Nanoscale characterisation of electronic and spintronic nitrides and arsenides

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Abstract. The limits of applicability of the nanoscale spatial resolution analysis techniques of EFTEM, CBED and dark field imaging as applied to ohmic contacts to AlGaN/GaN and Mn distribution within Ga₁₋ₓMnxAs epilayers are considered. EFTEM can be limited by acquisition times necessitating the post processing of images to compensate for sample drift. Complementary technique of assessment are required to address problems of peak overlaps in energy loss spectra or signal to noise problems for low elemental concentrations. The use of 002 dark field imaging to appraise Ga₁₋ₓMnxAs epilayers is demonstrated.

1. Introduction

The functional properties of advanced nitrides and arsenides for electronic or spintronic applications are strongly dependent on the microstructure of the device active regions. Detailed knowledge of structure and elemental composition on the nanoscale is therefore required for continued system refinement, to feedback into programmes to improve the control of the materials growth and processing whilst providing fundamental understanding of the material functional performance. The use of energy filtered TEM (EFTEM) for analysing the elemental composition of semiconductor device structures is well established, combining elemental sensitivity with high spatial resolution. However, the difficulties associated with the assessment of samples with low concentrations, coupled with problems of overlapping energy loss edges often emphasises the need for other complementary methods of analysis. By way of example, we consider the application of EFTEM, convergent beam electron diffraction (CBED) and dark field imaging to characterise two topical problems within electronic and spintronic semiconductors, i.e. ohmic contacts to AlGaN/GaN and Mn distribution within Ga₁₋ₓMnxAs, respectively.

The standard ohmic contact to AlGaN/GaN for high power field effect transistors is a multilayer structures based around an Al/Ti diffusion couple, separated from a top Au layer by a notional Ti, Ni, Pd or Pt barrier layer. Activation of the contact normally requires a rapid thermal anneal, with the formation of an interfacial Ti-nitride associated with the onset of ohmic behaviour [1]. Optimisation of the processing conditions for such contacts requires a clear understanding of the dynamic evolution of the contact-nitride interface. For this system the challenges associated with EFTEM mapping are initially considered.
Ga$_{1-x}$Mn$_x$As is presently viewed as a promising model ferromagnetic semiconductor system. Although ferromagnetism within Ga$_{1-x}$Mn$_x$As is theoretically possible at room temperature for layers with sufficiently high Mn content and hole concentrations [2], an optimum Curie temperature of 173K has been achieved to date for Ga$_{0.906}$Mn$_{0.094}$As, following annealing [3], being limited by problems related to the incorporation of Mn and its effect on the defect microstructure. Due to the low solid solubility limit of Mn within GaAs, the growth of Ga$_{1-x}$Mn$_x$As necessitates use of the non-equilibrium low temperature MBE technique, but this can result in the incorporation of high concentrations of As antisite defects, Mn clusters and interstitials, in addition to extended structural defects. Understanding the mechanisms responsible for the spintronic properties of this materials system requires a clear understanding of the form and location of Mn content within these layers. In this context, the limitations of EFTEM assessment are emphasised, with the need to apply 002 dark field imaging to appraise the Mn distributions.

2. Experimental
The first sample reported on here comprised a 100nm Au / 500nm Pt / 250nm Al / 500 nm Ti multilayer ohmic contact structure deposited on an AlGaN/GaN layer grown on an (0001) SiC substrate by metal organic chemical vapour deposition (MOCVD). The wafer was annealed for 60 seconds in flowing N$_2$ at 750°C. Transmission line measurements confirmed the ohmic behaviour of the contact. The second system reported on here comprised thin (50nm) and thick (1µm) Ga$_{1-x}$Mn$_x$As epitaxial layers with Mn compositions of either 2.2, 5.6 or 9 at% as determined by calibrated secondary ion mass spectrometry (SIMS), grown by MBE at indicated temperatures of 255, 210 or 185°C, respectively, on (001) oriented semi-insulating GaAs substrates, using As$_2$ to reduce the concentration of As antisite defects [4]. Buffer layers of 100nm thick, high temperature (580°C) GaAs followed by 50nm thick, growth temperature GaAs provided template material for Ga$_{1-x}$Mn$_x$As epitaxial growth. Magnetic measurements confirmed strong anisotropic ferromagnetism of these Ga$_{1-x}$Mn$_x$As layers with the easy and hard directions of magnetisation corresponding to the [1 1 0] and [1 1 0] directions, respectively, for unannealed samples [5].

Cross-sectional specimens for transmission electron microscopy were prepared by sequential mechanical polishing and dimpling, followed by argon ion milling and plasma cleaning. To complement conventional diffraction contrast imaging techniques, information on the chemical

Figure 1 (a-g) Elementally sensitive images derived from an EFTEM series of an ohmic AuPtAlTi (100nm/500nm/250nm/500nm) contact to AlGaN/GaN annealed at 750°C (h) line profile of the N and Ti signal across the interface plane.
distributions within the layers was obtained using electron energy loss spectroscopy (EELS) and EFTEM techniques using Jeol 2000fx and 4000fx instruments. The absolute crystal polarity of the GaAs substrates of the TEM sample foils was established using CBED [6]. 002 dark field imaging was used to appraise the Mn interstitial distribution within the Ga$_{1-x}$Mn$_x$As epilayers [7].

3. Results and Discussion

The elemental maps of the AuPtAlTi/AlGaN/GaN ohmic contact presented in Figure 1 illustrate both the strengths and weaknesses of the EFTEM technique. The maps shown were derived from six series totaling 150 images acquired over a range from 100 to 2500eV, with exposure times increasing from 0.06 to 3 seconds with increasing energy loss. The high spatial resolution offered by this approach is useful for highlighting the interfacial Ti rich layer, identified as being a Ti-nitride due to the spatial overlap with the N signal (Figure 1, f-h). The mapping of heavier elements such as Au and Pt is more complicated, as the signal to background ratio decreases with increasing energy loss, and the shape of the M-edges at 2049 and 2121 eV make separation of the contributions of these two elements problematic (figure 1 c,d). Using energy windows narrow enough to resolve the contribution from each element necessitates long acquisition times for each image and significant post acquisition processing is then required to compensate for sample drift of ~1.5 nm per minute. Drift compensation, e.g. by means of Fourier correlation between images is particularly important when considering thin interfaces, being required for the confident identification of the interfacial Ti-Nitride region shown in Figure 1, supported by subsequent HREM observations. Whilst it is apparent from these images that Au has diffused to the contact/nitride interface upon sample annealing, accurate mapping of the heavier elements requires the use of the complementary technique of EDX.

Figure 2 shows a 1µm thick Ga$_{0.944}$Mn$_{0.056}$As sample exhibiting structural anisotropy, with faint banded contrast on inclined {111}$_B$ planes and a rippled surface when observed in the absolute [110] projection. The inset CBED pattern confirms the crystal polarity. In this context, it is of particular interest to identify an appropriate combination of techniques to detect not just the presence of Mn, but to appraise the form in which the Mn is incorporated. It is known that the low temperatures required for the growth of Ga$_{1-x}$Mn$_x$As with significant Mn content lead to the production of a high density of interstitial Mn, which is a double donor that compensates holes, and is therefore considered detrimental to the magnetic properties of the layers. The challenge is to determine the ratios of interstitial and substitutional Mn throughout the grown layer. This is not possible using EFTEM in isolation and separation of the contribution of interstitial and substitutional Mn within Ga$_{1-x}$Mn$_x$As layers requires the use of the 002 dark field imaging technique, with theoretical calculation suggesting that the structure factor is not significantly affected by substitutional Mn, but is strongly increased by type 1 interstitials (four Ga nearest neighbours) and reduced by type 2 interstitials (four As nearest neighbours) [7]. Since type 2 interstitials are energetically favoured [9], it would therefore be expected that regions containing significant levels of Mn interstitials would appear dark compared to the GaAs substrate within 002 dark field images. The 50nm thick Ga$_{0.944}$Mn$_{0.056}$As/GaAs epilayer shown in Figure 3 is therefore consistent with an even distribution of interstitial Mn throughout the Ga$_{1-x}$Mn$_x$As layer. The next challenge is to appraise the concentration of interstitial Mn from a consideration of the image intensities.

Figure 3 acquired from a 50nm Ga$_{0.944}$Mn$_{0.056}$As epilayer is presented to illustrate another drawback of the EFTEM technique, in that low concentrations of Mn cannot be easily distinguished due to the poor

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**Fig. 2 [110] many beam bright field image of a 1 µm thick Ga$_{0.944}$Mn$_{0.056}$As epilayer. A polarity sensitive tilted CBED pattern is inset.**
signal to noise ratio. Image drift correlation was also required to associate the Mn and O signals at the sample surface, commensurate with the oxidation of surfactant Mn following post-growth exposure of the sample to the atmosphere.

In summary, EFTEM imaging techniques need to be used in conjunction with conventional diffraction contrast techniques to appraise the distribution of low concentrations of Mn within Ga$_{1-x}$Mn$_x$As epilayers in view of the differing proportions of substitutional and interstitial Mn present. It is recognised that EFTEM is essential for the appraisal of chemical distributions across the reaction interface of diffusion couple contacts to AlGaN/GaN following rapid thermal annealing. However, the limitations of this technique in terms of long acquisitions necessitating image post processing for the purpose of drift correction, combined with the problems associated with the overlap of some energy loss peaks, acts as a reminder for the use of other complementary methods of assessment to obtain a clear description of the sample chemical content.

References
[1] M. E. Lin, Z. Ma, F. Y. Huang, Z. F. Fan, L. H. Allen, and H. Morkoç, Appl. Phys. Lett. 64, 1003 (1994).
[2] T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, Science 287, 1019 (2000)
[3] K. Y. Wang et al, 2004, proceedings of the 27th International Conference on the Physics of Semiconductors.
[4] R. P. Campion, K. W. Edmonds, L. X. Zhao, K. Y. Wang, C. T. Foxon, B. L. Gallagher, C. R. Staddon, J Cryst Growth 247, 42 (2003)
[5] M. Sawicki, K-Y. Wang, K. W. Edmonds, R.P. Campion, C.R. Staddon, N.R.S. Farley, C.T. Foxon, E. Papis, E. Kaminska, A. Piotrowska, T. Dietl, B.L. Gallagher, Phys. Rev. B 71 121302 (2005)
[6] K. Ishizuka, J. Taftø, Acta Cryst. B40, 332-337, (1984)
[7] F. Glas, G. Patriarche, L. Largeau, and A. Lemaître, Phys. Rev. Lett. 93, 086107-1, (2004)
[8] K. M. Yu, W. Walukiewicz, T. Wojtowicz, I. Kuryliszyn, X. Liu, Y. Sasaki, and J. K. Furdyna, Phys. Rev. B 65, 201303 (2002);
K. M. Yu, W. Walukiewicz, T. Wojtowicz, I. Kuryliszyn, X. Liu, Y. Sasaki, and J. K. Furdyna, Phys. Rev. B 68, 041308 (2003).
[9] J. Mašek, J. Kudrnovský, and F. Máca, Phys. Rev. B 67,153203 (2003).
K.W. Edmonds et al., Phys. Rev. Lett. 92, 037201 (2004).