EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Status Report to the ISOLDE and Neutron Time-of-Flight Committee

IS630: Lattice sites, charge and spin states of Fe in $In_xGa_{1-x}N$ studied with emission Mössbauer spectroscopy

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Abstract

The ability to tune physical properties of binary group III-nitride semiconducting materials by alloying has opened a range of applications that include commercial full colour light emitting diodes, laser diodes, solar cells and high-power field effect transistors. Moreover, the incorporation of transition metal dopants in these materials has been employed to realize semi-insulating substrates and, more recently, has been envisaged for applications in spintronics and quantum information devices.

To date, a suite of temperature- and angle- dependent emission Mössbauer spectroscopy measurements following ^{57}Mn ($T_{½}$ = 1.5 min.) implantation have been undertaken as part of our project. The main focus is to investigate the nature (lattice location, charge and spin states) of Fe in $In_xGa_{1-x}N$ for $0 < x < 1$. The results of the preliminary data analysis show a decrease in the site population of magnetic contributions (sextets) with increasing x in these materials. This is accompanied by the evolution of a single line component, the nature of which remains one of the objectives of this project to unravel in addition to identifying Fe in different lattice sites and the effect dopants in nitrides ternary semiconductors. Comprehensive data analysis is current being undertaken.

A brief motivation, highlights of the preliminary results and several future experiments on virgin and doped (during growth and by ion implantation) $In_xGa_{1-x}N$ samples are planned to address outstanding questions which are discussed in this report together with additional complementary studies current underway at home institutions.

Remaining shifts: 4 shifts, (~1-2 runs ~ 2 years)

1 Introduction and a brief motivation

InGaN is a direct bandgap ternary semiconductor derived from two binary III-nitrides, InN and GaN, which is stable in the wurtzite structure [1]. The significance of InGaN alloys as active layers in optoelectronic devices emanates from the ability to change the relative abundance of Ga/In. This is accompanied by changes in the physical properties resulting in the possibility of tuning the band gap of $In_xGa_{1-x}N$ through the visible part of the spectrum. A summarised version of the motivation, with parts extracted from the proposal, is discussed.

Over the years, the exploitation of InGaN in optoelectronic devices and photovoltaics has been hampered by challenges imposed by the necessity of increasing the indium content [2]. In addition, similar to the binary constituents, GaN and InN, a critical issue has been *p*-type doping in $In_xGa_{1-x}N$ since the introduction of metallic elements such as Zn and Mg during growth has been observed to hinder acceptor doping due to the formation of complexes with hydrogen. Post-deposition thermal annealing in order to dissociate these complexes has proven useful in enhancing the release of free holes [3, 4]. In spite of $In_xGa_{1-x}N$ (mostly Ga rich) being used in actual commercial devices, basic knowledge of dopant lattice sites, their charge states and the formation of defects in $In_xGa_{1-x}N$ is still required to improve the efficiency/lifetime of current devices and expand its range of applications.

More importantly, intentional incorporation of Fe in nitrides has been employed to achieve semi-insulating buffer layer of GaN for high-electron mobility transistors [5]. Recent prospects for use include applications in spintronic devices [6] and in addition as spin qubits for quantum information processing [7]. The potential magnetic effects, charge and spin states of Fe impurities in GaN following ^{57}Mn* implantation in the temperature range, 100 – 800 K have been studied [8] using emission Mössbauer spectroscopy (eMS). The room temperature spectrum was analysed in terms of two main spectral components with the following assignments:

- high-spin Fe^{3+} on substitutional Ga sites showing slow paramagnetic relaxations, evident as magnetic structure (Fe_{Mag}) on the wings of the spectra as observed in ZnO [9, 10],
- high-spin Fe^{2+} on substitutional Ga crystalline sites (Fe_C), where the Fe^{2+} state is stabilized by nitrogen vacancies (V_N)[8].

The InN spectrum clearly revealed significant differences compared to $Al_xGa_{1-x}N$ [11] (including, GaN, $x = 0$), which forms the basis of the experiments initially proposed, most significantly, no magnetic structure on the wings of the spectrum. The initial analysis of the InN data required three spectral components; their tentative assignments are discussed in detail below, together with a comprehensive description of these differences and the prospective experiments required to fully understand the findings we observe in these materials. These are summarized here;

- The absence of magnetic features on the wings of the spectrum, as observed in $Al_xGa_{1-x}N$ suggesting the non-existence of high spin Fe^{3+} in InN. Instead, there is a single line (SL), a similar spectral component is evident in the Mn pre-doped $Al_xGa_{1-x}N$ [11] data which is tentatively attributed to Fe^{4+}. This could be interpreted as a consequence of acceptor-type defects created during the implantation process and suggest an alternative way of obtaining *p*-type doping in this system.
- The straightforward interpretation of the quadrupole-split doublet (Fe_X) with reference to the $Al_xGa_{1-x}N$ results is to assign this spectral component to Fe^{2+} stabilized by nitrogen vacancies. However, the observed isomer shift ($\delta_{RT} \sim 0.27$ mm/s) is too low to justify this interpretation. For covalent Fe^{2+} on In sites, one would expect $\delta_{RT} \sim 0.7$ mm/s. As indicated in the proposal and explained in detail, alternative explanations could include: (i) fast relaxing high-spin Fe^{3+}, (ii) low-spin Fe species, (iii) high-spin Fe^{2+}, or (iv) due to interstitial Fe.
- Moreover, an additional component, Fe_Y was required to fit the spectral feature at $v \sim 0.83$ mm/s. The right leg of this component is not immediately observable, as it falls under the more intense single line component. However, representing this by a doublet (as in GaN) with the isomer shift restricted to around 0.7 mm/s, results in the identification of this component as due to high-spin Fe^{2+}, presumably stabilized by V_N's in the neighbourhood of the probe atom. While this is the low intensity component in InN, it seems to be the dominating component in GaN, which could suggest that V_N is mobile in InN, while it is a stable defect in GaN [8].

2 STATUS OF EXPERIMENTS

2.1 Preliminary Results

As initially proposed, experiments M1, M3 and M4 have been carried out utilising ^{57}Mn ($T_{½}$ = 1.5 min.) and initial results are briefly discussed.

[M1] *Temperature series of ^{57}Mn eMS measurements*, for x = 0.03, 0.09, 0.16, 0.30 and 0.35 were undertaken at the low and high temperatures. Figure 1 shows RT spectra obtained from temperature series experiments measured for different concentrations of indium (x) together with the binary semiconducting materials. From visual inspection, there is a clear decrease in the contribution of the magnetic features located on the wings of the spectra with increasing indium composition. Furthermore, the nature of the dominant doublet seems to change in terms of asymmetry of the left and right peaks. This was initially attributed to Fe atoms in the 2+ state associated with nitrogen vacancy related defects (Fe_C) [8, 11]. Temperature dependence of the hyperfine parameters of Fe_C for low indium compositions mirrors that of GaN and AlGaN systems and analysis of higher In compositions is ongoing.

[M3] *^{57}Mn Angle dependent eMS measurements*, where samples are measured at different emission angles relative to the crystal axis. This method can easily distinguish between Fe in amorphous regions due to the implantation damage (no angular dependence) and Fe on regular lattice sites in non-cubic materials (angular dependence) [12]. Comprehensive analysis of the angle dependence data will give insights on the nature of Fe_X.

[M4] *^{119}In ($T_{½}$ = 2.1 min):* High temperature measurements on samples with concentration x = 0.16 and 0.30 were carried out and data analysis is current underway.

The limitations on outstanding experiments, M2 and M5 which were previously proposed will be discussed in the next section together with crucial planned experiments required to gain a deeper understanding of the lattice location and nature of the SL, Fe_X and Fe_Y components.

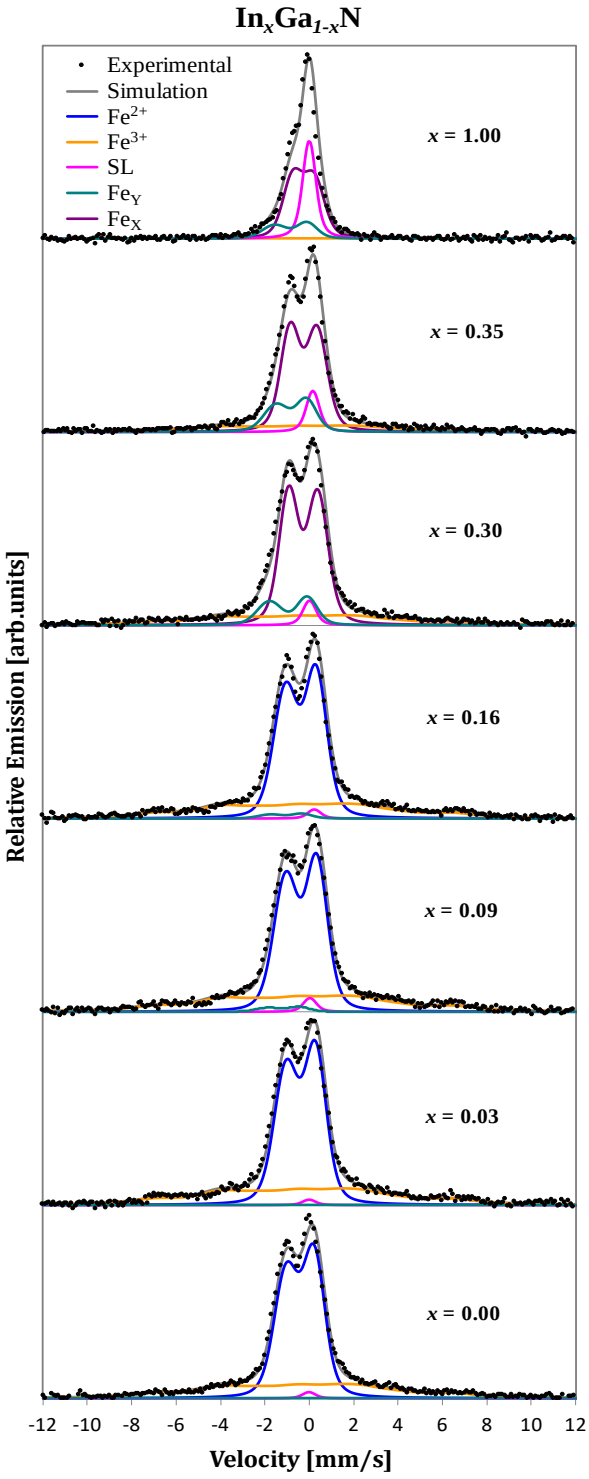

Fig 1: Room temperature eMS spectra of $In_xGa_{1-x}N$ obtained at an emission angle (θ_E) of 60° for values of x indicated.

3 REMAINING SHIFTS AND PLANNED EXPERIMENTS

The site population of the spectral components at room temperature as a function of indium (In) concentration are shown in Fig 2, obtained from the preliminary analysis, limited by the unavailability of samples with high In concentrations. The nature and behaviour of the single line (SL) becomes prominent at the expense of the magnetic features for higher indium composition.

3.1 Si, Mn and Mg doping

Central to the study is the possibility to ascertain the nature of the single line component and the effectiveness of *p*-type doping. eMS investigations with Si doped AlGaN samples [11], (since Si know as a donor in nitrides) have been carried out. The introduction of donor impurities is expected counteract the evolution of the single line and confirm the *p*-type conductivity hypothesis. As-grown samples doped with 0.5 at.% of Si will be prepared for a selected values of indium composition, *x*.

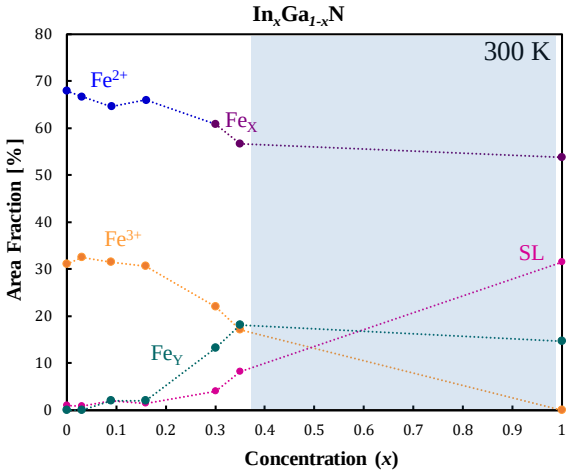

Fig 2: Area fractions of fitted components in $In_xGa_{1-x}N$ extracted for values of x indicated.

Due to limited samples with higher indium content (shaded region), an attractive alternative is to pre-implant ^{29}Si (offline) in InN with similar concentration of 0.5 at.%. This will be followed by eMS measurements at ISOLDE. Furthermore, a control virgin sample of InGaN will also be implanted with similar ^{29}Si concentrations to compare with as-grown samples and at the same time investigate the effects of pre-implantation. ^{29}Si is preferred instead of ^{28}Si to limit or avoid N_2 contamination during the implantation process. These implantations will be undertaken at KU Leuven in 2020.

Moreover, similar to the AlGaN systems, a number of as-grown InGaN samples with Mn and Mg dopants will be prepared for M1, M3 and M4 measurements to investigate the role of Mn and Mg in InGaN. Mg is a well-known dopant for achieving *p*-type conductivity in nitrides.

3.2 Outstanding Experiments

Some specific details on outstanding M2 and M5 experiments are discussed here, these have not been implemented. A modified set-up will be required to comply with future safety requirements to achieve M2 and the remaining 4 shifts will not allow for comprehensive studies. These experiments can offer additional insights:

[M2] *Rapid-cooling experiments (^{57}Mn)*, where samples are rapidly cooled to liquid nitrogen temperatures (~110 K) [13], immediately after implantation at temperatures ≥ 300 K. The eMS measurements at this temperature present an ability to study low temperature effects which are usually desired after high temperature implantations. This approach can be used to address the effects of mobile defects and enable the determination of Debye temperatures which are useful to support spectral component assignments;

- the hypothesis that Fe_X is due to interstitial Fe can be addressed by rapid cooling experiments which allow for an unambiguous determination of Debye temperatures of the spectral components.
- if defect-free environments are formed upon implantation at elevated temperatures, rapid cooling will allow us to identify whether fast spin relaxation is a possible hypothesis.

[M5] *^{57}Co ($T_{½}$ = 272 d)*: An alternative approach and of interest depending on availability is the utilization of long lived ^{57}Co for ^{57}Fe eMS for specific concentrations (*x*). This allows for a wider range of external sample conditions and post treatment (for example annealing and irradiations) of samples than is possible with the short-lived isotopes (^{57}Mn and ^{119}In).

A separate proposal and a letter of intent could be submitted in future for these experiments, respectively.

3.3 Complimentary and future studies

[C1] *DFT calculations.* *Ab initio* density functional theory calculations for Fe in different lattice environments and charge states are currently being undertaken to complement the experimental work in InGaN and AlGaN systems. The basic theoretical technique employed in the project will be quantum-mechanical calculations in the framework of density functional theory (DFT). These are envisaged to complement and clarify:

- the charge state and location of the SL component observed in InN, InGaN and Mn doped AlGaN,
- whether Fe_Y is due to high spin Fe^{2+} stabilized by nitrogen vacancies.

Furthermore, the observed isomer shifts of Fe_C/Fe_X will be tested and/or compared with the empirical model developed from previous Mössbauer studies of different semiconducting materials [14].

[C2] *^{57}Fe and ^{56}Fe implantations:* For selected samples, based on the results from the online eMS measurements (M1-M3), conversion electron Mössbauer spectroscopy (CEMS) on samples co-implanted with ^{57}Fe and ^{56}Fe (< 5 at.%) and (to be carried out at the University of the Witwatersrand and KU Leuven). Furthermore, ^{56}Fe implantation of different fluences are also planned to investigate the effects of concentration on the magnetic effects and spin-lattice/spin-spin relaxations rates.

[C3] *Additional Characterisation:* a wide range of pre- and post-characterization techniques to investigate mainly structural, optical, magnetic and/or electrical properties are currently being undertaken at home institutions.

4 BEAM REQUEST/ISOTOPES

The focus of the upcoming experiments is to employ mainly ^{57}Mn for emission Mössbauer Spectroscopy for temperature series and angle dependent measurements on doped samples (as grown and implanted), and any available with higher indium concentrations in addition to rapid cooling measurements on selected concentrations.

Table 1: Summary of proposed experiments.

Task	Isotopes	Time (hrs)	Rationale
M1/M3	^{57}Mn	26	~ Si and Mn doped plus any new higher concentrations
Calibration	^{57}Mn	6	~20%, based on experience

Summary of requested shifts: 4

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