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Electrical and optical properties of MOVPE InN doped with Mg using CP₂Mg

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ABSTRACT

The first trial of Mg-doping in the atmospheric-pressure MOVPE growth of InN has been made using CP₂Mg as a Mg source. Although Mg is incorporated in the InN films and its content is proportional to CP₂Mg/TMI molar ratio, all samples grown here show n-type conduction and the electron concentration is rather increased with increasing CP₂Mg/TMI molar ratio. The SIMS analysis reveals that C and H are also incorporated into the grown films. The AFM observation shows that the grain growth of InN is suppressed by the CP₂Mg supply. Both the contamination of C and H and the effect of the CP₂Mg supply to the grain growth are considerably reduced by selecting the substrate position on the susceptor.

1. INTRODUCTION

The interests in InN are being rapidly increased because excellent electron transport properties in InN are expected for high speed and high frequency electron devices. Optical devices operating in the wavelength region from ultraviolet to infrared, including a tandem solar cell, can also be fabricated by using InN-based alloys, since InN has a direct band gap of 0.7 eV. The major issue in the InN-based device technologies is the formation of pn junctions in InN. Undoped InN usually exhibits n-type conduction and the control of electron concentration has been established by adopting the Si doping [1]. Although a few studies were made of the Mg doping for MBE InN [2,3], p-type conduction has not yet been obtained. The reason for this has not been known and the effect of “the surface electron accumulation layer” to the Hall measurement data was discussed [3]. Compared with MBE InN, MOVPE InN has been still less studied and there have been no reports on acceptor doping for MOVPE InN. This paper reports the first experimental study on Mg doping of MOVPE InN using bis-cyclopentadienylmagnesium (CP_2Mg). The electrical and optical properties for Mg-doped InN will be described and discussed together with the SIMS data in this paper.

2. EXPERIMENTAL

Using an atmospheric-pressure MOVPE system with a horizontal reactor, InN is grown on a nitrided (at 900°C) (0001) sapphire substrates at 600°C at the pressure of 800 Torr. A 20 nm thick GaN layer grown at 550°C is used for a

buffer. Ammonia (NH_3), trimethylindium (TMI), triethylgallium (TEG) and bis-cyclopentadienylmagnesium (CP_2Mg) are used as sources. CP_2Mg /TMI molar ratio is changed from 0.001 to 0.3. Sapphire substrates are placed at a distance of 3, 9 or 15cm from the upstream end of the 18cm long carbon susceptor [4] in the horizontal reactor. The thickness of grown InN is about 0.5 μm . Carrier concentration and mobility are measured with the van der Pauw method. Photoluminescence (PL) spectrum is measured at room temperature by using a He-Cd laser (442 nm, 300 mW) as a excitation source and a LN-cooled InGaAs pin photodiode (Hamamatsu Photonics, G7754-01) as a detector. For Mg-doped GaN, it is well-known that the annealing in the N_2 atmosphere at around 700°C after the growth is essential to activate Mg atoms in the samples. For the preparation of ohmic contact to the samples using In metal, the annealing at 400°C for 10 min is performed. The grown films are also characterized by the atomic force microscopy (AFM) and the secondary ion mass spectroscopy (SIMS).

3. RESULTS AND DISCUSSION

For Mg-doped InN, on the other hand, such a high temperature annealing can not be applied because InN is easily decomposed. From the morphological investigation, the annealing even at 600°C in the N_2 atmosphere is found to deteriorate the Mg-doped InN obtained. Therefore, the data shown below are for samples without annealing after the growth.

Figure 1 shows the carrier (electron) concentration and Hall mobility of the Mg-doped InN as a function of CP_2Mg /TMI molar ratio. All samples grown with a

CP₂Mg/TMI molar ratio in the range 0-0.3 show an n-type conductivity, that is, no apparent compensation effect is observed. Especially, a marked increase in electron concentration and a marked decrease of Hall mobility are found when CP₂Mg/TMI molar ratio exceeds 0.05. However, it is noted that a slight decrease of carrier concentration exists for a CP₂Mg/TMI molar ratio in the range 0.03-0.05. This may be a glimpse of compensation effect. We need a detailed analysis of the samples grown in this CP₂Mg/TMI molar ratio range. Figure 2 shows the PL peak energy and intensity as a function of CP₂Mg/TMI molar ratio. The PL peak energy is shifted to a higher energy side with increasing CP₂Mg flow rate. This is due to the Burstein-Moss shift. When CP₂Mg/TMI molar ratio exceeds about 0.05, the PL intensity is also rapidly decreased. The results shown in Figs. 1 and 2 indicate that donor-type defects are introduced by the supply of CP₂Mg.

Figure 3 shows the results of secondary ion mass spectrometer (SIMS) analysis of the Mg-doped samples. The concentrations of impurities detected are normalized by those for non-doped one. One can see that Mg is incorporated in the films and its concentration is linearly increased with increasing CP₂Mg flow rate. The analysis also reveals that high concentration of C and H are incorporated in the samples and their concentrations are also almost linearly increased with increasing CP₂Mg flow rate. For the sample grown with a high CP₂Mg/TMI molar ratio (~0.2), O and Si are also detected. Figure 4 shows the relative contents of Mg, C, and H incorporated in InN samples grown at a different position on the susceptor. The horizontal axis shows distance from the upstream end of the 18cm-long carbon susceptor. The incorporation levels

of these impurities are rapidly decreased with increasing the distance. It is noted that the levels of C and H can be reduced to those for the nondoped samples when the growth is made at a position significantly far (15 cm) from the upstream end of the susceptor. This indicates that the design of susceptor and/or reactor is important for the successful doping of Mg into InN. Figure 5 shows the surface morphologies (AFM images) for a non-doped and Mg-doped InN. The grain size of grown InN is decreased by adding CP₂Mg to the source gas flow. Especially, the grain growth is seriously limited for a film grown near the upstream end of the susceptor (Fig. 5(b)). Such a film contains high contents of C and H. It is also noted that the effect of CP₂Mg to the grain growth is minimized by growing samples at a position significantly far (15 cm) from the upstream end of the susceptor (Fig. 5(c)). The high concentrations of C and H impurities detected for samples grown near the upstream end may be due to the adduct formation of CP₂Mg with NH₃ [5].

4. CONCLUSION

Mg-doped InN films have been grown with the atmospheric-pressure MOVPE using CP₂Mg as a Mg source. The Mg incorporation into grown InN is confirmed by the SIMS analysis. However, all samples grown here show n-type conduction and no apparent compensation effect is observed. A slight decrease of electron concentration is found for a CP₂Mg/TMI molar ratio in the range 0.03-0.05. This may be a glimpse of compensation effect. The SIMS analysis reveals that C and H are incorporated into the grown films together with Mg. The AFM

observation shows the grain growth of InN is affected by the CM_2Mg supply. The contamination of C and H and the effect to the grain growth by the supply of CP_2Mg are minimized by selecting the position of substrates on the susceptor. This suggests that the design of susceptor and/or reactor may be important for the successful doping of Mg into InN. Although the behavior of the Mg-doped InN is a little complicated, the data obtained here are believed to be an important step to realize p-type InN. Further investigations will be needed to clarify the growth mechanism and to understand the electrical optical properties for the MOVPE InN doped with Mg.

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FIGURE CAPTIONS

Fig. 1. Carrier (electron) concentration and Hall mobility for Mg-doped InN as a function of $\text{CP}_2\text{Mg/TMI}$ molar ratio.

Fig. 2. Photoluminescence peak energy and intensity of Mg-doped InN as a function of $\text{CP}_2\text{Mg/TMI}$ molar ratio

Fig. 3. Results of SIMS analysis of Mg-doped samples. The concentrations detected are normalized by those for non-doped one.

Fig. 4. Relative contents of Mg, C, and H incorporated in InN samples grown at a different position. The the horizontal axis shows distance from the upstream end of the 18cm-long carbon susceptor.

Fig. 5. Surface morphologies (AFM images; $3 \times 3 \mu\text{m}^2$) for non-doped and Mg-doped InN grown at a different position.

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Fig. 5. A. Yamamoto et al.