

Perturbed angular correlation spectroscopy of implantation-damaged indium nitride

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Introduction

Indium nitride (InN) is an important III-V semiconductor with many potential applications such as in high frequency transistors and laser diodes. The mobility, peak drift velocity and the saturation velocity of InN are predicted to be extremely high and superior to that of GaN [1]. Recently there have been reports suggesting that the band gap of this material could be as low as 0.7 eV [2] and that the band gap of the ternary compound $\text{In}_{1-x}\text{Ga}_x\text{N}$ ($0 \leq x \leq 1$) may be tuned to cover the whole of the visible spectrum. However, the magnitude of the electronic band gap of InN is still under debate and film growth is difficult due to the low dissociation temperature of InN. Furthermore, there are suggestions that the identification of the electronic band gap may be obscured by the presence of indium clusters in the material [3].

Indium nitride films, as grown, are generally found to be n-type, which is widely attributed to nitrogen vacancies. In order to make a p-n junction p-type material has to be also available. This is commonly achieved through doping by ion implantation. Information on ion implantation induced damage and annealing is limited [4]. The perturbed angular correlation (PAC) method, using the radioisotope probe $^{111}\text{In}/\text{Cd}$, is potentially an excellent technique to obtain such information. This technique can also identify even very small indium clusters because of its sensitivity to the local lattice environment.

For PAC spectroscopy, a radioisotope is introduced into the material as the probe. The directional correlation of the emitted γ -rays can then be detected providing information about the local electromagnetic fields in the immediate vicinity of the probing nuclei. These are a measure of the nature and crystallinity of the material. Although radioisotopes can also be introduced into a material by diffusion, the controlled ion implantation of a radioisotope probe has several advantages. They include accurate dosimetry of the number of probing nuclei and a high degree of control over the implantation depth.

With the exception of one study [5], no PAC data are available for InN films. In this work, indium nitride thin films have been implanted with the radioisotope probe $^{111}\text{In}/\text{Cd}$ as $^{111}\text{InO}^-$ ions. PAC spectroscopy has been performed on the implanted films and following annealing.

Experimental details

Two different types of InN films were studied in this work. The first set of films was grown using radio-frequency (RF-sputtering) reactive ion sputtering of a metallic indium target in a N_2 atmosphere [6]. These films were grown on glass slides over periods between one and two days. This resulted in oriented polycrystalline material. A transmission electron microscopy image of a typical film is shown in reference [7]. The c-axis of the columnar crystallites in these films is near-perpendicular to the substrate surface.

The second set of InN films was grown by Remote Plasma Enhanced Chemical Vapour Deposition (RPE-CVD) on sapphire substrates. Details of this growth system are given elsewhere [8]. The columnar structure of these films is evident from scanning electron microscope images. However, the diameter of the columns in this case is larger than that from RF-sputtering InN suggesting better crystallinity for RPE-CVD growth.

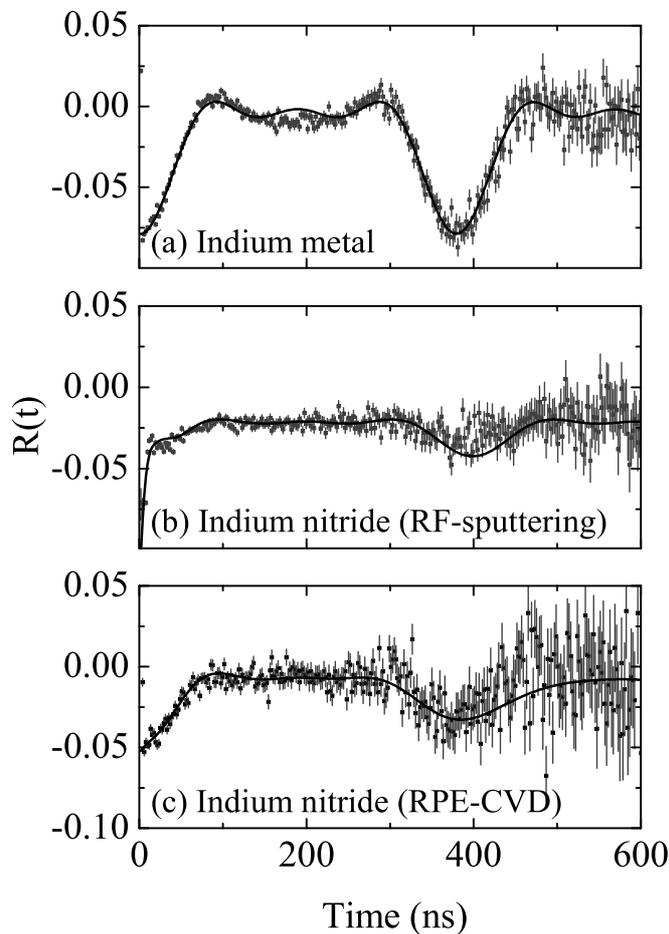


Figure 1: PAC spectra and fits for the $^{111}\text{In}/\text{Cd}$ probe in (a) an indium metal, (b) an InN film grown by RF-sputtering, and (c) an InN film grown by RPE-CVD. All measurements were performed in the as-implanted samples at room temperature.

X-ray diffraction on these films has verified the wurtzite structure of InN. The stoichiometry of these types of films has been precisely measured with heavy ion elastic recoil detection analysis showing that the films are slightly nitrogen-rich with nitrogen-to-indium ratios greater than unity [9, 10].

The radioisotope probe $^{111}\text{In}/\text{Cd}$ has been implanted into several InN films. The implantations were performed at the newly commissioned low energy radioisotope implanter at the Australian Defence Force Academy [12]. The probes were implanted as molecular $^{111}\text{InO}^-$ ions at an energy of 125 keV. The molecular $^{111}\text{InO}^-$ ion was chosen since the source output for this is three orders of magnitude larger than that for the elemental $^{111}\text{In}^-$ ion. The implantation depth of the probes, as estimated by SRIM [11], is 50 nm. The fluence of the implanted $^{111}\text{InO}^-$ ion was of the order of 10^{11} ions/cm 2 . Following the implantation the beam spot on all the samples was clearly visible as a discolouration of the film. This is due to the co-implantation of other ions with the same mass $A = 127$ with a measured approximate fluence of 2×10^{14} ions/cm 2 . The probe was also implanted into an indium metal sample for comparison.

PAC spectroscopy was performed using the conventional setup with four BaF_2 scintillation detectors [13]. For all measurements the c-axis of the InN films was aligned at 45° between two detectors. The anisotropy ratio function $R(t)$ was determined as described in reference [13].

The measurements were performed on the as-implanted films and after annealing at different temperatures. The RPE-CVD grown film was annealed for two minutes.

Results and discussion

Figure 1(a) shows the anisotropy ratio $R(t)$ measured for the indium metal sample. The data have been least square fitted with the appropriate theoretical perturbation function. The observed quadrupole interaction frequency of $\nu_Q = 16.6$ MHz is consistent with earlier measurements [14].

Figures 1(b) and 1(c) show the measured PAC spectra for the as-implanted InN films grown by RF-sputtering and RPE-CVD. These films show interaction frequencies in agreement with the result for indium metal. This is evidence for the presence of indium in both films. Using PAC spectroscopy, Lorenz and Vianden [5] have also reported the presence of indium clusters in an InN film grown by Plasma Induced Molecular Beam Epitaxy. In this case the film was implanted with $^{111}\text{In}^+$ ions. The implanted fluence is reported as 2×10^{13} ions/cm² which is also likely to include any parasitic beam of the same mass. After annealing the film they observed an interaction frequency of $\nu_Q = 153$ MHz with $\eta = 0.3$ which was interpreted as the $^{111}\text{In}/\text{Cd}$ probe on In lattice sites in InN.

The fit for the film grown by RF-sputtering, Fig. 1(b), indicates that about 16% of the probes are at the frequency corresponding to indium metal. The data for the film grown by RPE-CVD can be best fitted with a single frequency again corresponding to that of indium metal, see Fig. 1(c). The PAC results for both types of film indicate that in the implanted region the InN contains a large amount of metallic indium. This suggests that the observed discolouration after the radioisotope implantation is due to implantation-induced effusion of nitrogen from this region of the film. This is consistent with a previous study of a MBE-grown film, where exposure to a fluence of 5×10^{15} ions/cm² of mass $A = 127$ ions at 125 keV completely depleted the exposed region of nitrogen to a depth of 80 nm [4]. Importantly, a significant increase in the oxygen content has been observed in the implanted region due to the oxidation of metallic indium.

Figure 2 shows the anisotropy ratio $R(t)$ measured at room temperature for the InN grown by RPE-CVD after annealing at (a) 200 °C, (b) 400 °C, and (c) 600 °C, respectively. The spectra indicate the appearance of additional higher interaction frequencies which could be best fitted with hyperfine parameters ($\nu_{Q1} = 119$ MHz, $\eta_1 = 0.7$; $\nu_{Q2} = 154$ MHz, $\eta_2 = 0$) corresponding

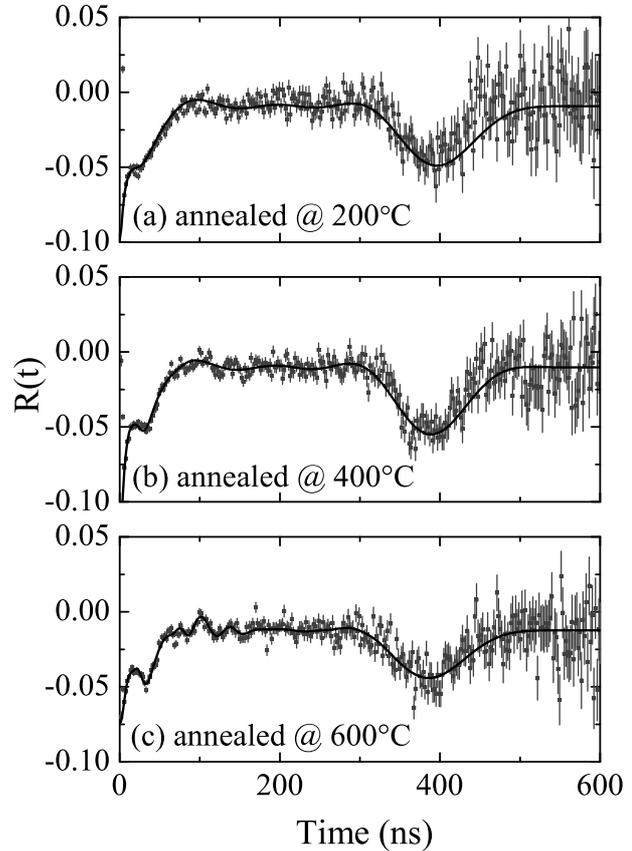


Figure 2: PAC spectra and fits for the $^{111}\text{In}/\text{Cd}$ probe in an InN film grown by RPE-CVD as measured after annealing at (a) 200°C (b) 400°C and (c) 600°C.

to ^{111}In probes in the indium oxide lattice [15]. With increasing annealing temperature the probe fractions corresponding to the higher interaction frequencies increase at the expense of the probe fraction corresponding to indium metal. The higher interaction frequencies are associated with a wide distribution of electric field gradients (EFGs) which indicate that the majority of the probe atoms are incorporated in highly distorted, non-unique environments in the lattice. For the wurtzite lattice, one should expect a vanishingly small EFG. The observed EFGs, however, are $6.08 \times 10^{21} \text{ V/m}^2$ (119 MHz) and $7.84 \times 10^{21} \text{ V/m}^2$ (154 MHz) which are an order of magnitude larger than the EFGs observed at Al and Ga sites in AlN and GaN, respectively [16, 17]. Hence the observed high interaction frequencies can be attributed to ^{111}In probes at indium sites of indium oxide lattice and seems to be consistent with elastic recoil detection analysis which showed complete depletion of nitrogen from the implanted region of an InN film and an increase in the oxygen content due to oxidation of the resulting metallic indium [4].

Conclusions

Indium nitride films have been implanted with the radioisotope probe $^{111}\text{In}/\text{Cd}$. The probe was implanted as molecular $^{111}\text{InO}^-$ ion. The PAC results have shown that nitrogen is depleted in the implanted region of indium nitride when implanted with mass $A = 127$ and energy 125 keV at a fluence of the order of $2 \times 10^{14} \text{ ions/cm}^2$. This is evidenced by observation of an interaction frequency corresponding to indium metal. With annealing, additional high interaction frequencies are observed. The magnitude of these frequencies are consistent with the previous observation by Lorenz and Vianden. In contrast to their interpretation, however, these interaction frequencies are attributed here to indium oxide. The indium oxide might have formed through the oxidation of the indium metal in the implanted region of the sample, which would be consistent with the results reported in reference [4].

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