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TEM assessment of As-doped GaN epitaxial layers grown on sapphire

M W Fay, I Harrison,[1] E C Larkins,[1] S V Novikov,[2] C T Foxon[2] and P D Brown

School of Mechanical, Materials, Manufacturing Engineering and Management

[1]School of Electrical and Electronic Engineering

[2]School of Physics

University of Nottingham, University Park, Nottingham NG7 2RD, UK

Abstract. TEM investigations of As-doped GaN layers grown by plasma-assisted molecular beam epitaxy on sapphire substrates reveal the presence of extensive regions of cubic stacking disorder within the hexagonal GaN matrix. Electron energy loss spectroscopy suggests the localization of As within grains immediately below domains containing stacking disorder, and additionally at the layer surface. This suggests that localised strain plays a role in the formation mechanism of the stacking faults.

1. Introduction

There is currently considerable theoretical and experimental interest in As-doped GaN. Three main reasons motivate such investigations. Firstly, the difference in the native crystal structures of GaAs and GaN and the large difference in their lattice parameters leads to a strong negative bowing of the Ga(As,N) band gap as a function of composition [1,2]. Secondly, As-doped GaN shows very strong room temperature blue emission at ~2.6eV, which raises the potential of using this material in blue light emitting diode (LED) applications [3-5]. Thirdly is the possibility of As-stimulated growth of zincblende GaN in a controlled fashion [6]. In this paper, we report on a TEM investigation of As-doped GaN films grown by PA-MBE that exhibit strong blue emission.

2. Experimental

As-doped GaN layers of varying thicknesses used in this study were grown on sapphire at a temperature of ~ 800°C, as described in detail elsewhere [7]. Active nitrogen for the growth was provided by an Oxford Applied Research (OAR) CARS25 RF activated plasma source. The nitrogen flux was about 3 x 10^{-5} mbar beam equivalent pressure (BEP). Arsenic, in the form of dimers (As_2) produced using a two-zone purpose made cell, provided a flux of about 7 x 10^{-6} mbar BEP. Prior to layer growth, the sapphire substrates were exposed to nitrogen at a temperature of ~800°C for 30 minutes in the same MBE reactor. Cross-sectional specimens for TEM were prepared by sequential mechanical polishing and dimpling, followed by argon ion milling to electron transparency. These specimens were examined using a JEOL 4000fx operating at 400kV equipped with a Gatan Imaging Filter (GIF) for chemical analysis. X-ray diffraction techniques were also used to study the structural properties of this sample set.

3. Results and discussion

X-ray diffraction studies previously confirmed that the As-doped GaN samples contained a mixture of phases, i.e. {0001} oriented hexagonal GaN, {111} oriented cubic GaN and {111} oriented cubic GaAs with respect to the growth plane [8]. The proportion of cubic GaN decreases rapidly with increasing film thickness suggesting that the majority of these domains are close to the epilayer/substrate interface. From the X-ray intensity of the GaAs peaks relative to GaN, it was concluded that GaAs constituted ~0.03% of the total volume of these films, with this fraction being roughly constant for films of different thickness. The volume fraction of cubic GaN was similarly determined to be 4-9% for samples with epilayer thicknesses ranging from 1 µm to 2.5 µm.

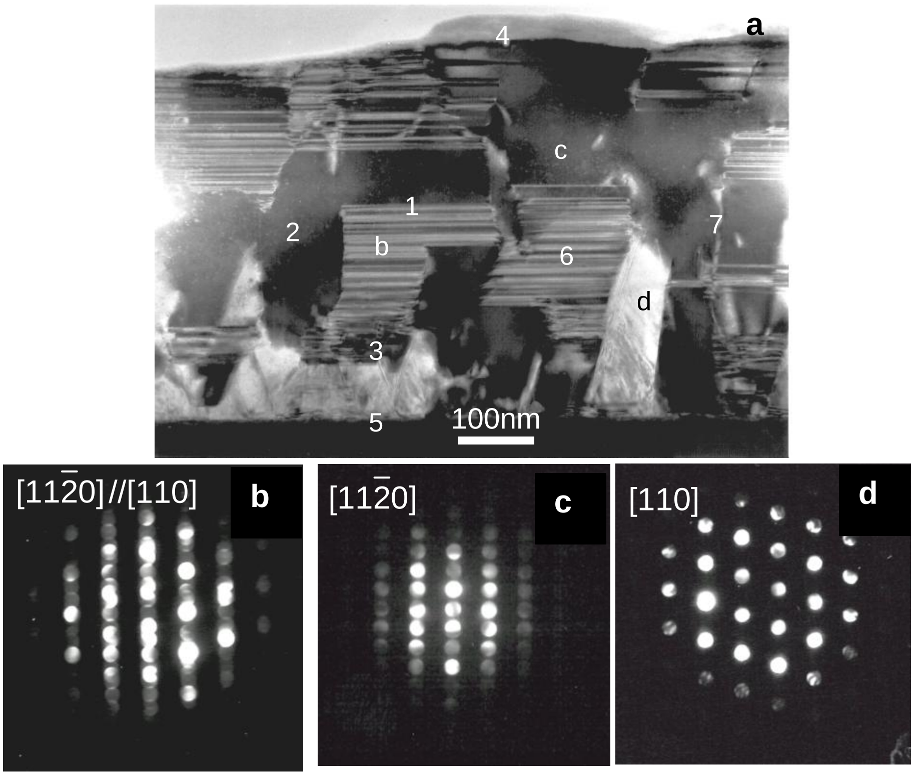

Figure 1. Focused probe diffraction patterns obtained from the areas labelled in (a) the bright field image for (b) a region containing stacking faults; (c) the wurtzite GaN<11 $\bar{2}$ 0> matrix and (d) a zincblende GaN<110> grain.

Cross-sectional TEM investigations revealed regions of stacking faults, up to 200nm wide on the scale of the layer subgrains (Fig. 1a). These stacking fault domains were established above the highly faulted regions near the substrate and were laterally defined by threading dislocations. Focused probe rather than selected area diffraction techniques were required to analyze these layer regions individually. Thus, converged probe diffraction patterns from the banded regions containing stacking faults confirmed the presence of both hexagonal and cubic GaN, with the orientational relationship

GaN<$11\bar{2}0$>$_{hex}$ // GaN<110>$_{cubic}$ (Fig 1). However, no evidence for the presence of GaAs was obtained from these diffraction patterns. A high density of grains of single crystal cubic GaN were identified near the epilayer/substrate interface, whilst regions free of stacking faults away from the substrate corresponded to hexagonal GaN. The tilted bright field image presented within Fig 1 emphasises the layer grain structure and the associated distribution of stacking faults. High resolution TEM imaging of mixed phase material regions confirmed the presence of basal plane cubic stacking disorder. The cubic stacking sequence was predominantly observed to be only one or two monolayers thick.

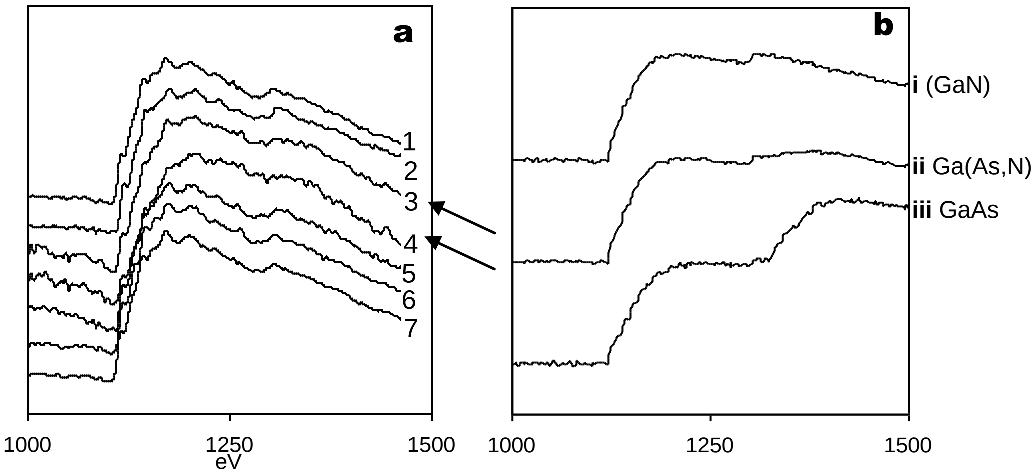

Figure 2. (a) Background subtracted EEL spectra, taken from various regions of the sample as shown in Fig. 2. (1) above stacking faults; (2) at the centre of a stacking fault free grain; (3) directly below a domain containing stacking faults; (4) a surface step feature; (5) at the GaN/sapphire interface; (6) at the centre of a grain containing stacking faults and (7) at a dislocation in the middle of the sample. The Ga $L_{2,3}$ edge at ~1100eV dominates these spectra. The Ga L_1 edge at 1298eV is present in all cases. Spectra 3 and 4 show an additional contribution due to the As $L_{2,3}$ edges. This feature takes the form of a gentle hump beyond 1298eV (arrowed). (b) Reference simulated spectra corresponding to (i) GaN, (ii) $GaAs_{0.25}N_{0.75}$, (iii) GaAs

Electron energy loss (EEL) spectroscopy was used to profile the distribution of As within these samples. Individual features were investigated for As content using a focused probe of ~20nm and even though the overall As content was extremely low it was identified and found to be concentrated at specific regions within the layer. Fig. 2 compares portions of the EEL spectra acquired from specific features within the sample shown in Fig 1. The spectra shown are dominated by the Ga $L_{2,3}$ edges and contain the position of the characteristic As $L_{2,3}$ edges which in two cases (Fig $2a_3$, $2a_4$) reveals the presence of low As content. The background prior to the Ga $L_{2,3}$ edges at 1115eV has been subtracted. Particular care was taken due to the overlap between the Ga L_1 edge at 1298eV, which is a hydrogenic edge, and the As $L_{2,3}$ edges at 1323 eV, which have a less clearly defined onset. In the absence of As, the Ga L_1 edge appears as a step-like feature, with a steady reduction with increasing energy (Fig. $2b_{iii}$). The presence of localised higher concentrations (>5%) of As would be expected to result in a visible change in the shape of this Ga L_1 tail beyond 1298eV, with a hump-like feature becoming more pronounced for increasing As content (Fig $2b_{ii}$). Such As-containing features were only reproducibly observed in spectra obtained from two types of feature within the sample, either directly below the grains containing stacking faults (Fig $1a_3$), or at step edge features on the surface of the GaN layer (Fig 1a_4). This distribution suggests that As is mediating the formation of stacking faults within the hexagonal GaN matrix whilst acting as a surfactant. However, in view of the projected volume of material analyzed it is not possible to determine from EEL spectroscopy whether these regions of As content are due to nanoscale GaAs grains, or a Ga(N,As) alloy.

Layer growth in the presence of As may result in the development of cubic GaN material in two ways. With a high concentration of As at the surface of the sample during growth, the arrival of Ga would initially tend to form cubic GaAs. It is suggested that, as the Ga-N bond is stronger than the Ga-As bond, the displacement of the As atom by N could then promote the localised formation of cubic GaN that subsequently propagate sideways on the basal plane, being confined by the subgrain boundary structures. Alternatively, the incorporation of As onto N sites would result in localised lattice strain which may introduce basal plane GaN stacking faults. It is noticed that As was detected at concentrations >5% in regions immediately below such domains containing stacking disorder, and hence it is considered that the high density of basal plane GaN stacking faults observed within these samples is more likely to have formed as a consequence of the increased lattice distortion in these grains. The lateral propagation of these monolayer thick stacking disorders is still crystallographically driven and this inference is supported by the observation that regions of stacking faults appear near the surface even though the surface layer itself is not flat. It is noted that stacking faults have recently been observed at the location of a GaAs interrupt within GaN [9], however, the study presented here is, to our knowledge, the first such TEM study on GaN layers grown with constant As flux.

4. Summary

The presence of As during the growth of hexagonal GaN by PA-MBE induces the formation of a high density of GaN stacking faults within the hexagonal GaN matrix. No planar GaAs stacking faults were identified. The limited precision of the analytical techniques used prohibit the unambiguous identification of a Ga(As,N) alloy within the faulted regions.

References

[1] Weyers M, Sato M and Ando H, Jpn J Appl Phys., Part 2 **31**, L853 (1992)
[2] Sakai S, Ueta Y and Terauchi Y, Jpn J Appl Phys, **32** 4413 (1993)
[3] Pankove JI and Hutchby JA, J. Appl. Phys. **47** 5387 (1976)
[4] Li X, Kim S, Reuter EE, Bishop SG and Coleman JJ, Appl Phys Lett **72** 1990 (1998)
[5] Winser AJ, Novikov SV, Davis CS, Cheng TS, Foxon CT and Harrison I, Appl. Phys. Lett. **77**, 2506 (2000).
[6] Cheng TS, Jenkins LC, Hooper SE, Foxon CT, Orton JW, Lacklison DE, Appl Phys Lett **66** 1509 (1995)
[7] Foxon CT, Novikov SV, Cheng TS, Davis CS, Campion RP, Winser AJ, Harrison I, J. Crystal Growth **219** 327 (2000)
[8] Andrianov AV, Novikov SV, Li T, Xia R, Bull S, Harrison I, Larkins EC and Foxon CT, phys. stat. sol. (b) **238**, No. 1, 204 (2003)
[9] Kim H, Andersson TG, Chauveau J-M and Trampert A, Appl. Phys. Lett. **81** 3407 (2002)