Discovery of nitrogen-excess in InN

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Compositional analysis of indium nitride thin films has been performed with Elastic Recoil Detection analysis using different beams. While significant depletion of nitrogen occurs during the analysis with 1 MeV/u ^{197}Au, the depletion is reduced for lighter beams so that rate of depletion with 1 MeV/u ^{109}Ag is smaller than that with ^{197}Au. The depletion is insignificant with the ^{32}S or it can even be avoided for indium nitride films with good structural properties. Thus, the compositional analysis is simplified and accuracy is improved. The combined results from these studies have shown that state-of-the-art indium nitride tends to have nitrogen-excess of up to a few at-%.

Introduction

Indium nitride (InN) films are of current interest because of their potential applications in high frequency devices and optoelectronics [1]. However, ideal growth conditions have not been identified and films often contain oxygen, carbon and hydrogen. The compositional analysis of InN films has been attempted with XPS and RBS, see for example Ref. [2-4]. However, it should be noted that XPS or SIMS can only provide qualitative compositional information due to the lack of standard samples for InN. RBS, though quantitative, is not suitable for InN [5].

We have demonstrated that accurate compositional analysis of InN is possible with Elastic Recoil Detection (ERD) analysis using heavy ions [6]. Despite the applicability of heavy ion ERD to the stoichiometric analysis of InN films, such analysis with 200 MeV ^{197}Au projectiles is complicated by the rapid and non-linear depletion of nitrogen. The depletion can, however, be monitored with a large solid angle gas ionisation detector so that the original nitrogen-to-indium ratio can be extrapolated with the bulk molecular recombination model. Thus the film composition can be derived.

The compositional analysis with ERD may be simplified if the depletion of nitrogen can be avoided. For other materials, it has been shown that ion-beam-induced depletion is correlated with the electronic energy loss of the projectile ions in the material [7,8]. Thus, it may be expected that projectiles with atomic numbers Z lower than ^{197}Au produce reduced or no nitrogen depletion during ERD analysis of InN. This would simplify the stoichiometric analysis, as no theoretical modelling would be required. This should also improve the accuracy of the measured film composition.

Experimental details and analysis

In this study InN films grown by different techniques have been analysed. The ERD measurements were performed with ^{197}Au, ^{109}Ag, ^{32}S and ^{19}F beams. The projectile ions, beam energies and their stopping powers in InN at that energy, as derived from SRIM [9], are given in the table shown below. It is apparent from the table that the electronic stopping power changes by an order of magnitude over this selection of beams.

Projectile	Energy (MeV)	Stopping Power ($eV/10^{15}$ atoms/cm^2)	
^{197}Au	200	4722	48
^{109}Ag	110	3139	18
^{32}S	42	1101	1.9
^{19}F	28	471	0.6

The projectile ions were delivered by the 14 UD pelletron accelerator at the Australian National University [10]. Ions recoiling from the samples during ERD

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analysis were detected at a scattering angle of $\theta = 45°$ using a position-sensitive gas ionization detector with a detection solid angle of $\Delta\Omega = 3.5$ msr. The angle between beam axis and sample normal was $\alpha = 67.5°$. Details of the technique are given in Ref. [11].

For typical InN films grown by Remote Plasma Enhanced Chemical Vapour Deposition (RPECVD), Fig. 1 shows the measured energy loss as a function of the measured energy for all detected recoil ions for (a) 200 MeV ^{197}Au, (b) 110 MeV ^{109}Ag, (c) 42 MeV ^{32}S and (d) 28 MeV ^{19}F projectile ions. The two-dimensional spectra shown in (a), (b) and (d) are for the same film and that shown in (c) is for a similar film from the same growth. All diagrams show that apart from In and N, O and C are also present in the films. For the ^{197}Au beam in Fig. 1(a), events associated with Si are from the substrate. It is evident that all the elements in the films are well separated down to the substrate interface. This allows the direct integration of the detected recoil yields Y_i (i=C,N,O,In) for C, N, O and In, and the extraction of individual recoil energy spectra. The C, N, and O recoils are also separated with the ^{109}Ag beam, see Fig. 1(b), however, the In recoils are not separated from Ag scattered by In. In this case the In yield was derived by integrating the In recoils and the scattered Ag projectiles together and considering the recoil and the scattering cross section of In and Ag, respectively. Interestingly, the C, N and O recoils are better separated with both the ^{32}S and ^{19}F beams compared to the ^{197}Au and ^{109}Ag projectiles, see Fig. 1(c) and Fig. 1(d). In these cases the information on the In content of the film was derived from the S and F atoms scattered off In atoms.

Since all the films essentially contain C, N, O and In, the atomic fractions of these elements are given by

$$f_i = \frac{Y_i}{d\sigma_i / d\Omega} \left(\sum \frac{Y_j}{d\sigma_j / d\Omega} \right)^{-1} \text{------ (1)}$$

where $d\sigma_i/d\Omega$ is the mean differential cross section for each element. In the case of the analysis with the ^{32}S and the ^{19}F beam, $d\sigma_{In}/d\Omega$ represents the scattering cross section for S and F scattered by In, respectively.

For several InN films grown by RPECVD, Fig. 2 shows the nitrogen-to-indium ratios η as a function of fluence ϕ during the ERD analysis. In the case of the ^{197}Au and the ^{109}Ag beam the ratio η decreases with ϕ. Since the indium content remains unchanged during ERD analysis, the decrease in η is due to the depletion of nitrogen from the film. The observed depletion is faster at the small fluences. The rate of depletion is faster for the ^{197}Au than for the ^{109}Ag beam.

The exposure with similar fluences of ^{32}S ions also results in the depletion of nitrogen from some InN films. However, in this case the depletion rate is much lower than that for the ^{197}Au or the ^{109}Ag

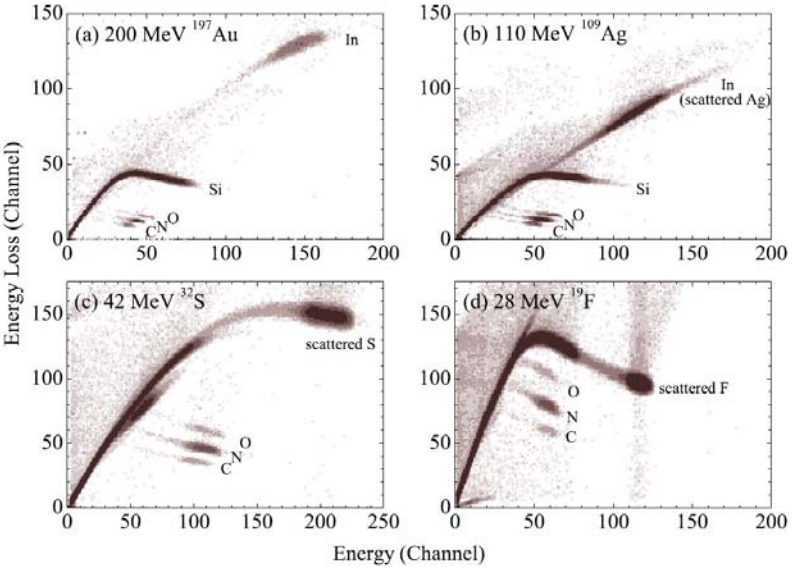

Fig. 1. Typical two-dimensional spectra from the ERD analysis of InN films grown on Si with RPECVD using (a) 200 MeV ^{197}Au (b) 110 MeV ^{109}Ag (c) 42 MeV ^{32}S and (d) 28 MeV ^{28}F projectile ions. Groups of events associated with different elements are labelled. Dark regions correspond to high count rates.

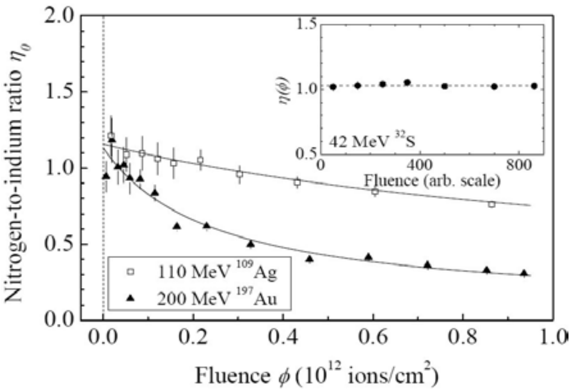

Fig. 2. Nitrogen-to-indium ratios $\eta(\phi)$ for InN films grown by RPECVD versus projectile fluence ϕ during ERD analysis with 200 MeV ^{197}Au, 110 MeV ^{109}Ag and 42 MeV ^{32}S projectile ions. The solid curves are the best fits with the bulk molecular recombination model. In the inset the dashed-line represents the average value of the nitrogen-to-indium ratio.

beam. Importantly, nitrogen depletion can be avoided for good quality films as it is shown in the inset of Fig. 2. Although nitrogen depletion was absent during the analysis with the ^{19}F ions, the composition could not be measured since for the selected energy the recoil cross sections are not in the Rutherford regime.

Where depletion of nitrogen did not occur, the film composition has been calculated directly from the ERD data using Eq. 1. In the case of depletion, the ratio $\eta(\phi)$ has been fitted with the bulk molecular recombination model to obtain the original nitrogen-to-indium ratio η_0 and then the film composition has been derived. It has been demonstrated in previous work that with this approach η_0 can be measured with an accuracy of ± 3% [6].

Nitrogen-rich indium nitride

The nitrogen-to-indium ratios η_0 of InN films, as obtained with ERD analysis, are plotted in Fig. 3. The η_0 for the films grown by RF-sputtering are in the range of 0.98 to 1.32. The film with $\eta_0 = 0.98$ has an oxygen content of about 26%. Thus it is possible that some of the oxygen is in the form of In_2O_3 and the actual InN is still nitrogen-rich.

The η_0 for the films grown by RPECVD are in the range of 1.01 - 1.69. Considering experimental uncertainty, two of the films may be stoichiometric, whereas all others have excess nitrogen. Importantly, the η_0 for the films from this growth has been found to be correlated with the growth temperature. The films grown below 400 °C are very nitrogen-rich, with $\eta_0 = 1.69$ for the film grown at 200 °C. In contrast, the films grown at higher temperature are close to stoichiometric with $\eta_0 = 1.01 - 1.06$.

The nitrogen-to-indium ratio in the films grown by Molecular Beam Epitaxy (MBE) ranges from 1.02-1.07. Considering the uncertainty, one of the films may be stoichiometric, whereas all others are nitrogen-rich. For the films grown by Metalorganic Chemical Vapour Deposition (MOCVD), the η_0 is in the range of 0.94 - 1.07. However, XRD and SEM have shown that the films with excess-indium have metallic In inclusions.

These data suggest that with all growth techniques nitrogen-rich InN material is obtained. The nitrogen-to-indium ratio excess of unity was unexpected since nitrogen vacancies and therefore nitrogen deficient material has been believed to be the source of donors producing the high conduction electron concentration observed for InN materials. Indeed, the InN films grown by RF-sputtering studied here have been found to have electron concentrations of more than 10^{19} cm^{-3} [12]. When grown in conditions

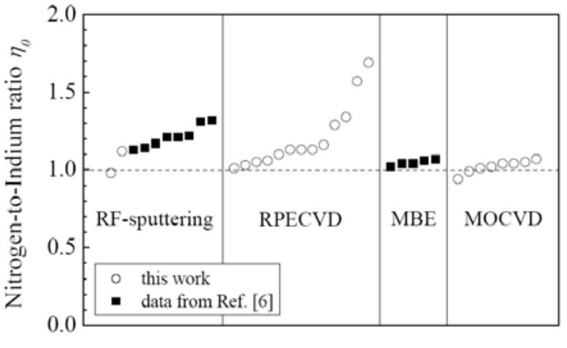

Fig. 3. Nitrogen-to-indium ratios η_0 for InN films from different growth techniques as measured with ERD.

of thermal equilibrium nitrogen loss is an inescapable consequence of film growth for InN. However, film growth by RF-sputtering does not occur in thermal equilibrium because of the high-energy ions created in the RF nitrogen plasma. Film growth by other techniques may also not occur under thermal equilibrium [12]. Highly nitrogen-rich InN grown by RF-sputtering may also be due to an over-nitrided sputter target.

Because of the fact that InN films, in general, have excess nitrogen, the common assertion that the observed high background concentration of electrons is due to nitrogen vacancies is difficult to explain. It may be speculated instead that indium vacancies exist or that nitrogen atoms occupy indium sites. This would be consistent with recent work by Laakso et al. [13] who have reported the presence of indium vacancies in InN films grown by MBE. Alternatively, the excess nitrogen may be on substitutional indium-sites. For InN films with a high level of excess nitrogen it may also be speculated that some of the excess nitrogen exists in molecular form interstitially or in voids.

Conclusions

Indium nitride films grown with a variety of techniques have been analysed with ERD using different projectile ions such as 200 MeV ^{197}Au, 110 MeV ^{109}Ag and 42 MeV ^{32}S. With this technique, all elements in the films can be simultaneously identified. Rapid and non-linear nitrogen depletion during the ERD analysis with very heavy ions, for example ^{197}Au or ^{109}Ag, is an issue for the correct and precise determination of the stoichiometry of InN films. However, the use of a gas ionisation detector with a large solid angle enables this depletion to be monitored as a function of incident projectile fluence. The depletion of nitrogen during the ERD analysis can be avoided by using a low-Z projectile. Experimental results have shown that the use of 42 MeV ^{32}S ions does not result in nitrogen depletion from films with acceptable stoichiometry and good crystal structure.

The InN films analysed have been found to have excess nitrogen, irrespective of the growth technique. For some types of film nitrogen excess is as high as 69%. This raises doubt about the common assertion that the observed high background concentration of electrons is due to nitrogen vacancies. It may be speculated instead that indium vacancies exist or that nitrogen occupies indium sites. Some of the additional nitrogen may also exist in molecular form interstitially or in voids.

Acknowledgment

The authors gratefully acknowledge technical support from the Department of Nuclear Physics at the Australian National University.

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