Hydrogen In Group-III Nitrides: An Ion Beam Analysis Study

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Abstract. The doping mechanisms of InN, a promising material for novel optoelectronic and electronic devices, are still not well understood. Unintentional hydrogen doping is one possibility that could explain the unintentional n-type conductivity in high-quality nominally undoped InN films. We measured a series of state-of-the-art InN samples grown by molecular beam epitaxy with 2 MeV 4He-ERDA and RBS, showing the presence of relatively high amounts of hydrogen not only at the surface, but also in a deeper layer. Strong depletion of hydrogen due to the analyzing beam was observed and taken into account in the analysis. Here, we report on the details of the analysis and show how the results correlate with the free-electron concentrations of the samples.

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INTRODUCTION

InN and related group-III-nitride alloys are key materials for contemporary and future optoelectronic and electronic devices such as high-brightness blue and white LEDs, multi-junction solar cells, high-frequency transistors, THz emitters and chemical sensors [1,2]. The doping mechanisms of InN are however still not well understood, and the origin of the unintentional n-type conductivity in InN is strongly debated. Unintentionally introduced hydrogen is a possible source of doping but until very recently it was believed that the amount of H in high-quality undoped InN films is insufficient to explain the observed free electron concentrations.

We measured a series of state-of-the-art InN samples grown by molecular beam epitaxy (MBE) with elastic recoil detection (ERDA) and Rutherford backscattering (RBS). Strong depletion of hydrogen due to the analyzing beam was observed, and taken into account in the analysis. For that purpose, consecutive spectra were collected, and the results were interpreted with the bulk molecular recombination model (BMR) of Adel et al. [3], allowing us to determine the initial and final concentration of hydrogen. The presence of relatively high amounts of hydrogen not only at the surface, but also in a deeper layer, is demonstrated and quantified. Here, we report on the details of the analysis, and show how the results correlate with the free-electron concentrations of the samples.

EXPERIMENTAL DETAILS

State of the art unintentionally doped InN films with (0001) orientation (c-plane) and different thicknesses, from 350 nm to 1600 nm, were grown by MBE on sapphire substrates. Different buffers were used, including GaN buffer layers [4], GaN templates [5], and low temperature InN buffer layers [6].

ERDA experiments were made using a 2 MeV 4He beam at 12º incidence with the surface of the sample. The Si surface barrier detector was located at a 24º scattering angle, so the outgoing angle is also 12º. Full experimental details are given elsewhere [7]. The depth resolution was around 35 nm at the surface, allowing us to clearly distinguish different layers within the depth probed.

The set-up had initially a 10 μm Kapton stopping foil. The large amount of 4He beam particles that was forward scattered and stopped on the foil created hydrogen recoils in the foil, that were detected and led
to a fairly large low energy background which reduced drastically the sensitivity to hydrogen in layers below the surface [8]. Therefore we replaced the Kapton by an 8 μm aluminium foil. RBS spectra were collected simultaneously with the ERDA, using a Si surface barrier detector located at a 160º scattering angle in the Cornell geometry. The beam was defined via a slit system. The beam height is fixed to be 0.6 mm, while its width can be adjusted between 0.2 and 1 mm. The area of the beam spot, necessary to calculate the beam fluence, was measured before each experiment by observing the beam spot on a Mylar foil.

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To study the depletion of hydrogen due to the analysing beam, spectra were collected consecutively in the same spot. While one spectrum for a given collected charge was stored, the beam was stopped by means of a shutter, so all the damage occurred during the actual measurements. From each sample, several spots were normally measured in this way. In total, 90 spots from 16 samples were measured, leading to many hundreds of spectra. We measured samples with different growth directions and present here the data for five c-plane samples. While H-incorporation in non-polar samples seems to show slightly different behaviour, the experimental aspects of the ERDA measurements including out-diffusion are comparable for differently oriented InN.

![Figure 1](image1.png)

**FIGURE 1.** a) RBS and b) ERDA data for one InN sample irradiated with a fluence of 13.1×10^{15} 4He/cm². For the ERDA, the simulations calculated with NDF and the Monte Carlo code are nearly indistinguishable.

RESULTS AND DISCUSSION

We show in Fig. 1 the RBS and ERDA spectra collected for a c-plane sample for a fluence of 13.1×10^{15} 4He/cm², the highest value for this given sample. Two separate regions are clearly distinguished in the ERDA data: a surface layer around 50 nm thick, containing high amounts of hydrogen, and a deeper sub-surface layer extending to the largest depth probed, with much less hydrogen.

The RBS data is used to determine the collected charge and thus normalise the ERDA data. This process relies on the known dead time corrections of the RBS and ERDA spectra; on an accurate calculation of pile-up [9], which changes the observed yield; and on the stopping power of 4He in InN. Given that using SRIM with the Bragg rule may lead to fairly large inaccuracies, we used experimental values for the stopping power that we measured for this purpose [10].

The data were analysed with the code NDF, which is capable of performing automated fits [11,12]. The maximum depth accessed by the experiment is ≈230 nm. For such depths the spectra collected for the initial low beam fluences have low statistics, with less than 1 count per channel on average. In this case, a χ² minimisation of the distance between the simulated curve and the data is very sensitive to the exact number of counts in each channel, and can easily lead to differences between the integral simulated and observed yield around 10%. Therefore, to analyse the data, first we made an automated fit that led to a good first approximation. Then, we manually adjusted the hydrogen content of the surface and of the deeper layer in order to obtain the same simulated and experimental total yield in the surface peak and in the low energy region, respectively.

![Figure 2](image2.png)

**FIGURE 2.** Hydrogen depth profile obtained by a direct conversion from the data using the known cross sections.
FIGURE 3. a) Surface hydrogen areal density and b) hydrogen concentration in the sub-surface region for one given InN sample as a function of the $^4$He fluence. The solid lines are the fits using the bulk molecular recombination model.

The simulations included the effect of double scattering events [8], which lead to a low energy background that must be considered in order to determine quantitatively the low hydrogen concentrations below the surface. To check the accuracy of the simulations made, we used the Monte Carlo code CORTEO [13], that intrinsically includes effects such as higher order plural scattering and multiple scattering, that can have an important influence on the result, at least in some experimental conditions such as ERDA with heavy ion beams [14]. The simulation obtained for the exact same depth profile as obtained with NDF is also shown in Fig. 1b). It is extremely close to the NDF simulation, which is about 3 orders of magnitude faster even including the dual scattering calculation, validating its results.

The hydrogen profile derived from the ERDA data in Fig. 1 is shown in Fig. 2. In this case, each data point was directly converted into a concentration value simply by using the known scattering cross section [15], after subtraction of the background due to double scattering and pile-up.

The hydrogen surface areal density and the hydrogen concentration in the $\approx 230$ nm thick layer below the surface are shown in Fig. 3 as a function of the beam fluence. Initially, there is a rapid decrease of the hydrogen content, which then stabilises. We analysed the data with the BMR model [3], which is based on the assumption that hydrogen effusion is due to breaking up hydrogen bonds due to the energy deposited by the beam, leading to recombination into H$_2$ molecules that easily escape the sample. According to this model the data points in Fig. 3 were fitted using equation

$$\rho(\Phi) = \frac{1}{1/\rho_f + (1/\rho_0 - 1/\rho_f) \exp(-K\Phi)}$$

where $\rho_0$ and $\rho_f$ are the initial and final hydrogen concentrations and $K$ is an effective molecular release cross section.

The BMR model has been previously applied to depletion of nitrogen in InN films irradiated with heavy ions [16]. In the same work, it was shown that nitrogen depletion only occurred for irradiation with ions as heavy as Ag or Au, and was not observed for irradiation with F and S beams. Therefore, we do not expect any loss of nitrogen due to irradiation with $^4$He. Furthermore, $^{35}$Cl-ERDA measurements on some samples have shown a N to In ratio very close to 1 within errors [17].

From the BMR model analysis we determine, for this sample, the release cross section, which is the fundamental parameter in the BMR model, to be $K=3.5$ Å$^2$ for depletion from the surface, and $K=5.2$ Å$^2$ for depletion from the deeper layer. These values have a large error due to the uncertainty in the beam cross section. Also, there is a fairly large variability, within a factor of 2, in the K values determined for different c-plane InN films, and even for different spots of the same sample. Nevertheless, the range of values obtained is of the order of magnitude expected [18,19].

We also determine the initial and final hydrogen concentration in the deeper sub-surface layer, to be 1.8 and 0.45 at.%, respectively. Large variations from sample to sample were observed, depending on the crystal orientation. Typically, c-plane films show final bulk concentrations from 0.2 to 0.45 at%. We note that, in different spots of the same sample, we have measured variations of up to 30%, which can be due to slightly different conditions of the sample surface.

We show in Fig. 4 the dependence of the bulk free electron concentration on the hydrogen concentration of the sub-surface layer in c-plane InN, showing scaling between the bulk electron concentration and the H concentration measured at depths extending to 230 nm. In Fig. 4 we used the hydrogen concentration with the highest charge corresponding to a fluence where out-diffusion already saturated since here the uncertainty is easier to estimate than for the initial point which relies on the validity of the BMR model and is subject of high statistical error. In fact, according to the BMR model hydrogen release ceases if H atoms are separated by more than a characteristic recombination distance. However, this would mean...
FIGURE 4. Bulk free electron concentrations vs. hydrogen concentration in the sub-surface region. The value for the film with the lowest free electron concentration represents the difference between hydrogen and carbon concentrations in the film [17].

derived from the last measured point that the saturation level should be the same for all InN samples, which is not observed, indicating that the BMR model may not be applicable to the present case despite the good fit to the experimental data and the reasonable values for the effective molecular release cross section $K$. The varying final hydrogen concentration for different samples suggests different incorporation sites for H in the InN lattice and out-diffusion takes place preferentially for weakly bonded H, possibly H decorating dislocations or grain boundaries. Also the presence of $H_2$ molecular hydrogen in the samples cannot be excluded. Assuming that higher out-diffusion takes place for samples with higher H concentrations the correlation of H vs. free electron concentration would be even more pronounced if the initial H-concentrations could be used. Our findings thus support the important role of unintentional hydrogen doping in the n-type conductivity of InN films [20].

SUMMARY

We studied the hydrogen content of MBE grown InN with ion beam analysis techniques, namely RBS and ERDA with a $^4$He beam. Strong depletion of the hydrogen content under the analysing beam was observed and a careful analysis of the data was necessary to obtain the hydrogen concentration. Two regions are clearly observed, one at the surface (up to 50 nm depth) with very high amounts of hydrogen, that are likely to be due to surface contamination, and a sub-surface region extending at least to the observable depth of around 230 nm, with smaller hydrogen concentrations, around typically the 1 at.% order of magnitude.

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