhenius plot of free hole concentration p for $x = 0.05$, 0.15, 0.22, and 0.35. Straight lines are linear fits of the experimental data of p by the following equation:

$$p = p_o\, e^{-\frac{E_A}{k_B T}} \qquad (1)$$

where E_A is the Mg energy level and k_B is the Boltzmann constant. The plot of E_A as a function of x for In$_x$Ga$_{1-x}$N:Mg alloys is shown in Fig. 5 along with other reported values [1, 17, 19]. It was found that E_A continuously decreases with an increase in x. Lower values of E_A are the main reason for higher values of p in $In_xGa_{1-x}N$:Mg alloys of higher x. An E_A value as low as 43 meV was measured in $In_{0.35}Ga_{0.65}N$:Mg. This value is ~4 times smaller than that of Mg-doped GaN. $In_xGa_{1-x}N$ materials with $x > 0.35$ are generally highly n-type and conversion of these materials to p-type by Mg doping is still very difficult. Our results indicate that p-type conductivity in InGaN:Mg could be further improved if a better control of the background electron concentration could be achieved. The issue of high background electron concentration in InGaN alloys with relatively high In content is currently under intensive investigation [11,12] and further improvement in the p-type conductivity of relatively high In content alloys is anticipated.

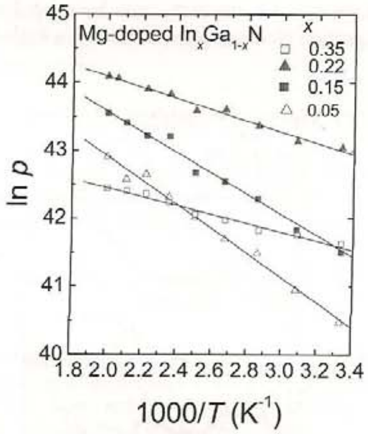

Figure 4. The Arrhenius plot of free hole concentration in Mg doped $In_xGa_{1-x}N$ alloys.

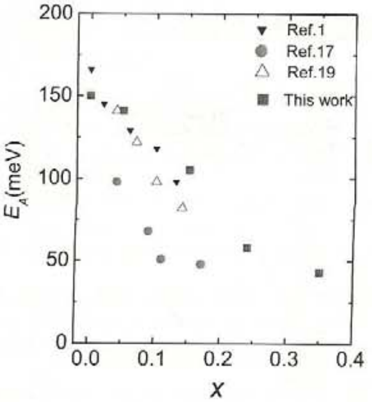

Figure 5. Energy level (E_A) of Mg acceptors in Mg doped p-$In_xGa_{1-x}N$ alloys as a function of In content x. Data from references available up to $x = 0.17$ are also included.

Figure 6 shows low temperature (10 K) PL spectra of $In_xGa_{1-x}N$:Mg for $x = 0, 0.05, 0.11$, and 0.22. We observed that the spectra for GaN:Mg is dominated by a broad emission band centered around 2.90 eV, which is a donor-acceptor-pair (DAP) type transition involving a deep donor, D^o, and an Mg-acceptor, Mg^o. Deep donors appeared in Mg doped GaN but disappeared in all InGaN:Mg alloys. One speculation is that the lower growth temperatures employed for InGaN alloys somehow suppresses the formation of these deep donors. A relatively weak feature in the higher energy side (with a peak at 3.29 eV) is a band-to-impurity type transition involving the conduction band (e^-) and acceptor (Mg^o) which is believed to dominate the spectra of GaN with light or moderate Mg doping. All p-type $In_xGa_{1-x}N$:Mg spectra except the GaN:Mg sample show the dominant peak with the same mechanism as that of the 3.29 eV line in GaN:Mg namely, a band-to-impurity transition involving the conduction band (e^-) and acceptor (Mg^o). An emission line at 3.29 eV also appeared in the spectra for samples with $x = 0.11$ and 0.22. This emission line is related to the SI-GaN template, which was lightly doped with Mg to achieve semi-insulation. From the PL peak positions observed here and the band-gap values already reported in the literature [11], we have estimated the acceptor level of Mg in our $In_xGa_{1-x}N$ epilayers, which is plotted in Fig. 7. As expected, Mg levels in $In_xGa_{1-x}N$ alloys decrease with In-content and are consistent with those obtained from the electrical measurement results shown in Fig. 5. The Mg impurity related PL emission intensity is found to decrease exponentially with In-content, as shown in Fig. 7. The PL emission intensity of Mg doped $In_{0.22}Ga_{0.78}N$ is almost three orders of magnitude lower than that of Mg doped GaN. The reduction in PL intensity may be related with the incorporation of impurities, which are also responsible for high background electron concentrations in high In content InGaN alloys.

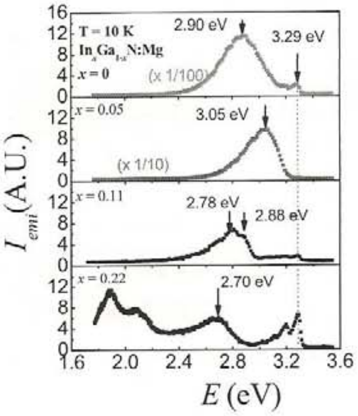

Figure 6. Photoluminescence spectra of Mg-doped p-type $In_xGa_{1-x}N$ alloys measured at temperature 10 K.

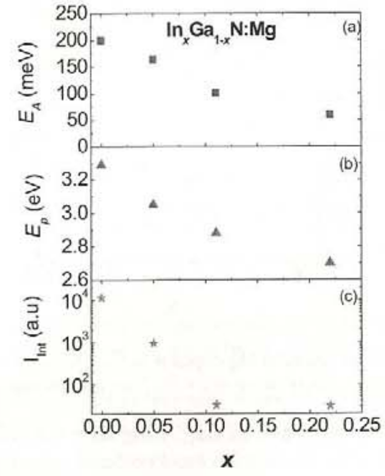

Figure 7. Mg acceptor energy levels E_A, peak position of Mg related emission E_p, and Integrated PL intensity I_{int} as functions of In content x. (a) E_A, (b) E_p, (c) I_{int}

4. SUMMARY

In summary, we have synthesized Mg-doped p-type $In_xGa_{1-x}N$ alloys by MOCVD for x up to 0.35 and analyzed their electrical and optical properties. P-type resistivity in Mg-doped InGaN alloys was found to be lower than that of Mg-doped GaN. Resistivity as low as 0.4 Ω-cm with a free hole concentrations as high as 5×10^{18} cm^{-3} was measured in Mg doped $In_{0.22}Ga_{0.78}N$. We have measured the Mg acceptor energy levels (E_A) in p-$In_xGa_{1-x}N$ alloys for x up to 0.35. E_A as low as 43 meV was obtained in Mg doped $In_{0.35}Ga_{0.65}N$. From low temperature PL measurements, we found Mg-acceptor levels for x up to 0.22 and the results are in close agreement with those obtained from electrical measurements. The difficulty of obtaining p-type InGaN in relatively high In-content is due to high background election concentrations caused by the lower growth temperature of InGaN alloys, which seems to promote the incorporation of donor like defects and impurities.

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