MRS Internet Journal Nitride Semiconductor Research

P- and N-type Doping of Non-Polar A-plane GaN Grown by Molecular-Beam Epitaxy on R-plane Sapphire

R. Armitage[1], Qing Yang[1] and Eicke R. Weber [1]
[1]*Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720,*

(Received Sunday, August 3, 2003; accepted Wednesday, September 3, 2003)

Non-polar a-plane GaN films doped with Si or Mg were grown by plasma-assisted molecular-beam epitaxy on r-plane sapphire substrates. The $(11\bar{2}0)$ orientation of the GaN epilayers was confirmed by x-ray diffraction. The layers were further characterized by atomic force microscopy, Hall effect, and photoluminescence measurements. The Mg-doped layers showed p-type conductivity, with a maximum hole concentration of 6×10^{17} cm^{-3} ($\mu = 2$ cm^2/Vs). Comparison with Mg-doping of N-polar c-plane GaN suggests the Mg sticking coefficient may be higher on the GaN $(11\bar{2}0)$ surface compared to the GaN $(000\bar{1})$ surface. The electron mobility obtained for a-plane GaN:Si (18 cm^2/Vs for $n = 1\times10^{18}$ cm^{-3}) was low compared to that of typical c-plane epilayers. The lower electron mobility is attributed to the higher density of structural defects in a-plane GaN.

1 Introduction

Almost all research on GaN to date has involved c-axis oriented wurtzite epilayers. With the polar c-axis aligned perpendicular to the film surface, the spontaneous and piezoelectric polarization effects cause strong internal electric fields at nitride heterointerfaces, e.g. InGaN/GaN quantum wells used for visible light emission. Built-in electric fields perpendicular to the heterointerface are generally undesirable for optoelectronic devices, as they cause separation of the electron and hole wavefunctions. The reduced overlap between these wavefunctions increases the carrier radiative lifetime and hence reduces the internal quantum efficiency.

To get around this problem, much attention has been focused on growth of the zincblende polytype of GaN, which is non-polar along the cubic [0 0 1] axis and therefore does not exhibit significant built-in electric fields at heterointerfaces. Unfortunately, the zincblende GaN polytype is metastable and it can only be grown successfully for a very narrow window of process conditions [1]. The difficulties in growth of zincblende GaN have hindered its further development for device applications.

Waltereit *et al.* [2] proposed a different idea to eliminate the internal electric fields due to polarization effects. Using $LiAlO_2$ substrates these authors grew wurtzite GaN epilayers with *m-plane* rather than the usual c-plane orientation. Wurtzite GaN epilayers with m-plane or a-plane orientation can be called “nonpolar” since the polar c-axis is parallel to the film surface. For this crystal orientation no significant built-in electric field exists within the quantum well.

The benefits of using non-polar GaN to eliminate internal electric fields was made clear by the work of Ng, [3] who compared the photoluminescence (PL) from AlGaN/GaN quantum wells grown in both the non-polar a-plane (on r-plane sapphire) and c-plane (on c-plane sapphire) orientations. Although the structural quality of the a-plane quantum well structures was inferior to that of the c-plane structures, the former actually showed much higher PL intensity. Time-resolved PL experiments showed a shorter radiative lifetime in the a-plane samples, as expected due to the absence of any carrier separation associated with internal electric fields [4].

The potential for improving light-emitting device efficiency with non-polar orientations of GaN has been clearly demonstrated in photoluminescence, but electroluminescence is required for practical applications. There have been no reports to date on p-type doping of a-plane GaN epilayers. Efficient light-emitting devices require highly conductive n- and p-type material. In particular, p-type doping of GaN is difficult and it has not yet been established that sufficient p-type conductivity can be obtained in non-polar GaN epilayers. Since the typical acceptor Mg is a volatile element with a sticking

© 2003 The Materials Research Society

https://doi.org/10.1557/S1092578300000491 Published online by Cambridge University Press

coefficient known to strongly depend on crystal polarity, it is expected that its incorporation behavior might be different for nonpolar versus c-plane epilayers.

2 Experimental Details

2.1 Growth

Growth runs were performed in a modified Riber 1000 molecular-beam epitaxy (MBE) system with a dc constricted glow discharge nitrogen plasma source [5] and effusion cells for gallium, silicon, and magnesium. The substrates were 8×8 mm pieces cut from a single-side polished 4" wafer of r-plane sapphire supplied by Union Carbide. Initially, the sapphire was treated in a solution of 3:1 H_2SO_4:H_3PO_4. Then the backs of the substrates were sputter-coated with titanium to facilitate heat absorption and temperature measurements inside the vacuum chamber. Just prior to loading into the chamber, the samples were ultrasonically cleaned in acetone and methanol, then mounted on the molybdenum sample holder using tantalum wires.

The sample temperature was estimated by radiation pyrometry, assuming an emissivity value of 0.9 for the titanium film on the back of the substrate. The substrate was initially outgassed for a few minutes at 820°C, then subjected to two *in-situ* cleaning cycles that involved deposition of a few layers of gallium metal at 550°C followed by heating to 770°C to desorb the gallium. This cleaning procedure yielded a streaky reflection high electron diffraction (RHEED) pattern from the r-plane sapphire.

For some of the layers, the growth was initiated with a nitridation procedure for 10 min at 820°C, with 20 sccm N_2 flow and a discharge current of 100 mA. These plasma conditions give an activated nitrogen flux sufficient for an N-limited GaN growth rate of ~150 nm/hour. Some growth runs were also tried without nitridation because the nitridation procedure was found to produce a spotty RHEED pattern, in agreement with the results of ref. 6. Although nitridation gave a spotty initial RHEED pattern from the substrate, the quality of the resulting GaN epilayers (as assessed by x-ray diffraction and Hall effect) was observed to be similar whether or not the nitridation procedure was employed.

Nitridation of a thin layer of Ga metal was previously found to produce an optimal nucleation layer for MBE growth of GaN on c-plane sapphire [6]. A similar buffer layer procedure was employed for growth on r-plane sapphire. A gallium metal layer was deposited at 500°C for 5 min with a Ga effusion cell temperature of 920°C. The Ga cell shutter was then closed and the Ga layer was annealed to the main layer growth temperature over an interval of 6 min with the nitrogen plasma source operating at 35 sccm, 100 mA. These plasma conditions correspond to an N-limited growth rate of ~300 nm/hour. The sapphire RHEED pattern completely vanished with the deposition of Ga metal. A spotty GaN RHEED pattern gradually appeared during the buffer layer annealing process in the nitrogen flux.

After completing the annealing process, the main GaN layer was grown with 980°C Ga effusion cell temperature and 750°C substrate temperature, with the same plasma conditions as those used for the buffer layer annealing. The growth duration was chosen between 3 and 4 hours, yielding films of 0.9-1.2 microns thickness as measured by stylus profilometry. The spotty RHEED pattern of the annealed buffer layer became streaky after a few minutes of main layer growth. The main layer growth conditions are believed to be nitrogen-limited based on the ex-situ observation of Ga metal droplets around the edges of the samples, which are at a slightly lower temperature than the substrate center. In MBE growth of c-plane GaN the presence of metallic Ga droplets on the sample surface is always associated with N-limited conditions, but we cannot be absolutely certain that this relationship also holds for a-plane GaN. The main layers were doped with either Si or Mg, with the Si effusion cell temperature 1020°C and Mg effusion cell temperatures from 350-400°C.

2.2 Characterization

Structural properties of the films were investigated by high-resolution x-ray diffraction using a Siemens D5000 instrument with Cu K_α radiation and a four-bounce Ge monochromator. Atomic force microscopy (AFM) was performed in the tapping mode using a Digital Instruments Nanoman instrument with standard Si cantilever tips. Hall effect measurements were performed using indium contacts in a four-corners square geometry with a magnetic field of up to 0.3 T and applied current values from 10^{-5} to 10^{-3} A. Hall data were obtained for several different values of the applied current and magnetic field strength to confirm the accuracy of the results. PL measurements were performed at 14 K with the sample mounted on the cold finger of a closed cycle helium cryostat. The excitation source was a 325 nm HeCd laser with power density of ~20 W/cm^2. The light was diffracted by a 0.85 m double-grating monochromator and detected with a photo-multiplier using the standard lock-in technique.

3 Results and Discussion

Figure 1 shows an x-ray θ-2θ scan for a GaN:Mg layer on r-plane sapphire. While the data presented are for a Mg-doped layer, Si-doped layers showed similar x-ray diffraction characteristics. The peak at 52.6° is assigned to the sapphire $(20\bar{2}4)$ reflection, and the peak at 57.9° is assigned to the GaN $(11\bar{2}0)$ reflection. Only background

© 2003 The Materials Research Society

https://doi.org/10.1557/S1092578300000491 Published online by Cambridge University Press

noise is present in the vicinity of 34.6°, the expected angle for a possible GaN (0002) reflection. These results indicate that the intended a-plane (non-polar) orientation of the GaN layer was in fact achieved. A ω-2θ scan for the GaN ($11\bar{2}0$) reflection is shown in Figure 2. This confirms the epitaxial orientation, but given the broad rocking curve (full-width half maximum of 20 arcmin) there is clearly a high degree of structural disorder in a-plane GaN epilayers. For comparison, our optimized c-plane samples on c-sapphire show a (0002) ω-2θ scan width of ~2 arcmin.

Analysis of the a-plane epilayers by AFM (Figure 3) revealed a surface morphology consisting of small (50-200 nm) but interconnected sub-grains. Due to the small sub-grain size, the overall root-mean squared (RMS) surface roughness is rather high (~20 nm) when imaged over a 10×10 micron area. However, the tops of the individual sub-grains are quite smooth with RMS roughness values of only 1-2 nm. The AFM experiments did not reveal any significant differences between the morphology of Mg-doped and Si-doped a-plane GaN films.

Hall effect results for Mg and Si-doped a-plane GaN epilayers are shown in Table I. The electron mobility observed for a-plane GaN layers is about a factor of 10 lower than typically obtained for c-plane GaN grown by MBE with the same Si doping level. Given the high degree of structural disorder revealed in x-ray measurements we conclude that the low electron mobility in a-plane GaN is probably related to a high density of extended defects that act as scattering centers. On the other hand, for Mg doping the p-type conductivity of a-plane epilayers is as high as is typically achieved in c-plane GaN:Mg. The hole concentration in a-plane GaN increases with increasing Mg effusion cell temperature, as expected. The decrease in hole mobility for high p-type doping levels is also typical of c-plane GaN:Mg. While the density of extended defects is higher in a-plane GaN, this does not significantly reduce the hole mobility compared to c-plane material.

It is noteworthy that in our MBE chamber we have never obtained a free hole concentration higher than 2×10^{17} cm^{-3} for c-plane GaN:Mg (N-face), while our preliminary experiments on a-plane GaN:Mg grown with similar substrate temperature and Mg flux already yielded significantly higher hole concentrations. This suggests that the Mg sticking coefficient on GaN ($11\bar{2}0$) may be substantially higher than on GaN ($000\bar{1}$), enhancing Mg incorporation and leading to higher free hole concentrations. Further systematic studies comparing a-plane and c-plane layers with identical growth conditions are necessary to confirm this preliminary finding.

Since Mg is highly volatile at the GaN growth temperature we would indeed expect the Mg incorporation behavior to be different for different crystal planes. Magnesium incorporation has already been shown to have a strong polarity dependence in c-plane GaN, with a much higher sticking coefficient on the Ga-face than the N-face [7]. Furthermore, excessive Mg flux can invert Ga-face material to N-face, making it difficult to control Mg incorporation for either polarity of c-plane GaN [8].

As an independent check for the Hall effect results indicating p-type conductivity, the samples were also characterized by photoluminescence (Figure 4). Due to the rather poor structural quality of the a-plane GaN layers, some key luminescence features such as the excitonic peaks cannot be resolved. However, the luminescence spectrum of a-plane GaN:Mg is clearly dominated by shallow donor-acceptor pair (DAP) luminescence centered at ~3.3 eV. In c-plane GaN:Mg samples individual peaks are usually resolved corresponding to the zero phonon DAP transition (3.27 eV) and its phonon replicas [9]. Evidently due to the poor structural quality of the a-plane GaN:Mg sample in Figure 4 the zero-phonon DAP peak and its phonon replicas are so broad that they appear as one convoluted feature. There also appears to be another band centered at ~2.9 eV which overlaps with the low-energy side of the shallow DAP-related transitions. These luminescence characteristics are usually associated with p-type GaN:Mg [9]. The absence of any yellow luminescence (~2.2 eV) in Figure 4 is also consistent with a p-type GaN sample. The ~2.2 eV band is usually observed in n-type but not p-type GaN [10].

4 Conclusions

Magnesium and silicon-doped a-plane (non-polar) GaN epilayers have been grown on r-plane sapphire by plasma-assisted MBE. The structural quality of the a-plane GaN layers was inferior to that of typical c-plane layers, as has also been found by other groups attempting to grow a-plane GaN [3] [11] [12]. The electron mobility in a-plane GaN:Si was only 18 cm^2/Vs for an electron concentration of 1×10^{18} cm^{-3}, compared to about 200 cm^2/Vs for c-plane epilayers of similar Si doping level. On the other hand, the p-type conductivity of a-plane GaN:Mg layers is as high as is typically found for c-plane GaN:Mg. A maximum hole concentration of 6×10^{17} cm^{-3} was observed for the Mg cell temperature of 400°C, with mobility of 2 cm^2/Vs. A preliminary comparison with p-type doping results on N-face c-plane GaN suggests the Mg sticking coefficient on GaN ($11\bar{2}0$) may be higher than on GaN ($000\bar{1}$). It therefore appears that control of magnesium doping in

© 2003 The Materials Research Society

https://doi.org/10.1557/S1092578300000491 Published online by Cambridge University Press

MBE growth may be easier for a-plane than for c-plane epilayers. Despite the rather poor crystal quality of a-plane GaN films achieved to date, the present results prove in principle that sufficiently high p- and n-type conductivity can be obtained for applications in light-emitting diodes, and there might even be an opportunity to achieve higher p-type doping levels compared with c-plane GaN films.

ACKNOWLEDGMENTS

This work was funded by the US Department of Energy project "Improving the Efficiency of Solid State Light Sources" under contract no. DE-FC26-01NT441202. Additional support is acknowledged from the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

[1] H. Okumura, K. Ohta, G. Feuillet, K. Balakrishnan, S. Chichibu, H. Hamaguchi, P. Hacke, S. Yoshida, *J. Cryst. Growth* ***178***, 113-133 (1997).

[2] P. Waltereit, O. Brandt, M. Ramsteiner, R. Uecker, P. Reiche, K. H. Ploog, *J. Cryst. Growth* ***218***, 143 (2000).

[3] H. M. Ng, *Appl. Phys. Lett.* ***80***, 4369 (2002).

[4] H.M. Ng, personal communication

[5] A. Anders, N. Newman, M. Rubin, M. Dickinson, E. Jones , P. Phatak , A. Gassmann , *Rev. Sci. Inst.* ***67***, 905-907 (1996).

[6] Y. Kim, N. A. Shapiro, H. Feick, R. Armitage, E. R. Weber, Y. Yang, F. Cerrina, *Appl. Phys. Lett.* ***78***, 895 (2001).

[7] L. K. Li, M. J. Jukovic, W. I. Wang, J. M. Van Hove, P. P. Chow, *Appl. Phys. Lett.* ***76***, 1740 (2000).

[8] G. Namkoong, W. A. Doolittle, A. S. Brown, *Appl. Phys. Lett.* ***77***, 4386 (2000).

[9] A. K. Viswanath, E. Shin, J. I. Lee, S. Yu, D. Kim, B. Kim, Y. Choi, and C. -H. Hong, *J. Appl. Phys.* ***83***, 2272 (1998).

[10] W Gotz, NM Johnson, J Walker, DP Bour, H Amano, I Akasaki, *Inst. Phys. Conf. Ser.* ***142***, 1031 (1996).

[11] S. Iyer, D. J. Smith, A. Bhattacharyya, K. Ludwig Jr, T. D. Moustakas, *Mater. Res. Soc. Symp. Proc.* ***743***, L3.20 (2002).

[12] M. D. Craven, S. H. Lim, F. Wu, J. S. Speck, S. P. DenBaars, *Appl. Phys. Lett.* ***81***, 469 (2002).

FIGURES

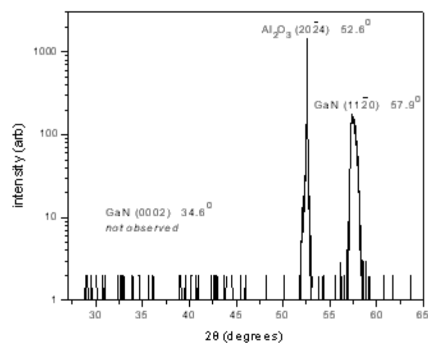

Figure 1. X-ray θ-2θ scan for a GaN:Mg epilayer on a-plane sapphire.

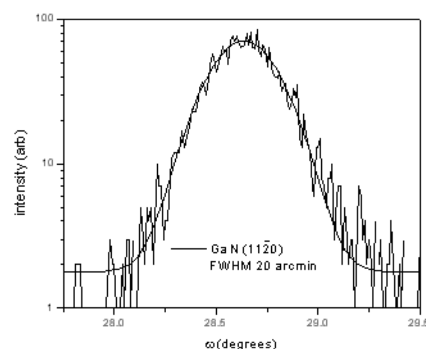

Figure 2. X-ray ω-2θ scan for a GaN:Mg epilayer on a-plane sapphire. The solid curve indicates a Gaussian fit to the experimental data.

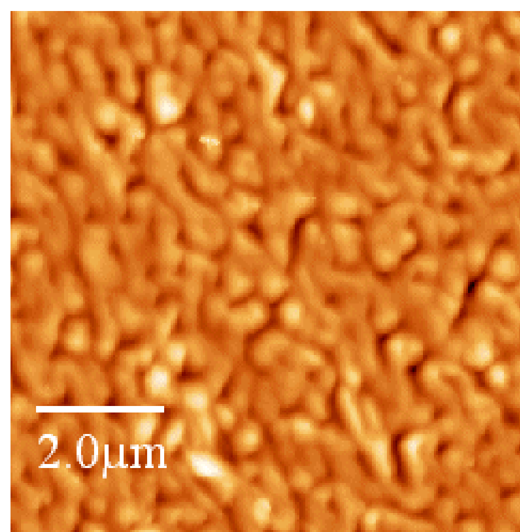

Figure 3. Atomic force microscopy image for a ~1 micron thick a-plane GaN:Mg epilayer on r-plane sapphire.

© 2003 The Materials Research Society

https://doi.org/10.1557/S1092578300000491 Published online by Cambridge University Press

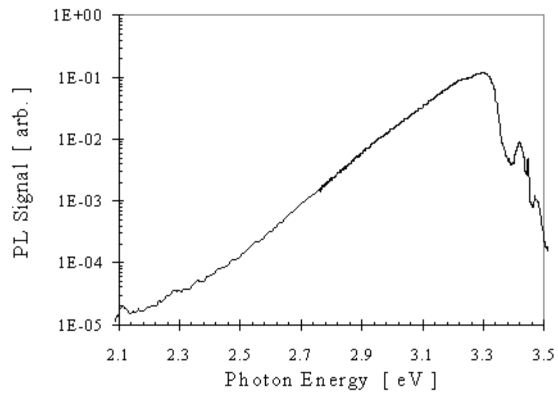

Figure 4. Photoluminescence spectrum (14 K) for an a-plane GaN:Mg epilayer.

TABLES

Table I. Hall effect results for Si-doped and Mg-doped a-plane GaN epilayers.

Effusion cell temperature	Carrier Concentration	Mobility
T_{Si} = 1020°C	$1x10^{18}$ cm^{-3}	18 cm^2/Vs
T_{Mg} = 350°C	$3x10^{17}$ cm^{-3}	5 cm^2/Vs
T_{Mg} = 400°C	$6x10^{17}$ cm^{-3}	2 cm^2/V

© 2003 The Materials Research Society

https://doi.org/10.1557/S1092578300000491 Published online by Cambridge University Press