Properties of InN grown by remote plasma enhanced chemical vapour deposition

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Abstract—We have investigated the properties of indium nitride (InN) grown at various temperatures on c-plane sapphire substrates using remote plasma enhanced chemical vapour deposition (RPECVD). The optical absorption spectra show a broad range of the apparent band-gap from 0.90 to 2.18 eV, depending on the growth temperature. These two extreme apparent band-gaps are similar to the controversial values of 0.7 and 1.9 eV quoted in the InN band-gap debate [1-3]. Along with optical absorption results, the influence of growth temperature on growth rate, and carrier concentration is discussed. The correlations between the carrier concentration, and shallow-donors (oxygen and hydrogen) in InN are also analysed.

Keywords—InN, band gap; growth rate; carrier concentration; Burstein-Moss effect; oxygen incorporation

I. INTRODUCTION

InN has attracted great attention for applications in InGaN based optoelectronic devices [4], quantum spintronic devices [5], Li-ion thin-film batteries [6], solar cells [7], and high-speed electronics [8]. Despite recent progress, InN is still the least understood of the nitride semiconductors and many of its fundamental characteristics are not well known, especially the band gap of this promising material. The physical reasons for the difference between the recently reported value of 0.7 eV band-gap and the previously reported much higher band-gap of 1.9 eV are not yet clear. There are several possible explanations for the observed variation in band-gap including quantum size effects [9], Burstein-Moss effect [10,11], and defect centres [12-14].

In this paper the influence of Burstein-Moss effect, and oxygen and hydrogen incorporation is explored for RPECVD grown InN. These samples have been analysed by optical absorption measurements, scanning electron microscopy (SEM), secondary ion mass spectroscopy (SIMS), and Hall measurements.

II. EXPERIMENTAL

InN films were grown directly on c-plane sapphire substrates using RPECVD at temperatures between 200 and 550 °C. The precursors were nitrogen plasma radicals and trimethylindium (TMI), with nitrogen as the carrier gas. Samples were grown at a pressure of 1.0 Torr.

Cross section images obtained with a LEO Supra 55VP SEM were used to measure sample thicknesses. A Cary UV-Vis-IR spectrophotometer was used for the optical absorption measurements. The carrier concentration of each sample was determined through Hall measurements using the van der Pauw method with a specimen dimension of 4×4 mm. SIMS measurements were carried out at the Australian Nuclear Science and Technology Organisation (ANSTO) using a Cameca IMS-5F dynamic system. The samples used for Hall and SIMS measurements were taken from comparable regions of the InN films.

III. RESULTS AND DISCUSSION

Fig. 1 shows that the growth rate under the chosen conditions increases with growth temperature until reaching a maximum of 0.153 ± 0.011 μm/h at around 500 °C. This dependence is primarily due to the number of available indium precursor species on the substrate surface waiting to chemically interact with nitrogen radicals. Higher growth temperatures enhance the decomposition of TMI, resulting in greater growth rates. With a further increase in the growth temperature to 550 °C, however, the growth rate drops significantly suggesting that thermal decomposition is also evident at this higher temperature [15-17].

Fig. 2 shows that both the band-gap and the carrier concentration have a strong growth temperature dependence. At the lowest growth temperature of 200 °C the InN film has the highest band-gap energy and n-type carrier concentration of 2.18 eV and 5.1×10^19 cm^-3, respectively. However, for the sample grown at 550 °C the band-gap appears to be much lower at 0.90 eV with a 3.6×10^19 cm^-3 carrier concentration. The thermal decomposition occurring at 550 °C, as discussed earlier, appears to have a minimal affect on the temperature dependence of the band-gap and electron concentration. Apparently, a correlation between the band-gap energy and the carrier concentration is evident. This dependence could be due to a Burstein-Moss shift, for which suggests the position of the absorption edge shifts to shorter wavelengths when the dopant concentration increases. Fig. 3 shows a typical \( E_G + E_F \) versus


0-7803-8820-8/05/$20.00 © 2005 IEEE

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carrier concentration plot used when a strong Burstein-Moss effect is expected. The result indicates that the InN samples grown in this work agree with the trend for Walukiewicz et al.’s MBE samples and their apparent Burstein-Moss effect calculation [11]. The finding of Fig. 3 suggests that the RPECVD InN samples analysed in this work may have similar properties to the MBE samples.

Oxygen as a potential donor is a possible source of carriers for a Burstein-Moss effect. The qualitative analyses of the oxygen content in all the samples were investigated using SIMS and a known reference sample characterised by heavy ion elastic recoil detection (HIERDA) [18] as per previous work. As shown in Fig. 4, there is a decrease in oxygen content for increasing growth temperature to 450-500 °C, however at 550 °C the oxygen content increases. We believe this is associated with the growth rate decrease shown in Fig. 1. Interestingly, the low oxygen content suggests that oxygen incorporation may not be the primary shallow-donor in this material.

Along with oxygen, hydrogen is also a possible candidate as the dominant shallow-donor in InN [13]. The normalised SIMS H/In ratio spectra for all InN samples are displayed in Fig. 5, and show a similar growth-temperature dependence in comparison to oxygen, but with the minima at the highest growth temperature of 550 °C. This trend seems to correlate the hydrogen concentration and the carrier concentration, however, the two spectra at 250 and 300 °C share a similar hydrogen content that does not coincide with the carrier-concentration shift shown in Fig. 2. Therefore, the hydrogen impurity may not be the primary shallow donor in these InN samples either. The significance of the hydrogen incorporation in all the samples has yet to be quantitatively determined, though this will be done in the near future.

Other effects such as strain [19], and stoichiometry [20] may also have an influence on the carrier-concentration shift, and these will also be the target of future study.

Figure 1. Growth rate for InN samples grown at different temperatures.

Figure 2. Plot of band gap and carrier concentration against growth temperature.

Figure 3. The $E_{\text{g}}$+$E_F$ versus carrier concentration plot for InN samples.

Figure 4. Oxygen concentration of InN samples as a function growth temperature.
We have reported results for InN samples grown by RPECVD having a wide range of band-gap energy from 0.90 to 2.18 eV. The effect of InN thermal decomposition is evident above a 500 °C growth temperature, however this does not seem to influence either the band-gap energy or carrier concentration, which are functions of growth temperature. All the samples analysed show an apparent Burstein-Moss effect.

Comparison of carrier concentration and SIMS depth profiles show that oxygen incorporation does not account for the apparent Burstein-Moss effect.

ACKNOWLEDGMENT

P. P.-T. Chen would like to acknowledge the support of a Macquarie University ICS PGRF grant for sample characterisations. Authors would also like to acknowledge an award for SIMS time provided by the Australian Institute of Nuclear Science and Engineering.

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