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Microstructural characterisation of zinc-blende Ga\(_{1-x}\)Mn\(_x\)N grown by MBE as a function of Mn flux

Y Han\(^1\), M W Fay\(^1\), S V Novikov\(^2\), K W Edmonds\(^2\), B L Gallagher\(^2\), R P Campion\(^2\), C R Staddon\(^2\), C T Foxon\(^2\) and P D Brown\(^1\)

\(^1\) School of Mechanical, Materials and Manufacturing Engineering and
\(^2\) School of Physics and Astronomy, at the University of Nottingham, University Park, Nottingham NG7 2RD, UK

Email: emxyh@nottingham.ac.uk

Abstract. Zinc-blende Ga\(_{1-x}\)Mn\(_x\)N epilayers grown by plasma assisted molecular beam epitaxy as a function of Mn flux have been assessed using a variety of structural characterisation techniques. Increasing Mn flux is associated with the build up of a Mn surfactant layer during the early states of growth and a transition from zinc-blende single phase growth to zinc-blende/wurtzite mixed phase growth.

1. Introduction

III-V ferromagnetic semiconductors are gaining interest because of their potential application within spintronic device structures. However, a Curie temperature well above 300K is required for such material systems to be of widespread technological use. In particular, theoretical prediction of the Curie temperature for various semiconductors [1] suggests, for example, that a \(T_c\) value above room temperature is possible for zinc-blende GaN containing 5 at% Mn and a hole concentration of \(3.5 \times 10^{20}\) cm\(^{-3}\). Accordingly, attention is presently being given to the development of p-type Ga\(_{1-x}\)Mn\(_x\)N ferromagnetic semiconductors.

In practice, establishing p-type conductivity is found comparatively easier within zinc-blende Ga\(_{1-x}\)Mn\(_x\)N than wurtzite Ga\(_{1-x}\)Mn\(_x\)N, where the transition metal species is responsible for both the ferromagnetic properties and the p-type behaviour. By way of example, high p-type zinc-blende Ga\(_{1-x}\)Mn\(_x\)N layers with carrier concentrations exceeding \(10^{18}\) cm\(^{-3}\) and a detected ferromagnetic signal over 400K, attributed to a second phase material, have been obtained by plasma assisted molecular beam epitaxy (PAMBE) [2]. In view of the limited solid solubility of Mn in GaN and the metastability of zinc-blende GaN epitaxial layers, establishing appropriate conditions for the growth of uniform alloys of Ga\(_{1-x}\)Mn\(_x\)N while maintaining cubic epitaxy becomes an intriguing challenge. It is known that GaN grown in the presence of As promotes the formation of single phase zinc-blende material [3], whilst growth in the presence of Fe is considered to favor the formation of mixed phase material [4]. Hence, for the Ga\(_{1-x}\)Mn\(_x\)N materials system, the impact of Mn on the epitaxial growth of zinc-blende GaN needs to be understood.

In this paper, the influence of Mn flux on the microstructural development of Ga\(_{1-x}\)Mn\(_x\)N grown by PAMBE is assessed using the combined technologies of reflection high energy electron diffraction (RHEED) and conventional transmission electron microscopy (TEM).
2. Experimental

Zinc-blende Ga\textsubscript{1-x}Mn\textsubscript{x}N epilayers were grown on semi-insulating (001) oriented GaAs substrates at 680°C by PAMBE. Briefly, the GaAs substrate was heat treated at ~600°C under As flux for 10 minutes to remove the protective oxide layer and a GaAs buffer layer of thickness ~0.15µm was deposited to provide a clean surface for epitaxy. Following initiation of the N plasma, the Mn and N shutters were opened whilst the As shutter was closed. The substrate temperature was then ramped up to 680°C and maintained for 2 hours during Ga\textsubscript{1-x}Mn\textsubscript{x}N epitaxial growth. Activated nitrogen was supplied using an Oxford Applied Research RF plasma source and arsenic was produced from a two-zone purpose made cell. An overall chamber pressure of 2-3×10\textsuperscript{-5} mbar and a Ga flux of 2×10\textsuperscript{-7} mbar were maintained to provide slightly N-rich growth conditions, considered to be beneficial for Mn incorporation into the zinc-blende GaN lattice [5]. The Mn flux was varied from 0 to 25×10\textsuperscript{-9} mbar corresponding to Mn concentrations of 0 to ~6.6 at% as verified by calibrated secondary ion mass spectrometry (SIMS) measurements. The growth conditions for the sample set investigated are summarised in Table 1.

The near surface crystal structure of the epilayers was initially assessed by RHEED using a modified Jeol 2000fx TEM, with as-grown specimens mounted vertically, immediately beneath the projector lens. The bulk epilayer crystal structure was further assessed by X-ray diffraction (XRD) using a Philips X-pert Diffractometer. Sample morphology was assessed using an FEI XL30 scanning electron microscope (SEM) operated at 15-20kV. Cross-sectional specimens for TEM investigation were then prepared using sequential mechanical polishing and argon ion beam thinning. They were investigated using conventional diffraction contrast techniques using Jeol 2000fx and 4000fx instruments. The absolute polarity of this sample set was assessed using CBED applied to the GaAs substrate [6].

| Sample | T\textsubscript{g} / °C | N\textsubscript{2} / ×10\textsuperscript{-5} mbar | Ga flux / ×10\textsuperscript{-7} mbar | Mn flux / ×10\textsuperscript{-9} mbar | Estimated Mn concentration from SIMS/ at% |
|--------|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| A      | 680             | 2-3                         | 2                           | 0                           | 0                           |
| B      | 680             | 2-3                         | 2                           | 0.495                       | 0.04                        |
| C      | 680             | 2-3                         | 2                           | 1.65                        | 0.22                        |
| D      | 680             | 2-3                         | 2                           | 4.95                        | 1                           |
| E      | 680             | 2-3                         | 2                           | 25                          | 6.6                         |

3. Results and discussion

The predominant formation of zinc-blende Ga\textsubscript{1-x}Mn\textsubscript{x}N was confirmed by XRD spectra obtained across the sample set. SEM observations indicated that samples grown without Mn (sample A) or under a low Mn flux (sample B) exhibited smooth surfaces, whilst the surfaces of samples grown under higher Mn flux (samples C, D and E) became rougher. Pairs of RHEED patterns recorded along orthogonal <110> projections are presented in Figures 1a to 1f, corresponding to samples A, B and E, respectively. All the epilayers demonstrated predominant cubic epitaxy with streaks and/or extra spots indicating varying degrees of stacking disorder on inclined \{111\} planes and/or mixed phase growth. In particular, a transition from single phase cubic growth under low Mn flux to cubic/hexagonal mixed phase growth under high Mn flux was observed. Increasing degrees of anisotropy in the epilayer defect microstructure was also apparent with increasing Mn flux (e.g. Figures 1e,f).

By way of example, for sample A grown in the absence of Mn flux, clear, sharp spots were observed for both <110> orthogonal projections, indicative of single phase cubic epitaxy. For samples grown with low Mn flux (e.g. sample B), faint streaks along <111> directions for both orthogonal projection were observed, indicative of stacking faults on inclined \{111\} planes. For samples A, B and C, no obvious anisotropy in the orthogonal <110> RHEED patterns was detected. For samples D and E grown under conditions of higher Mn flux, dominant diffraction spots from both cubic and hexagonal material were identified, with diffraction spots due to the hexagonal phase becoming strongest for sample E grown under the highest Mn flux. The indexing of Figure 1f is clarified with
reference to the schematic diagram of Figure 1g which illustrates the orientation relationship between
the two phases, with $[\{11\}$ // $[\{01\}$ and $\{11\}$ // $\{00\}$. Such a symmetrical epitaxial relationship
does not occur for the orthogonal $[10]$ projection of this sample, because rotation of the hexagonal
phase through 90° would not provide a low index crystallographic orientation, and consequently just
the $[11]$ diffraction pattern is apparent within Figure 1e. It is noted that this orientation relationship
and the anisotropic distribution of hexagonal spots are consistent with those of Ga$_{1-x}$Mn$_x$N samples
grown under higher N:Ga ratios [5]. In addition, for the sample grown under highest Mn flux (sample
E), streaks preferentially aligned along the $[11]$ direction for just the $[11]$ sample projection were
observed, indicating the preferential alignment of inclined planar defects on the set of $[11]$ planes
inclined to the growth surface (Figure 1f). This figure was indexed absolutely following subsequent
polarity measurements on the associated TEM sample foil, with reference to the electron beam
emerging upwards out of the pages.

TEM investigations across the sample set demonstrated the presence of highly faulted defect
microstructures in all the specimens. By way of illustration, Figures 2a and 2b present 002 zinc-blende
weak beam dark field, cross-sectional TEM images for samples B and E, respectively. Sample B with
a layer thickness of ~200 nm has a relatively flat growth surface indicating a relatively steady growth
mode under conditions of low Mn flux. However, a very rough growth surface and a large variation in
epilayer thickness from ~100 nm to 200 nm is apparent for sample E. a-MnAs inclusions (arrowed i)
at the interface extending into the GaAs buffer layer and associated voids (arrowed ii) were also
identified, as reported elsewhere [7]. The bright line delineated at the position of the Ga$_{1-x}$Mn$_x$N/GaAs
interface in Figures 2a and 2b is tentatively attributed to scattering from remnant oxide and/or small
nucleation grains. Further, a distinct nucleation layer of 30 to 40 nm in thickness (arrowed iii) was
apparent, followed by a transformation to mixed phase columnar grains containing stacking faults on
inclined close packed planes. Selected area electron diffraction (SAED) and diffraction contrast
imaging experiments performed to clarify the distribution of phases throughout sample E (e.g. Figures
2c to 2e) confirmed the presence of hexagonal grains through the bulk of the epilayer, rather than just
being associated just with the epilayer surface in addition to the predominant cubic grains [5]. No
evidence for the presence of hexagonal Ga$_{1-x}$Mn$_x$N was found within the initial nucleation layer.

It is known that zinc-blende GaN can be stabilised on a variety of substrates using carefully
controlled growth conditions. Due to the volatile nature and low partial pressure of N, the GaN growth
front is always Ga terminated, independent of crystal polarity and the Ga:N growth ratio [8]. The high
mobility of Ga adatoms on the growth surface associated with the MBE growth conditions is promoted
by weak Ga-Ga bonding. The effective diffusion of Ga is compromised by the incorporation of surface
N atoms, deteriorating by a large amount under high N-rich growth conditions, leading to a rough
growth surface with reduced crystal quality [9]. For the sample set examined here, all the samples
were grown under slightly N-rich conditions. Hence, a modest level of surface roughness and epilayer
faulting is to be expected. However, the effect of increasing levels of Mn flux is to severely degrade
the structural quality of the epitaxial layers.

Even though the Mn incorporation efficiency is comparatively low, being controlled by the Mn
flux and growth temperature, an increasing level of Mn incorporation with increasing Mn flux is
evident. In this context, the development of a Mn surfactant layer is envisaged being associated with a
transition of the initial cubic nucleation layer into mixed phase growth, consistent with Mn acting to

Figure 1. 200kV RHEED patterns for as-grown Ga$_{1-x}$Mn$_x$N. (a,b) Sample A; (c,d) sample B and (e,f,) sample E
recorded along orthogonal <110> projections. (g) Schematic illustration corresponding to Figure 1f denoting
diffraction spots due to zinc-blende Ga$_{1-x}$Mn$_x$N (open circles) and wurtzite Ga$_{1-x}$Mn$_x$N (solid dots).
It is suggested therefore that purposely reducing the Mn flux to lessen the Mn accumulation on the growth surface after layer initiation might be beneficial to maintain the cubic epitaxy of Ga$_{1-x}$Mn$_x$N at these higher levels of Mn flux.

In summary, a high Mn flux has a dominant effect on the growth of zinc-blende Ga$_{1-x}$Mn$_x$N, leading to the development of a mixed phase growth regime.

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