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Nanoscale characterisation of MBE-grown GaMnN / (001) GaAs

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Summary: The growth of cubic (Ga,Mn)N/(001)GaAs heterostructures by plasma assisted molecular beam epitaxy has been appraised as a function of Ga:N ratio, Mn concentration and growth temperature. The combined analytical techniques of EFTEM, EDX, CBED and dark field imaging have been used to appraise the Mn distributions within (Ga,Mn)N epilayers. Improved incorporation efficiency of Mn is associated with growth under N-rich conditions, but Mn incorporation may be enhanced under Ga-rich conditions at reduced growth temperatures. The surfactant behaviour of Mn during the growth of this spintronic system determines the resultant alloy composition.

1 Introduction

Ferromagnetic semiconductors raise the possibility of spintronic devices that combine electronic and magnetic properties. Practical spintronic applications require p-type material and a Curie temperature (T_c) above room temperature [1,2]. Theoretically, ferromagnetism at room temperatures is achievable within (Ga,Mn)N for very high Mn concentrations [3]. However, the low solid solubility of Mn in GaN limits the development of these systems. T_c values exceeding room temperature have been reported for (Ga,Mn)N, although the source of the ferromagnetic signal has not been definitively identified [4,5]. The requirement for p-type (Ga,Mn)N material is most practically achieved by growing the cubic phase using plasma assisted MBE (PAMBE) on (001)GaAs [2]. The growth conditions, combined with a large lattice parameter mismatch between substrate and epilayer, result in highly faulted structures. Detailed knowledge of the structure and elemental composition on the nanoscale is required for continued refinement of these spintronic material systems, both to feedback into growth programmes to improve the control of the materials growth and processing, and to underpin fundamental understanding of the material functional properties.

The effect of varying the growth parameters of III-V ratio, Mn flux and temperature on the structure and Mn incorporation of (Ga,Mn) N layers has been investigated using 12kV reflection high energy electron diffraction (RHEED) in-situ within the PAMBE growth chamber and 200kV RHEED ex-situ within a JEOL 2000fx TEM, energy dispersive X-ray (EDX) and energy filtered TEM (EFTEM) elemental analysis, selected area electron diffraction (SAED) and conventional imaging modes. Ex-situ RHEED and EDX analysis were carried out in a JEOL 2000fx transmission electron microscope operating at 200kV, EFTEM analysis was carried out using JEOL 2010F and 4000fx transmission electron microscopes.

2 Results and discussion

(Ga,Mn)N layers grown using PAMBE have been consistently found to be p-type by measuring the electrical properties of free-standing layers using Hall-effect measurements in a Van der Pauw geometry [2].

Varying the Ga:N ratio was found to produced a marked structural difference in the layers. Under N-rich conditions, RHEED analysis confirmed the presence of both zincblende and wurtzite material, with a high density of stacking faults on one set of {111} planes (Fig. 1a). RHEED analysis of Ga-rich layers, after the chemical removal of Ga droplets, revealed a smoother surface with single zincblende structure (Fig. 1c). However, EDX analysis confirmed that Mn was only incorporated in the layers under N-rich and nearly 1:1 growth conditions.

The presence of α-MnAs inclusions into the GaAs buffer layer were confirmed using EDX and SAED. It is considered that the inclusions formed due to the migration of Mn from the growth layer to the buffer layer. The orientation relationship between MnAs and the GaAs substrate was found to be affected by the Ga:N ratio, with N-rich conditions being associated with ($[11\bar{2}0]$MnAs//[110]GaAs) orientational relationship, whilst Ga-rich conditions produced ($[11\bar{2}0]$MnAs//$[1\bar{1}0]$GaAs).

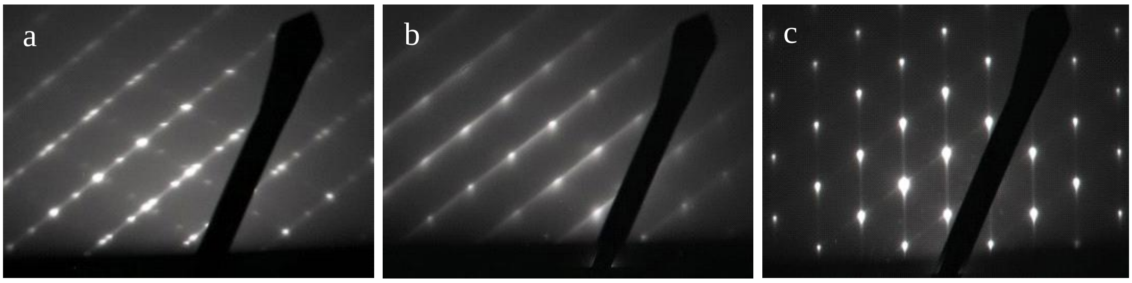

Fig. 1. Ex-situ RHEED patterns obtained from (Ga,Mn)N layers grown using PAMBE under a) N-rich, b) 1:1 and c) Ga-rich conditions at 680°C.

Increasing Mn flux was associated with the build up of a Mn surfactant layer during the early stages of PAMBE growth, with a transition from zinc-blende single phase growth to zinc-blende/wurtzite mixed phase growth, as shown in figure 2. High Mn flux produced samples with a ferromagnetic signal above 400K, however the exact nature of the origin of the signal has not been definitively identified. Secondary phases and Mn clusters are expected to be a significant contributor to this additional Mn content within the GaMnN alloy. EFTEM analysis has revealed the presence of Mn-rich regions at grain interfaces.

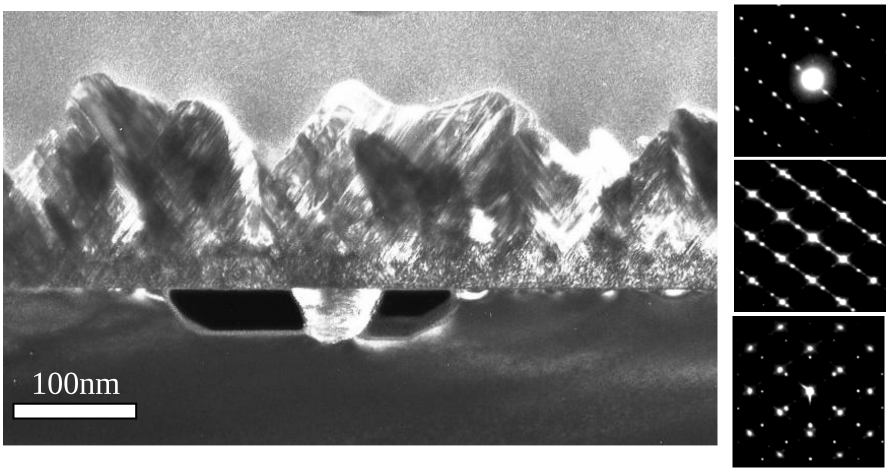

Fig. 2. a) Cross section image of a (Ga,Mn)N layer grown under Mn-rich conditions (nominally 6.6at%). b-d) SAED patterns taken from the top, middle and bottom of the layer respectively, showing the transition from zincblende to wurtzite structure via zincblende/wurtzite mixed phase growth.

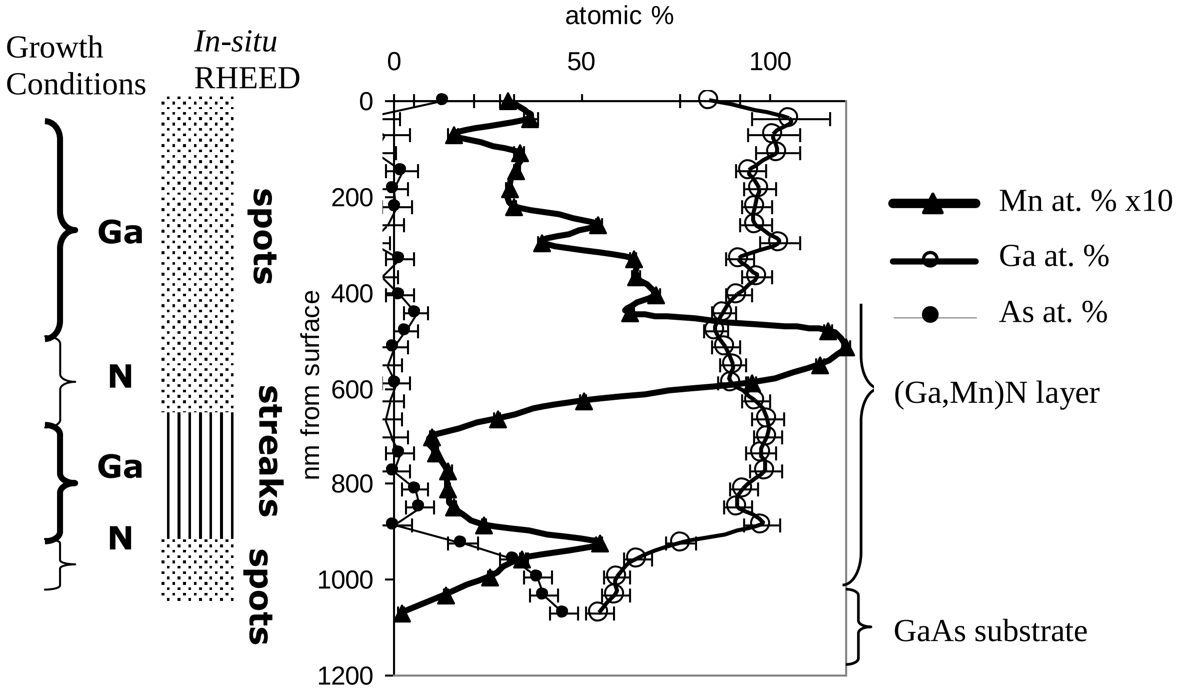

Fig. 3. The effect of alternating the III-V ratio during growth of a (Ga,Mn)N layer, as investigated using *in-situ* RHEED and EDX line profiles

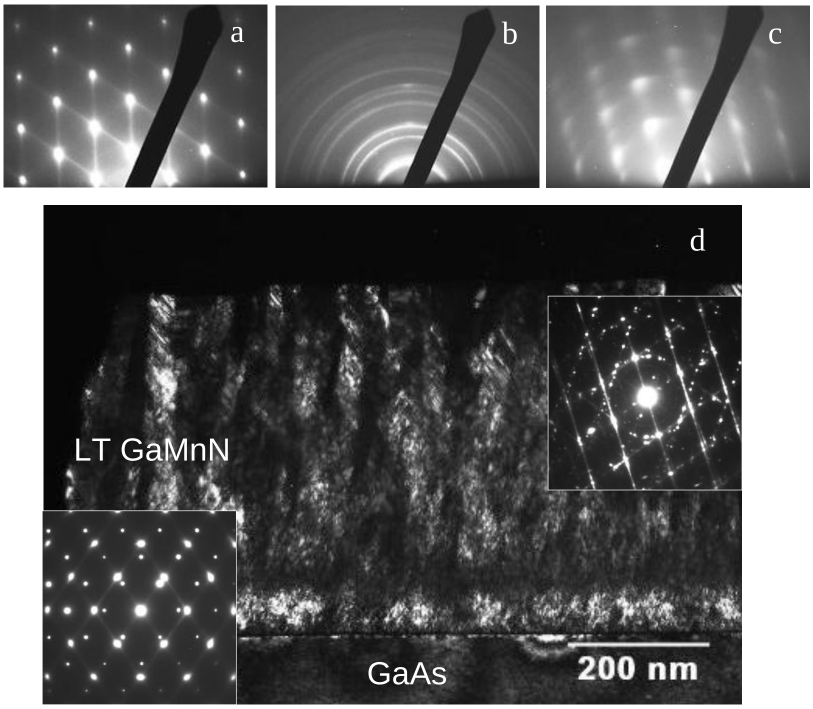

Fig. 4. *ex-situ* RHEED patterns obtained from layers grown with Ga rich conditions at a) 680°C, b) 340°C and c) 265°C**;** d) dark field image showing the structure of a (Ga,Mn)N layer grown at 265°C, with inset diffraction patterns of the initial (Ga,Mn)N nucleation layer (bottom left) and the low temperature (Ga,Mn)N layer (top right)

The elemental composition through a (Ga,Mn) N layer grown using alternating N and Ga-rich conditions to a thickness of ~1100nm was appraised by EDX line profiles (figure 3). 12kV in-situ RHEED patters allow comparison of the chemical profile with the near surface crystal structure of the layer during PAMBE growth at 680°C The initial growth phase of (Ga,Mn)N under N-rich conditions produced a layer with a significant level of Mn incorporation. However, switching to Ga-rich growth conditions resulted in a drastic reduction in the level of Mn incorporation, along with an improvement in the structural quality of the layer, indicated by the streaks in the *in-situ* RHEED. Returning to N-rich growth conditions at ~500nm layer thickness caused a transition back to a rough growth mode, and the incorporation once again of significant levels of Mn. A subsequent switch back to Ga-rich growth conditions continued to show a rough growth mode, with significant but reduced Mn incorporation.

The effect of growing (Ga,Mn) layers at reduced temperature was also investigated. Under N-rich growth conditions, reducing the temperature from 680°C was simply associated with the transformation from single crystal cubic growth to polycrystalline cubic and hexagonal mixed phase growth [6]. Under Ga-rich conditions, lowering the growth temperature to 340°C led to a transition from single crystalline to polycrystalline growth (figure 4b). However, further reducing the growth temperature to 265°C results in a recovery from polycrystalline growth to a mixed phase growth with close packed planes for both cubic and hexagonal GaMnN roughly parallel to the growth surface, as shown by 200kv ex-situ RHEED (figure 4c). This was accompanied by an improved Mn incorporation, as confirmed by EDX line profiles indicating the uniform incorporation of Mn under such non-equilibrium conditions [6].

3 Conclusions

The microstructure and elemental concentrations of (Ga,Mn)N layers grown by PAMBE under a range of conditions have been investigated. N-rich and nearly 1:1 Ga:N growth conditions are associated with the incorporation of Mn into the GaN lattice. Ga-rich growth conditions are associated with a slightly improved (Ga,Mn)N microstructure, but with little incorporation of Mn into the GaN lattice. Under conditions of increasing Mn flux, the build up of Mn on the growth front creates a surfactant layer, resulting in enhanced levels of Mn incorporation but mixed phase growth. Growth of a layer under alternating Ga or N rich conditions confirmed the surfactant behaviour of Mn during the growth of this spintronic system. Low temperature growth under N-rich conditions led to polycrystalline mixed phase growth. (Ga,Mn)N films adopt a tilted mixed phase growth mode with an improved Mn incorporation under Ga-rich conditions at low temperature.

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