Accurate Stoichiometries of Polycrystalline Indium Nitride Films from Elastic Recoil Detection

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Indium nitride thin films for potential application in high power, high frequency devices have been grown with reactive ion sputtering. The film stoichiometries were measured with ERD. The beam-induced nitrogen depletion during ERD analysis has been found to be severe and non-linear with ion fluence. A model has been developed which reproduces the experimental data and allows extrapolations of the original nitrogen content. All films studied have been found to be nitrogen-rich and have large band gaps ranging from 2.14 - 2.3 eV. The amount of excess nitrogen correlates with the band gap energy suggesting a Moss-Burstein effect.

1. Introduction

The controlled growth of thin films of the group-III nitride semiconductors GaN and InN is vigorously being studied because of their wide-ranging technological potential. InN material is emerging as a strong candidate for applications in high power transistor devices because of its potentially large peak electron velocity. The use of InN in its polycrystalline form may entail cost-benefits and allow use of substrates other than sapphire. More importantly, higher mobilities have been reported for polycrystalline material than for single crystal material [1].

Routine growth of reproducible InN polycrystalline films and their technological application requires the detailed understanding of film stoichiometry and the role of impurity elements such as oxygen and carbon. Previous study of GaN has demonstrated the analytical potential of the Elastic Recoil Detection (ERD) technique for films of group-III nitrides [2]. Building upon earlier work, the application of the technique has been extended to the analysis of polycrystalline InN films to evaluate the efficacy of ERD for this material and to correlate the measured stoichiometries to other properties.

2. Experimental Details

Several polycrystalline InN films were grown in a reactive ion sputtering system. The films were grown on glass and the growth periods were in the range of 24-48 hours. The electronic band gaps of the films were measured with a Cary double beam transmission spectrophotometer. The films were analysed with ERD using 200 MeV ^{197}Au ions. Details of the ERD technique are given elsewhere [3]. The recoil ions were detected at a scattering angle of 45° with a gas ionization detector with a detection solid angle of 3.5 msr.

For a typical sample, the measured energy loss signals ΔE of the recoil ions as a function of ion energy E are displayed in Fig.1. All the relevant elements C, N, O, and In are well separated in the spectrum, permitting extraction of energy spectra and integration of recoil yields. The N and In yields associated with the films have been divided by the respective recoil cross-sections to obtain N/In ratios. The energy spectra for these elements were compared with SIMNRA simulation to determine the number of incident ions and atomic fractions of O and C in the films. A typical total energy spectra and the optimised

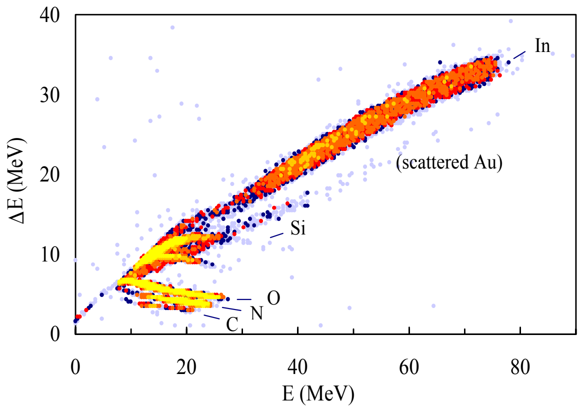

Fig.1: A 2D spectrum from the ERD analysis of a typical polycrystalline InN film grown on glass. The labels indicate groups of events associated with a specific element.

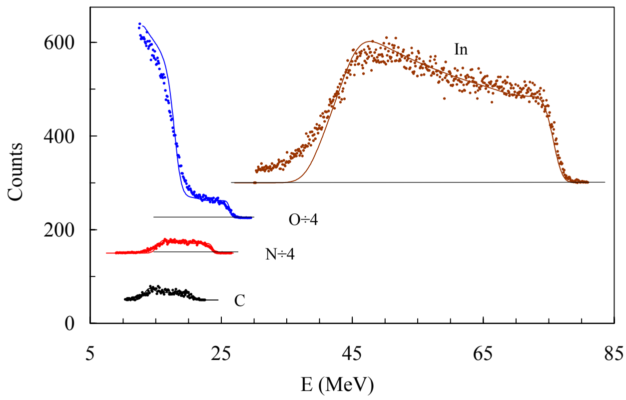

Fig.2: Energy spectra for recoil ions from sample A in comparison with a simulation using the program SIMNRA, which agrees well with the data. For clarity the spectra have been shifted upwards by constant numbers of counts.

SIMNRA simulation are displayed in Fig. 2. The atomic fractions obtained are indicated in Table 1.

3. Results and Discussion

For two representative samples, Fig. 3 shows the measured N/In and N/Ga ratios as a function of projectile ion fluence during ERD analysis. The data for N/Ga are from previous work [2]. Since the count rate for the group-III element is essentially constant with incident fluence in both cases, the decrease of the ratio is due to the loss of nitrogen from the film. The nitrogen depletion is near-linear for GaN, allowing reliable extrapolation of the original value. For InN, however, the depletion is non-linear and rapid. Without knowledge of the functional relation between nitrogen content and incident fluence, a reliable determination of the initial nitrogen concentration would not be possible. However, the nitrogen depletion data were found to agree with a nitrogen depletion model, which assumes formation of N_2 molecules as the crucial step of the depletion process. This model suggests a functional relation between the nitrogen concentration and incident ion fluence I with two free parameters a and b. The function has the form:

$$\frac{N}{In}(I) = \frac{1}{a.I + b} \qquad (1)$$

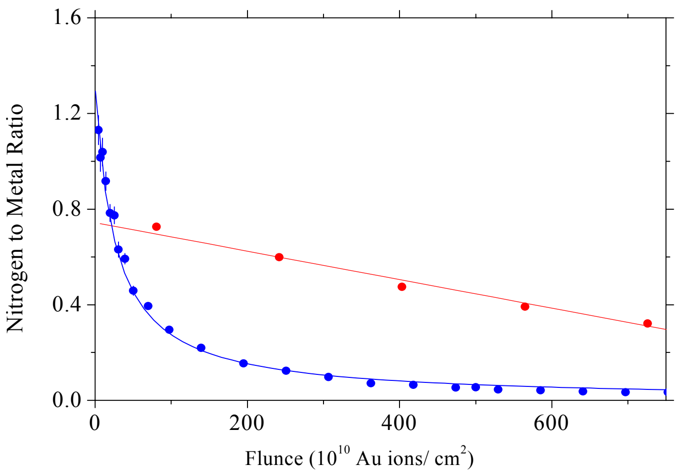

Fig.3: N/Ga (red symbols) and N/In (blue symbols) ratios versus the fluence of projectile ions during ERD analysis for a GaN and an InN film, respectively. The data for GaN can be approximated with a straight line (red). The strong depletion of N in the case of InN is well reproduced by a two-parameter function derived from a depletion model for nitrogen. The best fit with this function is shown as a blue curve.

Similar approaches have previously been successfully applied to beam-induced hydrogen depletion [4]. The quality of fits using Eq. 1 is demonstrated in Fig. 3. The model has been used to extrapolate the original N/In of the films. They are given in Table 1. The experimental uncertainties of the ratios are better than ±3%, which has been confirmed by repeating analysis of sample B.

Table 1: The measured stoichiometries and band gaps E_g of the polycrystalline InN films studied.

Sample	A	B		C
N/In(0)	1.31±0.03	1.32±0.04	1.30±0.03	1.14±0.03
C (%)	0.8	0.8		0.8
O (%)	10.7	9.3		9.3
Eg (eV)	2.3	2.27		2.14

Table 1 shows that the measured N/In ratios are considerably larger than unity, which have been also confirmed by Raman Spectroscopy [5]. The fact that the films are nitrogen-rich may be unexpected since nitrogen vacancies have been believed to be the source of donors producing the high background electron concentration observed for InN materials. Indeed, the material studied here has been found to have charge carrier concentrations of up to 2×10^{20} cm^{-3}. When grown in conditions of thermal equilibrium; nitrogen loss is an inescapable consequence of film growth for InN. However, film growth by RF sputtering, as employed in this work, does not occur in thermal equilibrium because of the energetic ions created in the RF nitrogen plasma. The high nitrogen incorporation into the films may thus be understood.

The electronic band gaps of the film analysed are much larger than the accepted band gap of 1.89 eV. Furthermore the measured values correlate with the excess nitrogen content of the film. This is significant, since the Moss-Burstein effect is known to cause an apparent increase of the band-gap. The excess nitrogen thus appears to act as the donor of charge carriers.

4. Conclusion

In comparison to GaN films, the stoichiometric analysis of InN films with ERD poses a greater experimental challenge, since nitrogen depletion caused by the incident beam is much more severe. The use of gas ionisation detectors with large solid angles allows this depletion to be monitored. However, without knowledge of the functional relation between the observed non-linear nitrogen depletion from the film during analysis and the fluence of the incident beam, a reliable measurement of the initial nitrogen concentration would be impossible. The experimental data presented here are consistent with a nitrogen depletion model which assumes the formation of N_2 molecules as the defining step of the depletion process. This model suggests a straight-forward functional relation between nitrogen concentration and projectile fluence, which allows reliable extrapolations of the initial N/In ratio of the film. For all samples analysed this ratio has been determined with an uncertainty of better than ±3%.

The ERD analysis showed that the material studied here is extremely nitrogen-rich. The amount of excess nitrogen correlates with the magnitude of the band gap, while the observed charge carrier concentration is large. This suggests that the excess nitrogen acts as a donor and that the Moss-Burstein effect increases the band gap from its nominal value of 1.89 eV to the observed values in the range of 2.14 - 2.3 eV.

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