# Characterisation of AlGaN epilayers on (0001) sapphire grown by LP−MOVPE

**C. McAleese** 1), M.J. Kappers 1), F.D.G. Rayment 1), D.M. Graham 2), P. Dawson 2), E.J. Thrush 3), C.J. Humphreys 1)

1) Department of Materials Science and Metallurgy, University of Cambridge, CB2 3QZ, UK , 2) Department of Physics, UMIST, PO Box 88, Manchester, M60 1QD, UK , 3) Thomas Swan Scientific Equipment Limited, Buckingway Business Park, Cambridge, CB4 5UG, UK

## *Summary*

Crack−free $Al_xGa_{1-x}N$ epilayers with Al contents up to x=0.40 have been grown by LP−MOVPE on c−plane sapphire substrates, using low temperature AlN nucleation layers. A silane treatment during nitridation of the sapphire surface has been found to improve the crystalline quality of a 2 µm thick AlGaN epilayer with x=0.17, substantially reducing the XRD peak widths, and leading to the removal of an impurity or defect peak in the LT−PL spectrum. This treatment is responsible for an increase in the average grain size of the AlN nucleation layer, and leads to a greater compressive strain in the AlGaN layer.

## *Introduction*

AlGaN is a wide bandgap semiconductor alloy of great importance for ultraviolet optoelectronic applications such as solar−blind photodetection, biochemical detection, solid−state white lighting, and lithography. It is of paramount importance for deep−UV (<340 nm) light−emitting devices to exclude the use of GaN buffer layers or SiC substrates which would drastically reduce the light extraction efficiency due to absorption. To circumvent this problem, thick crack−free AlGaN layers, grown directly on sapphire substrates, are required. This immediately poses a materials problem since AlGaN/GaN heterostructures are generally of superior quality to those grown directly on sapphire, although cracking and fracture can be significant in the former. Good quality $Al_xGa_{1-x}N$ layers with x<0.70 have already been grown on sapphire using low−temperature nucleation layers of GaN [1, 2], AlGaN [3, 4] or AlN [2, 5, 6], and the incorporation of strained−layer superlattice structures [5] seems particularly encouraging. Despite these advances many materials development issues for the AlGaN alloy system still need to be addressed, such as the reduction in defect density and impurity incorporation, the presence of spontaneous alloy ordering, and improvements in n− and (especially) p−type conductivity. In this paper we report on the optimisation of the growth of $Al_xGa_{1-x}N$ alloys grown on c−plane sapphire substrates, and the characterisation of their structural (AFM, XRD, RBS), optical (LT−PL, LT−PLE spectroscopy), and electrical properties (Hall−effect measurements).

## *Growth*

AlGaN epilayers were grown in a 6×2" Thomas Swan Close−Coupled Showerhead reactor on (0001) sapphire substrates, with trimethylaluminium (TMA), trimethylgallium (TMG) and ammonia ($NH_3$) used as the Al, Ga and N precursors respectively. The sapphire wafer was treated in a flow of ammonia and hydrogen at 1050 °C, resulting in nitridation of the sapphire surface, before ramping down the temperature to 700 °C to deposit a 30 nm AlN nucleation layer (NL). The high temperature AlGaN epilayer was subsequently grown at 1040 °C and a pressure of 50 Torr. The TMG flux was kept constant in all cases, and the Al content of the layers was varied by changing the TMA flow rate; the V/III ratio was controlled by adjusting the $NH_3$ flow rate. In a number of experiments, the sapphire surface was dosed with silane for 120 seconds during the nitridation treatment. The growth was monitored in−situ using a laser interferometer operating at 635 nm. Surface roughening, depending on the length scale of the roughness, results in the decay of the average reflectance and/or the amplitude of the oscillations. Figure 1 shows the effect of changes in the V/III ratio on the rate of roughening during epilayer growth; a relatively high V/III ratio of 2600 was found to be necessary for HT epilayer growth, to prevent surface roughening and the formation of large pits on the surface. Another parameter which strongly affects the surface roughening rate is the growth temperature. As mentioned by Omnes et al [1], the surface morphology is very sensitive to temperature, and it was also found here that there appears to be a narrow window of little more than 10 °C in which smooth surfaces are obtained. Outside this range, the surface roughens and the reflectance decreases with time in a similar manner to that shown in Figure 1.

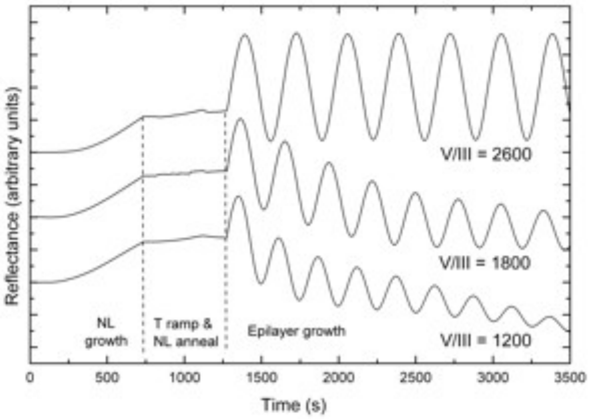

Figure 1: Interferometer traces from AlGaN epilayer growth at different V/III ratios.

Using a V/III ratio of 2600 at a temperature of 1040 °C, a range of smooth, crack−free $Al_xGa_{1-x}N$ layers have been grown, with thicknesses up to 1.7 µm and 2 µm for x=0.38 and x=0.17 respectively. This is by no means the limitation in thickness, as cracking has not been observed in any of the AlGaN samples prepared in this study, a finding in contrast to the observations of Zhang et al [5], where cracks were observed in samples thicker than 1.2 µm for x=0.20. Hall effect measurements indicated that the AlGaN layers were highly resistive when undoped, but with Si doping using silane, a carrier mobility of 128 $cm^2$ /Vs with a carrier concentration of $3.5\times10^{18}$ $cm^{-3}$ has been achieved for 1.2 µm $Al_{0.15}Ga_{0.85}N$.

### ***X−ray Diffraction Analysis***

The composition and strain state of the AlGaN layers has been determined from the *a* and *c* lattice parameters, derived from XRD reciprocal space mapping of the (0002) and (10−15) reflections, using a biaxial strain model to determine the variation of lattice parameters with strain. The strain along the *c*−axis (growth direction), $\epsilon_{zz}$ , is given by [7]:

$$\epsilon_{zz} = -\frac{2C_{13}}{C_{33}}\epsilon_{xx} = -\nu\epsilon_{xx}$$

where $\epsilon_{xx}$ is the strain in the basal plane, $C_{ij}$ is the elastic stiffness tensor in Voigt's notation and $\nu$ is Poisson's ratio. The elastic moduli are assumed not to vary significantly with composition, as they are similar for AlN and GaN [8] and the values used here are 103 GPa and 405 GPa for $C_{13}$ and $C_{33}$ respectively [9]. The lattice constants used are: $a_{GaN}$ = 3.1893 Å, $c_{GaN}$ = 5.1851 Å, $a_{AlN}$ = 3.1130 Å, $c_{AlN}$ = 4.9816 Å, and the variation with composition has been assumed to be linear, i.e. in accordance with Vegard’s Law. The composition can then be determined from:

$$x = -\frac{ac(1+\nu) - ac_{GaN} - a_{GaN}c\nu}{ac_{GaN} - ac_{AlN} - a_{AlN}c\nu + a_{GaN}c\nu}$$

where c and a are the measured lattice parameters of the AlGaN layer. All the AlGaN samples grown were found to be under biaxial compressive strain, presumably due to epitaxial growth on the AlN NL, which has smaller lattice constants. As a further independent measure of the composition, one sample has been tested with Rutherford Backscattering (RBS), giving a value of x=0.37, in reasonable agreement with a calculated Al content by XRD of x=0.40.

It was found that the crystalline quality of the AlGaN layers can be improved considerably by dosing the sapphire surface with silane during the nitridation stage prior to NL growth. Two samples with x=0.17 and thickness 2 µm, one with 120 s silane dosing (sample A), the other without this pre−treatment (sample B), were studied in more detail. The full width at half maximum intensity (FWHM) of an XRD omega scan (rocking curve) about the (0002) reflection was reduced from 1270 arcsecs (sample B) to 630 arcsecs (sample A) when this silane treatment was used. Since the (0002) rocking curve is sensitive to the tilt component of sub−grains in the mosaic structure, further rocking curves were taken for the (10−11) reflection, which is more sensitive to the twist misorientation. The FWHM of this reflection was reduced from 3030 arcsecs (B) to 2130 arcsecs (A), demonstrating the crystal quality to be improved in general. Furthermore, the silane treatment appears to have an effect on the strain state of the epilayer; sample A with the treatment was found to have a higher compressive strain than the untreated sample (B). A further noticeable feature from the X−ray data was the pronounced asymmetry in the (0002) omega/2theta scan for sample A, which was absent in sample B, indicating a proportionally greater amount of material with larger c lattice parameter throughout the thickness of sample A. Presumably, the AlGaN near the interface with the AlN is under considerable compressive strain, and this relaxes slightly with increasing thickness of the AlGaN layer, but at a slower rate and ultimately to a lesser extent in sample A. The difference in average compressive strain between the two samples induced by the silane treatment is still apparent after 2 µm of epilayer growth.

### ***LT−PL Analysis***

The AlGaN epilayers have also been characterised with low temperature (T = 6 K) photoluminescence spectroscopy (PL) and photoluminescence excitation spectroscopy (PLE). In Figure 2 are shown PL spectra for samples A and B and the PLE spectrum for sample A; as can be seen by comparing the PL and PLE spectra, the main spectral feature is assigned to recombination of bound or localised excitons. Also at around multiples of ~90 meV below the main peak are seen peaks that are assigned to phonon−assisted exciton recombination. A significant difference in the PL spectrum of samples grown with and without silane treatment can be observed. For sample B, an additional low energy feature at 3.66 eV is apparent, and it should be stressed that this is not due to phonon−assisted recombination of localised or bound excitons. At present, the assignment of the low energy recombination is unclear, other than that it is most likely to be associated with recombination involving some defect(s) or impurities. Furthermore, the difference in the peak energy of the excitonic emission is not the same in samples A and B; this may reflect either some small difference in Al content or the difference in the strain state of the AlGaN epilayers as revealed by the XRD measurements.

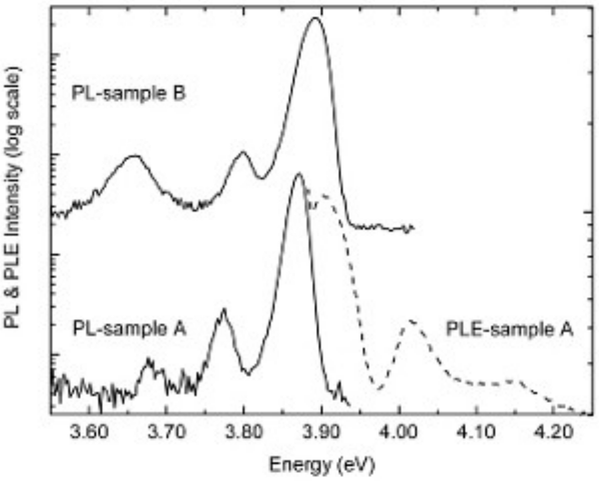

Figure 2: Comparison of LT-PL spectra for samples A and B, together with LT-PLE spectrum for sample A.

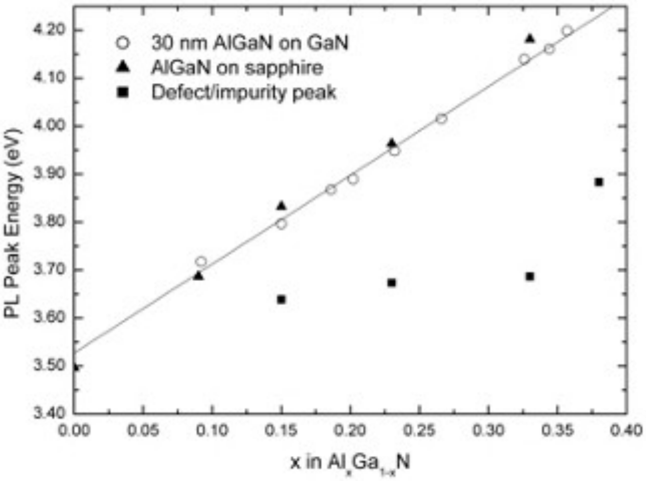

Figure 3: Variation in AlGaN epilayer LT-PL peak energy and defect/impurity peak energy with Al content

A plot of the peak energy for the localised exciton emission versus the Al content is shown in Figure 3, together with the low energy peak positions. As the Al content is increased, the strength of this defect/impurity peak, which is observed for layers with x>0.15 grown without silane dosing during nitridation, increases relative to the AlGaN peak, such that by x~0.33, the defect peak dominates the spectrum. PL peak energies from 30 nm AlGaN layers on GaN are also shown in Figure 3; the peak energies of the thicker AlGaN layers can be seen to follow a similar trend to the AlGaN/GaN heterostructures.

## ***Discussion***

The silane treatment clearly improves the quality of the crystal, judging from the XRD and PL data. It has been reported [10] that a similar silane treatment, which was used for GaN NLs, resulted in a change in the density and size of the GaN islands after the NL anneal, suggesting that the treatment results in a partial masking of the surface with a thin layer of $SiN_x$. AFM scans of the annealed AlN NLs show that the layer is continuous, but the average grain size is greater in the case of the silane−treated sample (see Figures 4 a and b).

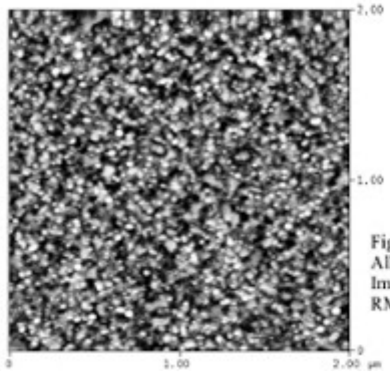

Figure 4a: AFM image of AlN NL without silane treatment. Image z range 12 nm. RMS roughness 1.22 nm.

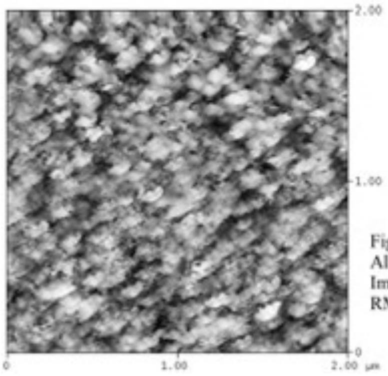

Figure 4b: AFM image of AlN NL with silane treatment. Image z range 7 nm. RMS roughness 0.68 nm.

Since the growth of the high temperature AlGaN epilayer is immediately 2D, the morphology would strongly depend on the underlying NL, hence a larger average grain size in the NL could be leading to an improvement in crystal quality. Twigg et al [11] report that for GaN growth on AlN NLs, a reduction in the density of extended defects in the NL increases the GaN grain size and improves the structural and electrical properties of the layer. TEM investigations are being carried out to determine whether a similar process is responsible for the effects observed here.

## ***Conclusions***

AlGaN epilayers up to 2 µm thick with smooth, mirror−like surfaces have been grown on (0001) sapphire substrates, using low temperature AlN nucleation layers, with Al contents up to x=0.40. It was found that dosing the sapphire surface with silane during the nitridation stage resulted in substantially improved crystalline quality, as characterised by XRD and LT−PL. This was accompanied by an increase in compressive strain of the AlGaN, and appears to be due to an increased grain size of the AlN.

## ***References***

[1] F. Omnes, N. Marenco, B. Beaumont, Ph. de Mierry, E. Monroy, F. Calle, E. Munoz, J. Appl. Phys. 86 (1999) 5286.
[2] S.R. Lee, A.F. Wright, M.H. Crawford, G.A. Petersen, J. Han, R.M. Biefeld, Appl. Phys. Lett. 74 (1999) 3344.
[3] D.K. Wickenden, C.B. Bargeron, W.A. Bryden, J. Miragliotta, T.J. Kistenmacher, Appl. Phys. Lett. 65 (1994) 2024.
[4] A. Krost, J. Blaesing, F. Schulze, O. Schoen, A. Alam, M. Heuken, J. Cryst. Growth 221 (2000) 251.
[5] J.P. Zhang, H.M. Wang, M.E. Gaevski, C.Q. Chen, Q. Fareed, J.W. Yang, G. Simin, M. Asif Khan, Appl. Phys. Lett. 80 (2002) 3542.
[7] R. Dupuis, Darpa website: http://www.darpa.mil/mto/suvos/workshop.html
[8] M. Schuster, P.O. Gervais, B. Jobst, W. Hosler, R. Averbeck, H. Riechert, A. Iberl, R. Stommer, J. Phys. D: Appl. Phys. 32 (1999) A56
[9] A. Polian, M. Grimsditch, I. Grzegory, J. Appl. Phys. 79 (1996) 3343.
[10] A.F. Wright, J. Appl. Phys. 82 (1997) 2833.
[11] S. Haffouz, P.R. Hageman, V. Kirilyuk, L. Macht, J.L. Weyher, P.K. Larsen, Mat. Sci. & Eng. B97 (2003) 9.
[12] M.E. Twigg, R.L. Henry, A.E. Wickenden, D.D. Koleske, J.C. Culbertson, Appl. Phys. Lett. 75 (1999) 686.