Accurate Stoichiometries of Polycrystalline Indium Nitride Films from Elastic Recoil Detection

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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 [1]. For example, GaN films are used in the manufacture of blue and white light emitting diodes, blue lasers, ultraviolet detectors and high power transistor devices. InN material is emerging [2] as a strong candidate for applications in high power transistor devices because of its potentially large peak electron velocity. Polycrystalline films of GaN and InN may offer alternatives for many applications. Polycrystalline GaN films can be produced at considerably lower deposition temperatures 650°C than material of single crystal quality [3], permitting the use of substrates other than sapphire or SiC. The use of InN in its polycrystalline form may also entail cost-benefits. More importantly, in this case higher mobilities have been reported for polycrystalline material than for single crystal material [4,5].

Routine growth of reproducible polycrystalline films of group-III nitrides and their technological application requires the detailed understanding of film stoichiometry, grain-size, and the role of impurity elements such as oxygen and carbon. In an effort towards such an understanding, a correlation has been established between oxygen incorporation and grain-size for polycrystalline GaN films deposited with remote plasma enhanced laser induced chemical vapour deposition [3].

The stoichiometric information was obtained with Elastic Recoil Detection (ERD) using an incident beam of 200 MeV ^{197}Au ions [6]. The measurements demonstrated the analytical potential of the ERD technique for films of group-III nitrides, if the effects of beam-induced nitrogen depletion are understood and monitored during analysis. The particular advantage of ERD is its sensitivity to nitrogen and to all other light elements. Building upon this 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.

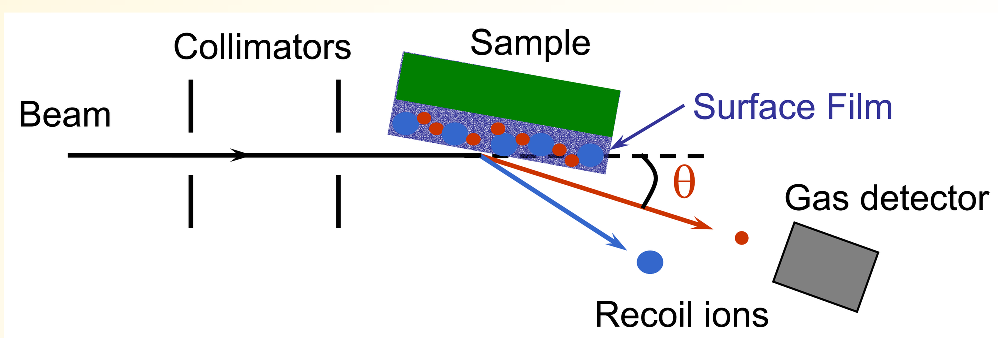
Film Growth

- Polycrystalline InN films were grown in a reactive ion sputtering system.
- The system was operated at 13.56 MHz.
- The growth periods used were in the range of 24-48 hours.
- Films were grown on glass.
- Band gaps of the InN films were measured with a Cary double beam transmission spectrophotometer.

Elastic Recoil Detection (ERD) Analysis

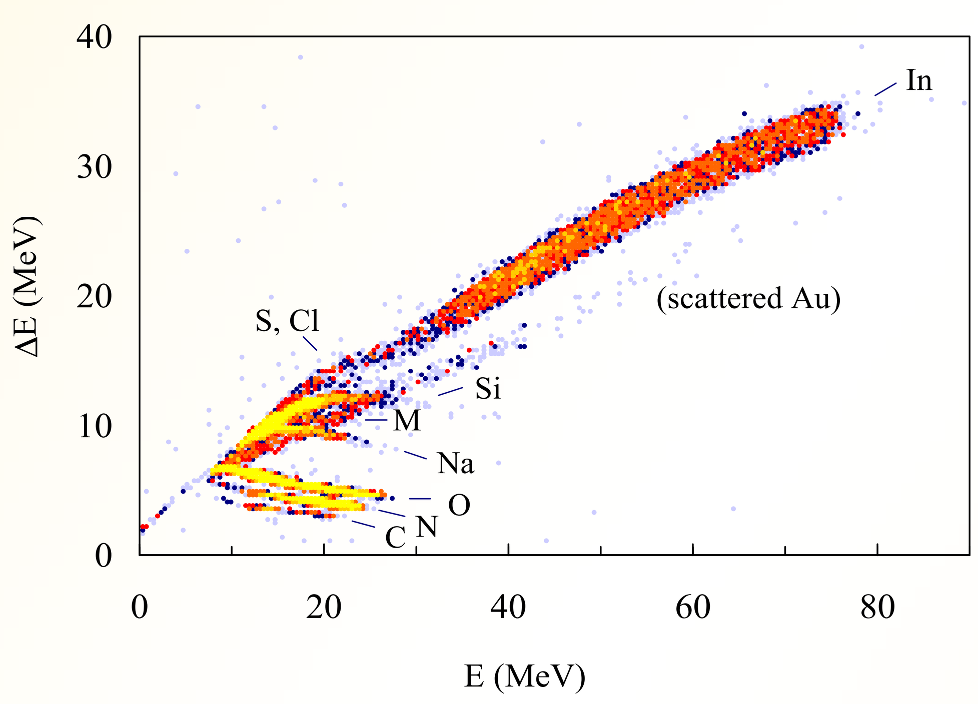
Principle

- Projectile ions strike the sample.
- Constituent nuclei recoil and are ejected.
- Recoil ions detected with a gas ionization detector.



Experiments

- ERD analysis with a projectile beam of 200 MeV ^{197}Au ions, so that all elements in the sample could be distinguished to a depth of 1 µm.
- The recoil ions were detected at a scattering angle of 45° using a gas ionization detector with a detection solid angle of 3.5 msr [7].
- The energy loss signals from the recoil ions are plotted as a function of ion energy.
- Energy spectra for recoil ions C, O, N, and In are integrated to obtain yields for each element.
- N and In yields have been divide by respective recoil cross-section to give the N/In stoichiometric ratios.



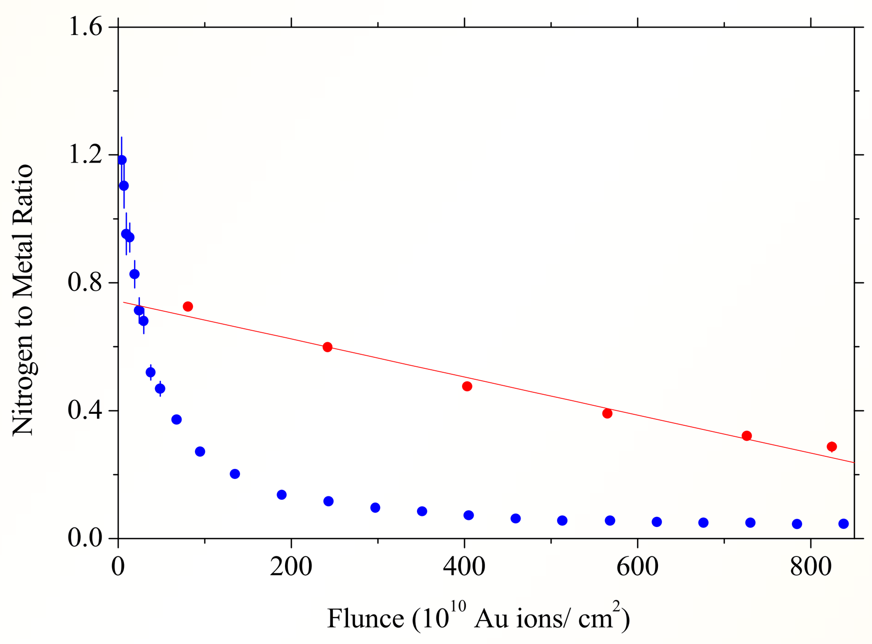
A two-dimensional spectrum from the ERD analysis of a typical polycrystalline InN film grown on glass.The energy loss signals ΔE of the recoil ions as a function of ion energy E. The labels indicate groups of events associated with a specific element. In addition to In and N significant amounts of O and C are present in the film, while the substrate contains Si, O, Na, Mg and traces of S and Cl.

Nitrogen Depletion

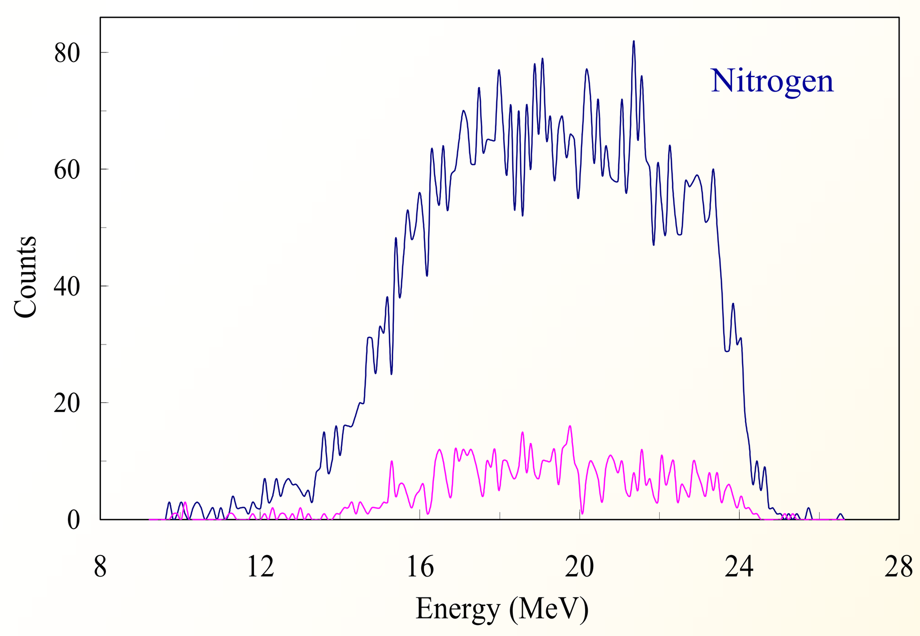
- In the previous study of GaN[4], linear nitrogen loss during the ERD analysis was observed.
- In the case of InN, unlike GaN, a rapid and non-linear nitrogen loss during the analysis is observed.

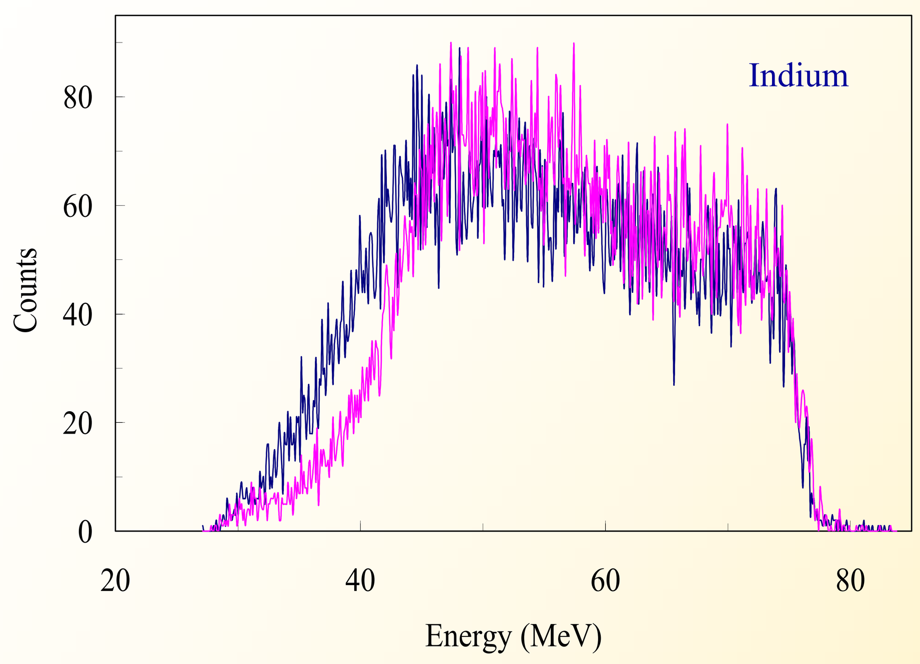
Problem?

- For the reproduction of films, understanding of film stoichiometry is necessary.
- Without knowledge of the functional relation between nitrogen content of the film and incident fluence, a reliable determination of the initial nitrogen concentration would be impossible.



N/Ga (red symbols) and N/In (blue symbols) ratios as a function of fluence of projectile ions during ERD analysis for a typical GaN and InN films respectively. Nitrogen loss from GaN is linear so that it can be approximated with a linear fit. However nitrogen loss from InN is non-linear and rapid.

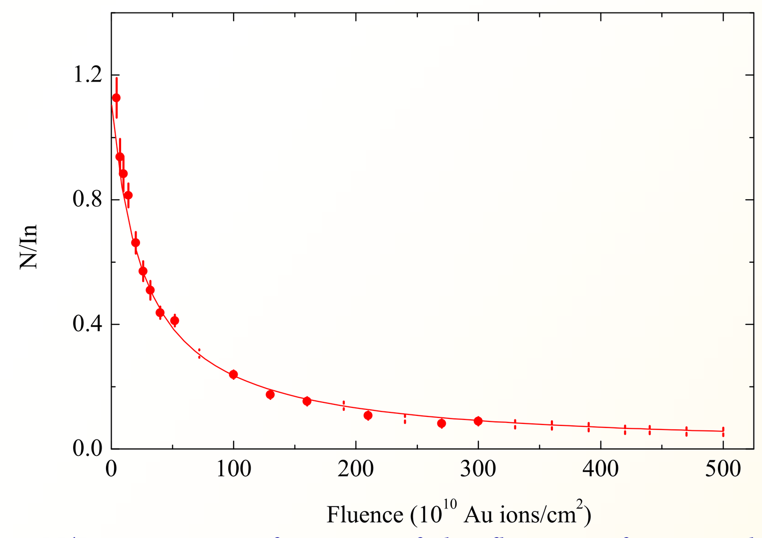




Energy spectra for N and In recoil ions measured at the beginning (blue symbols) and during (red symbols) the ERD analysis. The spectra indicate strong nitrogen depletion during the analysis but indium remains constant.

Nitrogen Depletion Model

- 2-parameter nitrogen depletion model has been derived, which assumes the formation of N_2 molecules as the crucial step of the depletion process.
  N/In(I) = 1/(a I + b) where I is the incident ion fluence and a & b are free parameters.
  (Similar approaches have previously been successfully applied to hydrogen depletion during ion beam analysis [8])
- Nitrogen depletion data agree with the model
- The validity of the model has also been confirmed in ERD measurements of crystalline InN films. This shows that the observed nitrogen depletion is not specific to polycrystalline material and that extrapolations using this function are reliable.
- The experimental uncertainties of the original N/In ratios extrapolated using the model are better than ± 3. This has been confirmed by repeating the ERD analysis of sample B.



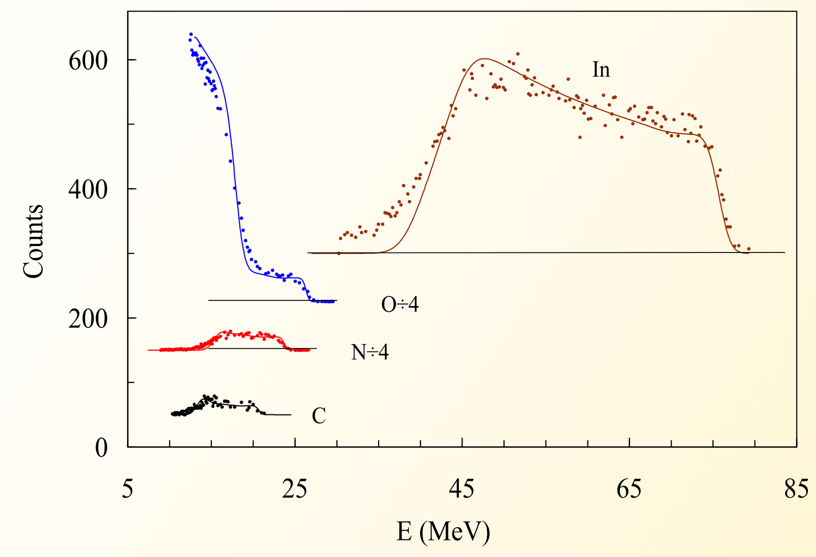
N/In ratio as a function of the fluence of projectile ions during ERD analysis of a typical InN sample. The strong depletion of nitrogen is well produced by a two-parameter function derived from a nitrogen depletion model. The best fit with this model is shown as a solid curve.

SIMNRA Simulation

Energy spectra have been extracted for the elements In, N, O and C, which have been compared with simulations from the code SIMNRA[9]. The simulations have been adapted to the experimental data to extract the atomic fractions of O and C in the films.

Sample ID	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
E_g (eV)	2.3	2.27		2.14

The measured stoichiometries and band gaps of the polycrystalline InN films studied.



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 number of counts.

Results and Discussion

- The measured N/In ratios are considerably larger than unity. The excess of nitrogen in the films has been confirmed by Raman Spectroscopy [2].
- 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 of film growth for InN. However, film grown by RF sputtering 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 as measured are also much larger than the accepted band gap of 1.89 eV for InN. 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 [10]. The excess nitrogen thus appears to act as a donor of charge carriers.
- Foley [4] has measured and identified a donor level at 50 meV for polycrystalline InN. If that donor level is the main source of carriers, it is so far below the conduction band that it can only be 1.8% ionised at a carrier concentration of 2×10^{20}cm^{-3}. The donor level would have to be at 38% of the total concentration of InN molecules to supply that many carriers. This value is of the order of the excess nitrogen present in the films. Indeed, the material studied here has been found to have charge carrier concentrations of up to 2 $\times10^{20}$cm$^{-3.}$ When grown in conditions of thermal equilibrium nitrogen loss is an unescapable consequence

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 decrease of the initial nitrogen content of 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. For all samples analysed this ratio has been determined with an uncertainty of better than ±3%.
- The atomic fractions of other elements in the film can also be quantified with the ERD technique, so that the stoichiometry of the material can be fully established. This is crucial for the development of the low temperature growth of polycrystalline InN films, where significant amounts of carbon and oxygen are incorporated into the film.
- The ERD analysis showed that the material studied 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. The magnitudes of the nitrogen excess and the charge carrier density are consistent with a donor level at 50 meV below the conduction band being the main source of the charge carriers.

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