Compositional Studies of InGaN Epilayers and Magnesium−doped GaN Grown by MOVPE, Using Wavelength Dispersive X−ray Spectrometry

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Introduction

Indium gallium nitride ($In_xGa_{1-x}N$) alloys and p−type magnesium−doped GaN (Mg:GaN) form essential functional layers in III−nitride optoelectronic devices[1]. Challenges arise both in growth and characterisation of these materials[2]. The optical emission properties of $In_xGa_{1-x}N$ are governed by several factors: gross alloy composition, physical form of the material (eg. thin quantum well versus thick epilayer), and spontaneously formed nanostructure. This study concerns measurements of the composition of relatively thick $In_xGa_{1-x}N$ layers, which are complicated by strain originating from lattice missmatch between the $In_xGa_{1-x}N$ and underlying GaN buffer layers. We focus particularly on the correlation between composition and growth temperature. Meanwhile optimisation of Mg:GaN for electrical−injection light−emitting devices is also very dependent on accurate compositional analysis. Here methods are required to quantify magnesium atom concentrations, henceforth denoted as [Mg], in GaN in the <0.1 atomic percent range. In contrast to more ideal dopants, the relatively deep magnesium acceptor level in the GaN bandgap means that [Mg] values are ~100 times higher than achievable mobile hole concentrations.

Electron probe microanalysis using wavelength−dispersive X−ray analysis (WDX) is a technique with allows spatially−resolved quantification of the elements present in almost any beam−stable solid material. Although most commonly applied to bulk samples such as minerals, it is also an ideal method for characterisation of thin films. The application of WDX to $In_xGa_{1-x}N$ and Mg:GaN films offers advantages over alternative methods of compositional analysis. For example, inferences about the composition of $In_xGa_{1-x}N$ layers from luminescence spectroscopy and simpler types of X−ray diffraction study are complicated by the effects of strain, which may also vary with depth[3]. Currently the main measurement technique for [Mg] in Mg:GaN is secondary ion mass (SIMS) spectroscopy, which is both destructive and reliant on custom ion−implanted standards. WDX has not to our knowledge been applied to this problem before, but possesses adequate sensitivity, and can be calibrated using easily obtained standards.

Film growth and development of WDX procedures

$In_xGa_{1-x}N$ and Mg:GaN samples were grown on sapphire (0001) substrates, under conditions producing wurtzite−phase GaN/In_x $Ga_{1-x}N$ with (0001) orientation. A horizontal−flow, single−wafer Aixtron 200/4 RF−S MOVPE reactor was employed. Precursors were trimethylgallium (TMGa), ammonia, trimethylindium (TMIn) and magnesocene (Cp_2Mg). All metal sources were supplied by Epichem Metalorganics, and this study included comparisons of solid and solution TMIn and Cp_2Mg. The solid sources were used in reverse−flow bubblers. Solution sources were prepared by adding a high−boiling liquid amine and alkane to TMIn and Cp_2Mg respectively.

Procedures for growth initiation on sapphire, heteroepitaxial growth of ~1 µm undoped GaN layers, and reflectance−based measurements of growth rates and film thickness, were as described previously[4]. $In_xGa_{1-x}N$ layers typically ~200 nm thick were grown onto GaN buffers, at temperatures between 760 and 882°C. Precursor flow rates were 14.2 µmol/min for TMIn, 22 µmol/min for TMGa, and 0.22 mol/min for ammonia, while the growth ambient was nitrogen. Mg:GaN was grown on similar buffer layers, but in a hydrogen ambient, at a standard temperature of 1130°C. Cp_2Mg flow rates were varied, with standard TMGa flow rates of 53µmol/min,

and ammonia flow rates of 0.055 mol/min. GaN buffer layers, Mg:GaN and $In_xGa_{1-x}N$ were all grown at 200 mbar pressure. Mg:GaN doped samples were treated after growth by a rapid thermal annealing process, to increase their conductivity and minimise charging during WDX.

WDX studies were conducted using a Cameca SX100 electron microprobe analyser, equipped with three X−ray spectrometers[5]. $In_xGa_{1-x}N$ analyses employed conditions described previously, using the L_{alpha} X−ray peaks of indium and gallium, plus the nitrogen K_{alpha} peak for full quantification. InAs and GaN samples were used for standardisation. Measurement of [Mg] in Mg:GaN used the magnesium K_{alpha} peak, and standardisation methods as discussed below. A thallium acid phthalate (TAP) diffracting crystal, with 2d = 2.575 nm, was employed. Both $In_xGa_{1-x}N$ and Mg:GaN analyses were concerned with determining average compositions over beam illumination areas of ~160 nm diameter, although other studies indicate lateral inhomogeneities are detectable in $In_xGa_{1-x}N$ layers similar to those examined[6]. Rutherford backscattering (RBS) measurements of composition were made over large area compared to the WDX analyses, under conditions discussed elsewhere[7].

The thickness of thin−film samples is a very important consideration in WDX. This study assumed all film surfaces to be ideally planar, although atomic force microscopy indicates significant texture in the case of $In_xGa_{1-x}N$ samples[4]. For our $In_xGa_{1-x}N$ layers the typical thickness was 200 nm, and for Mg:GaN layers it was 1 µm. To make accurate quantitative analyses, the accelerating voltage must be selected so as to confine the electron beam within the depth of interest, while simultaneously exciting emission of the X−rays required. Measurement conditions were selected with the aid of Monte−Carlo simulations of electron trajectories. At 6 kV the penetration depth is ~160 nm, and at 10 kV it is ~400 nm, making these voltages suitable for the $In_xGa_{1-x}N$ and Mg:GaN samples respectively. For $In_xGa_{1-x}N$ analyses, the beam current was 20 nA. This was increased for Mg:GaN to 30 nA, to obtain better signal to noise ratios.

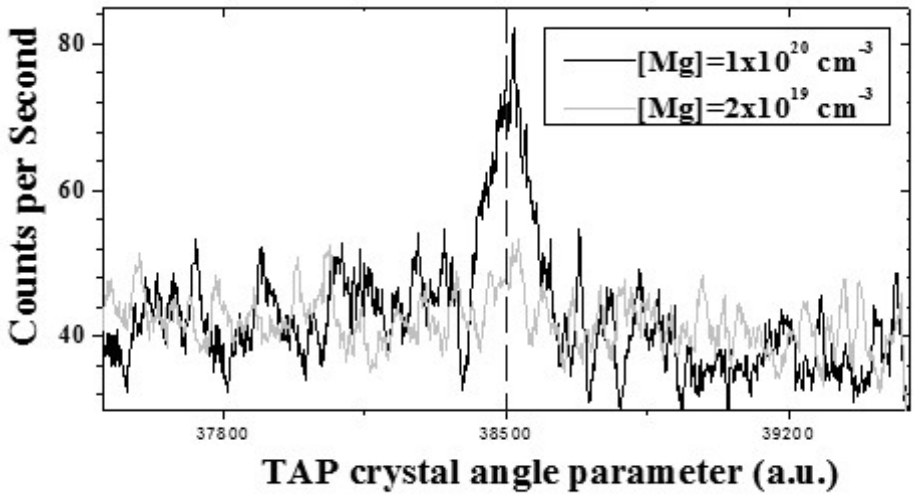

Figure 1 -WDX scan through Mg peaks with short collection time

Application of WDX to measurements of the dopant element in Mg:GaN requires particular care in choice of analysis conditions. The low magnesium concentrations dictate long scan times over the magnesium K_{alpha} region in order to obtain adequate peak to background ratios. Fig. 1 illustrates spectra obtained under identical conditions from light−emitting diode (LED) structures in which [Mg] differs by a factor of ~5. These data highlight the need for careful background subtractions. This scan is a qualitative analysis consisting of 1000 points with a short collection time for each point. Quantatative analysis involves recording the signal counts from only the peak position and background points either side of the main peak for a longer period time to increase the signal to noise ratio. Selection of magnesium standards is also an important issue. MgO has been adopted in this work, although its non−conductive character requires that it must be carbon−coated to avoid charging, and this factor allowed for in Mg:GaN analyses. Results discussed below have also been checked by analysis of a Mg:GaN sample examined

by SIMS, doped to ~2 x 10^{19} cm^{-3} .

Illustrative WDX results

Fig. 2 shows the measured indium contents in a range of $In_xGa_{1-x}N$ epilayers grown over more than two years. Circular datapoints were obtained by WDX, while triangular datapoints were measured by another technique unaffected by strain, RBS. There is a robust trend between the indium content and growth temperature, which is fitted to a straight line on the plot. Where samples have been analysed by both WDX and RBS, there is good agreement between the techniques. Samples grown both with solid and solution TMIn lie on the same trend line, indicating effective saturation of the carrier gas passing through the bubbler in each case. The scatter in the data is thought to be mainly attributable to changes in precise growth conditions, associated with reactor hardware changes, rather than errors in compositional measurements. The ability to control indium content by systematic changes in growth temperature has been exploited in several series of growths of $In_xGa_{1-x}N$ quantum well structures[8], which have emitted at wavelengths from 365 to 750 nm. The dependence of indium incorporation on growth temperature can be rationalised by assuming strong competition between growth and indium desorption.

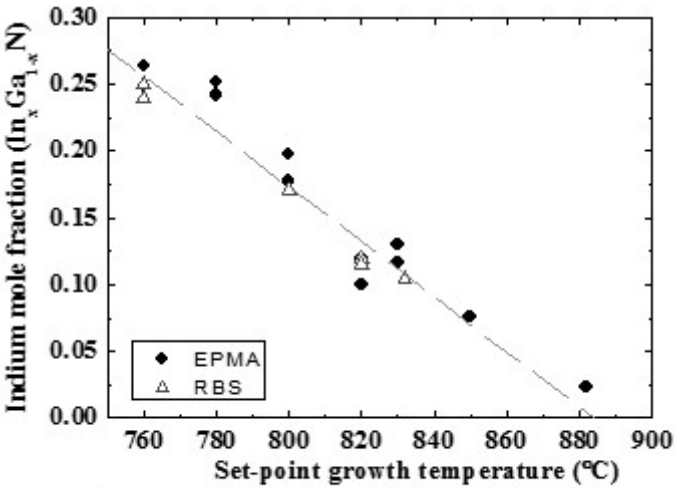

Figure 2 - Variation of indium composition with growth temperature

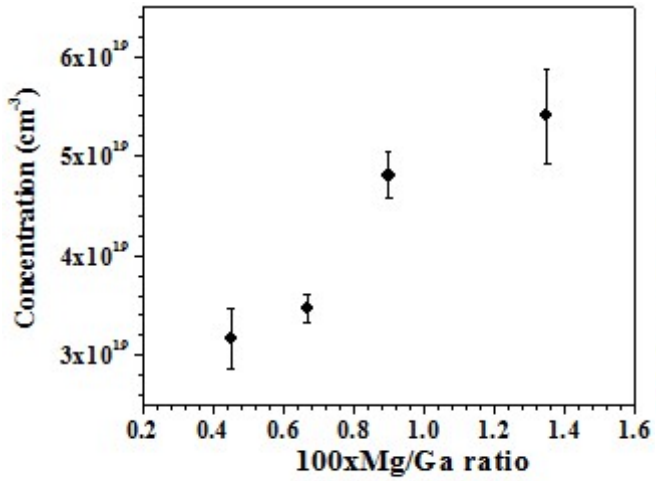

Figure 3 - WDX measured [Mg] variation with Mg:Ga gas-phase ratios

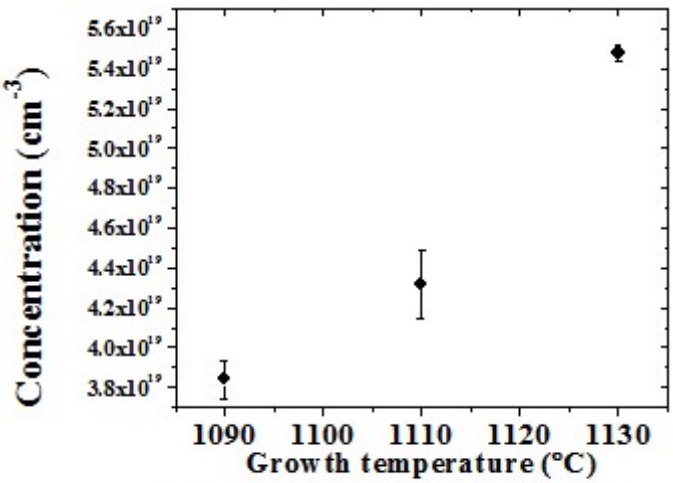

Figure 4 - WDX measured [Mg] variation with growth temperature

Applying WDX to Mg:GaN, we were able to measure [Mg] values over a global range of 5 x 10^{18} to 1.2 x 10^{20} cm^{-3}. These dopant levels correspond to mass percentages ranging from 0.00325 to 0.06825%. Figs. 3 and 4 show representative results. The horizontal axes on both plots show gas−phase Mg:Ga ratios, calculated assuming saturated uptake of Cp_2Mg, while error bars for [Mg] are based on scatter between repeat measurements. Fig. 3 illustrates the use of WDX to investigate the dependence of [Mg] on Cp_2Mg molar flow rate, for samples grown at 1130°C in consecutive runs, using the solid dopant source. The expected increase in magnesium incorporation with precursor flow rate is observed. However, comparisons with more recent work using solution Cp_2Mg suggest that the carrier gas flow through the bubbler did not achieve saturation, which would lead to irreproducible doping behaviour over a long term. Results obtained using the solution source are illustrated in Fig. 4, which shows the dependence of [Mg] on growth temperature, with the gas−phase magnesium to gallium ratio of 0.010 and other

conditions kept constant. The trend seen suggests that the decomposition kinetics of Cp_2Mg may still be a limiting factor on magnesium incorporation at GaN growth temperatures.

Further work has successfully applied WDX to [Mg] measurements in LED structures and Mg:$In_xGa_{1-x}N$. Currently we are correlating [Mg] measurements by WDX with electrical properties of Mg:GaN and Mg:$In_xGa_{1-x}N$, using Hall and transmission line methods. One limitation of both WDX and SIMS is that these techniques analyse average [Mg] values over micro−scale volumes, and so do not provide information on the localisation of significant proportions of incorporated magnesium in nano−scale pyramidal inversion domains in Mg:GaN[9].

Conclusions

The application of WDX to compositional analysis of $In_xGa_{1-x}N$ epilayers has been demonstrated with reference to a series of samples grown at different temperatures, and having a maximum x value of ~0.27. Growth temperature exerts a dominant influence on the extent of indium incorporation when other growth conditions are standardised. With careful attention to experimental detail, WDX can also be applied to measurements of [Mg] in Mg:GaN test structures and LEDs, at dopant concentrations in the $10^{19}-10^{20}$ cm^{-3} range. This technique has genuine potential for use in the optimisation of p−type GaN and $In_xGa_{1-x}N$ for device structures.

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