Structural characterization of GaN and $GaAs_xN_{1-x}$ grown by electron cyclotron resonance-metalorganic molecular beam epitaxy

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Electron cyclotron resonance-metalorganic molecular beam epitaxy has been used to deposit GaN and $GaAs_xN_{1-x}$ layers on various substrates. This paper will report on the structural characterization of this material, as measured by x-ray diffraction and cross-sectional transmission electron microscopy. $GaAs_xN_{1-x}$ layers grown on GaAs appear to be cubic while those grown on GaP are surprisingly hexagonal. The hexagonal phase is also observed under some growth conditions in material grown on GaAs, however, the cubic phase can be obtained by optimizing the parameters which affect the initial nucleation. Conditions such as pre-deposition annealing and growth temperature are critical in determining the phase and crystallinity of the resulting layers. Because of the reduced mismatch between GaN and GaP, the cubic phase of GaN can be more easily nucleated on GaP substrates than on GaAs wafers using similar growth conditions. However, the films under all growth conditions are fine-grained polycrystalline. The impact on film quality of various strain dissipation schemes, such as grading the group V species across the As (or P)–N interface, will also be discussed.

I. INTRODUCTION

The growth of III–V nitrides is becoming of increasing importance due to their potential for use as visible optical devices and high-power electronic devices.[1,2] Though a great deal of information is available regarding their growth by metalorganic chemical vapor deposition (MOCVD)[1–6] and to a lesser extent molecular beam epitaxy (MBE)[1,2,7–13] little is known about the use of metalorganic molecular beam epitaxy (MOMBE) for deposition of nitride materials.[14,15] One of the advantages of MOMBE is its ability to grade the group V composition over a wide range for all of the potential elements of interest.

In order to take advantage of the processing, materials and device technologies already in place, it is highly desirable to deposit the group III nitrides on other III–V substrates. GaAs substrates, for example, have received a significant amount of attention.[1,2,7,8,16] Though cubic material has been obtained, large defect densities are often observed due to the severe lattice mismatch between the GaN and the GaAs.[2,8] One potential method of grading out the lattice mismatch between the group III nitrides and III–V substrates is the use of mixed Group V layers such as $GaAs_xN_{1-x}$ or GaP_xN_{1-x}. Neither material has to date been studied extensively. Sato and Weyers[6] reported on the growth of low nitrogen content, $1-x\sim0.035$, cubic $GaAs_xN_{1-x}$ alloys by metalorganic chemical vapor deposition (MOCVD) on GaAs substrates. The crystalline quality was reported to be excellent. Similarly, Igarashi and Okada[17] and Igarashi[18] have studied the growth of low nitrogen content, $1-x\sim0.065$, GaP_xN_{1-x} alloys on sapphire substrates. No information is available on the growth of nitrogen-rich alloys for either of these materials.

Another promising approach to improving the crystal quality of cubic nitrides grown on III–V substrates is the use of GaP rather than GaAs substrates since the lattice constant of this material is closer to that of GaN.[19] Thus far, only poly-crystalline hexagonal material has been obtained on GaP substrates for either (111) or (100) (Ref. 19) orientations. No analysis by scanning electron (SEM) or transmission electron (TEM) microscopy has yet been reported. In this article we will discuss the growth of the nitrogen-rich mixed group V alloy $GaAs_xN_{1-x}$ by MOMBE on both GaAs and GaP substrates. In addition we will report, for the first time, on the deposition of cubic GaN on GaP substrates. Deposition on GaAs substrates under similar growth conditions is also discussed for comparison.

II. EXPERIMENAL

Samples were grown on 2 in. diam (100) GaAs or GaP substrates in an INTEVAC Gas Source Gen II using In-free mounting. Triethylgallium (TEG) was used as the Ga source for all of the layers and was transported with either H_2 or He carrier gas. Prior to growth of the GaN, 1000 Å homoepitaxial buffer layers were deposited. AsH_3 and PH_3 decomposed in a catalytic cracker held at 1100 °C were used as the As and P sources respectively. Nitrogen was derived from a nitrogen plasma generated from 13 sccm of N_2 at 200 W in a Wavemat ECR MPDR610. Film thicknesses ranged from 4000 to 8500 Å and except where indicated were grown at a rate of 140 Å/min. Calibration with an infrared pyrometer indicated that the actual surface temperature of the GaAs was ~20–25 °C below that recorded by the substrate thermocouple. Since GaP is more transparent to the radiation emitted by the substrate heater, the heating efficiency of these substrates is expected to be poor. Consequently, GaP substrates were loaded with a GaAs backing wafer in order to make physical contact to the GaAs which would absorb the radiation from the heater. Calibration of the GaP surface tem-

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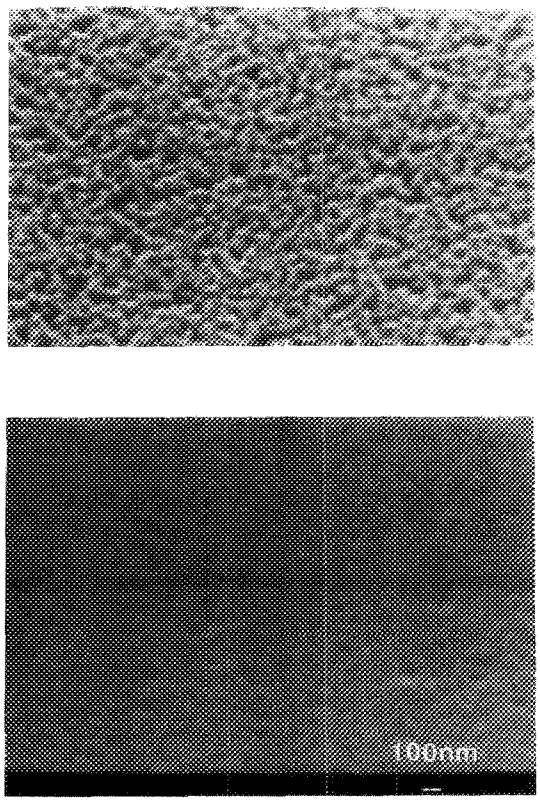

FIG. 1. SEM micrographs of $GaAs_xN_{1-x}$ grown at 700 °C on GaAs (top) and GaP (bottom).

perature was not possible with the pyrometer, though it is to be expected that the temperature is significantly lower than that of the GaAs. However, based upon the decomposition rate of the TEG, it is clear that this difference is less than 100 °C otherwise the growth rates observed on GaP at 525 °C would be drastically different from those measured on GaAs at 525 °C. Surface morphologies were examined using Nomarski optical and scanning electron (SEM) microscopes. X-ray diffraction (XRD) scans were obtained using Cu $K\alpha$ radiation in a single-crystal powder diffractometer. Selected area diffraction patterns (SADP) were taken in a JEOL 200CX transmission electron microscope as were cross-sectional photomicrographs obtained with $g=220$.

III. RESULTS AND DISCUSSION

As discussed previously, mixed group V materials would appear to be a potential method for reducing the problems associated with the severe lattice mismatch between the group III nitrides and the most commonly available III–V substrates. In order to be of help, however, these materials themselves must be of reasonable quality. As shown in Fig. 1, $GaAs_xN_{1-x}$ grown on GaAs with an N_2/AsH_3 ratio of ~18 exhibits a rough surface morphology usually indicative of fine-grained poly-crystalline material. On GaP, the AsH_3 flow was increased to 2 sccm so that an alloy with roughly the same lattice constant as GaP would be deposited if the alloy obeys Vegard's law and if the sticking coefficients for both elements were the same. Obviously both of these assumptions are at best rough approximations. Unfortunately, though the surface morphology improves significantly when GaP substrates are used in conjunction with a higher AsH_3 flow rate of 2 sccm, the surface texture still would suggest a polycrystalline layer. TEM analysis of both samples in fact confirms the polycrystalline nature of these films. From this data it is clear that changing the composition will not alone allow for deposition of high quality layers. Careful control of the initial nucleation conditions will also be required. However, it is interesting to note that the $GaAs_xN_{1-x}$ layer deposited on GaAs does appear to be cubic, as evidenced by the appearance of the c-GaN (200) peak at 39.8225°, as seen in Fig. 2. The SADP for this layer also indicates the presence of cubic material, and is confirmed by DIFFRACT simulation, though significant streaking is observed. Surprisingly, the $GaAs_xN_{1-x}$ layer grown on GaP appears to be hexagonal in spite of the reduced mismatch. Though certainly further work is needed to improve the crystallinity of the $GaAs_xN_{1-x}$ alloy, it is encouraging that cubic material on GaAs can be obtained. In addition to the potential use of this material as an interlayer or as a contact material, it may be useful as a method of tailoring the bandgap below that which can be obtained in GaN.

Given the poor crystallinity of the thick $GaAs_xN_{1-x}$ layers on GaAs, it is not surprising that a GaN layer grown on a thin, ~500 Å, graded $GaAs_xN_{1-x}$ buffer is polycrystalline as well. It is somewhat surprising, however, that the layer is hexagonal, as evidenced by the intense peak at ~35° in the XRD scan in Fig. 3, and not cubic. Initially it was assumed

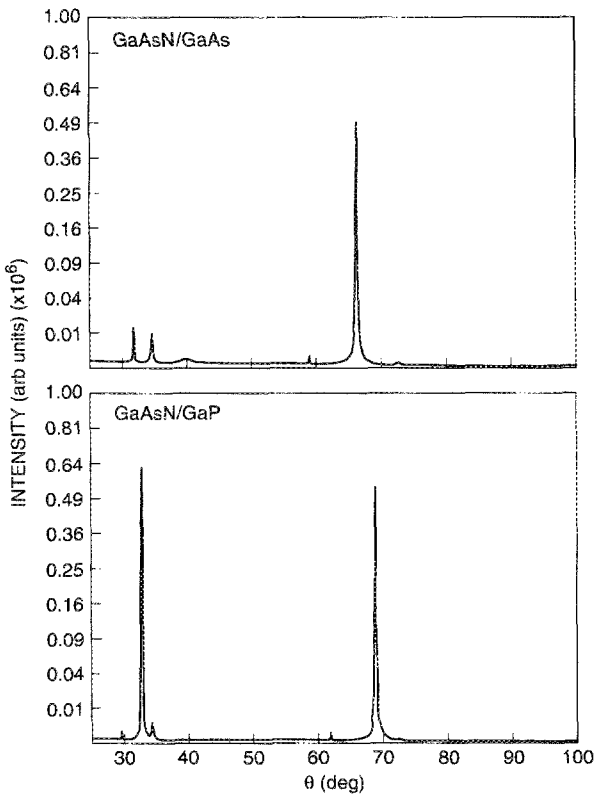

FIG. 2. XRD scans of $GaAs_xN_{1-x}$ grown at 700 °C on GaAs (top) and GaP (bottom).

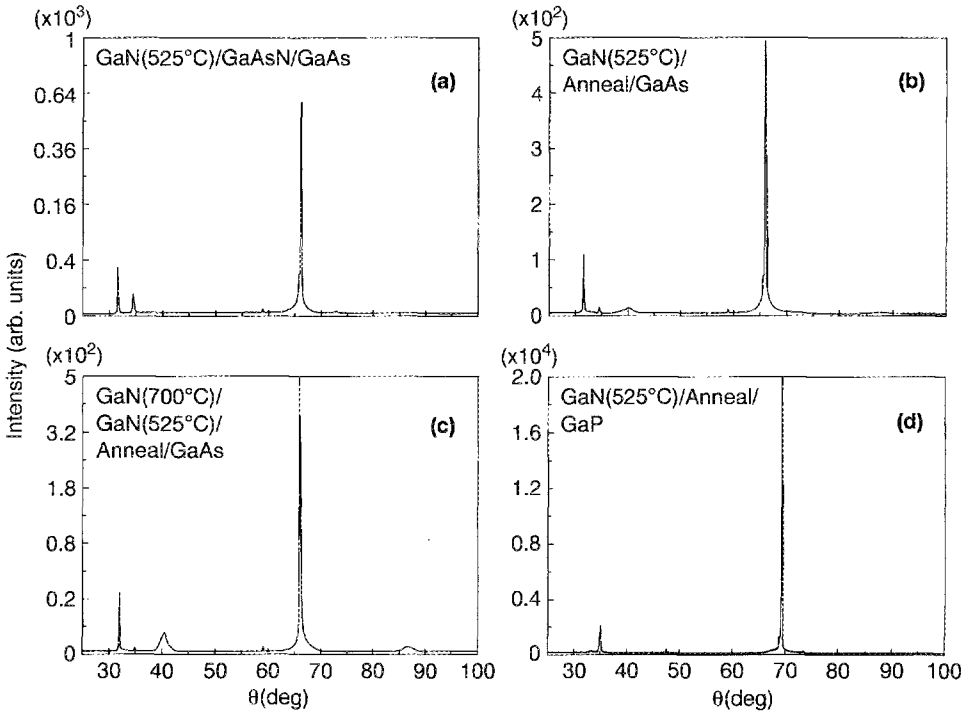

FIG. 3. XRD scans of GaN grown on either GaAs (a)–(c) or GaP (d). Scan in (a) was taken from a sample with a graded $GaAs_xN_{1-x}$ buffer while the other samples were grown with a 15 min *in situ* anneal under a nitrogen plasma. Samples depicted in (a), (b), and (d) were deposited at 525 °C. The layer shown in (c) was deposited at 700 °C after deposition of a thin, ~500 Å, GaN buffer layer at 525 °C.

that the low temperature employed for the growth of the GaN layer might have been responsible for this behavior rather than the presence of the $GaAs_xN_{1-x}$. However, when the graded interlayer is replaced with an *in-situ* anneal at 700 °C under a nitrogen plasma, some evidence of cubic material, namely a small peak at ~40°, can be seen in the XRD pattern even though the layer is grown at 525 °C. This peak can be enhanced by increasing the growth temperature to 700 °C such that only cubic material can be confirmed from the XRD scan. Unfortunately, though, the SADPs of the interfaces of samples grown at both temperatures show clear evidence of hexagonal as well as cubic GaN as shown in Fig. 4. Thus, while it appears that nitridation of the GaAs surface is more effective at inducing the cubic phase on GaAs than is the incorporation of a thin graded group V layer, clearly this is not sufficient to produce only cubic material.

With GaP substrates, it would appear from the XRD pattern, shown in Fig. 3(d), that only hexagonal material is obtained as evidenced by the appearance of the strong peak at ~35° and the absence of a peak at ~40°. SADP of the bulk of the layer, shown in Fig. 5(a), would seem to confirm this, showing primarily *h*-GaN (100). However, SADP of the interface, seen in Fig. 4(c), clearly shows only *c*-GaN with B=(110) and the orientation relationship is GaN [001]// GaP[001], GaN (001)//GaP (001). Spots due to twinning can also be observed. This is the first observation of cubic GaN on GaP, and suggests a transition from cubic to hexagonal during the course of the growth rather than immediate nucleation of the hexagonal phase. In this sample this transition occurs after ~1500 Å of growth suggesting that the condi-

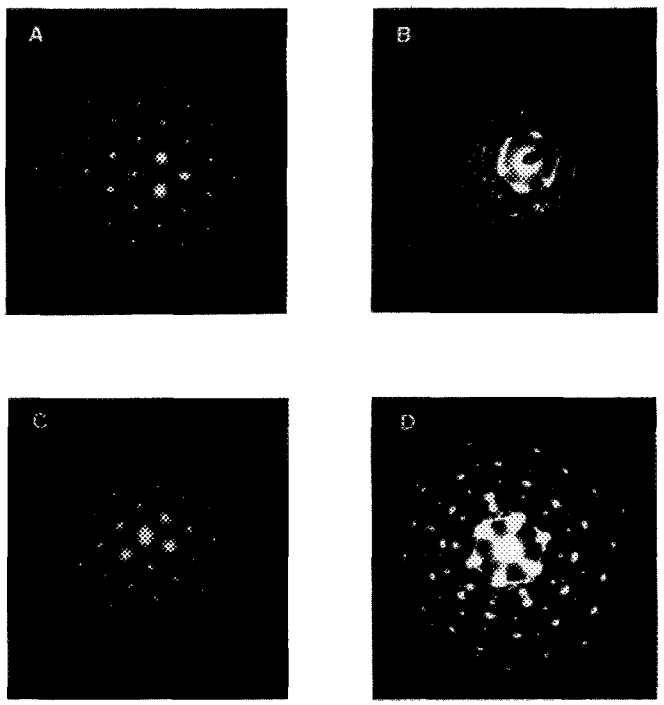

FIG. 4. SADP of GaN layers grown at 700 °C (b) or 525 °C (a), (c), and (d) on GaAs (b) and (d) or GaP (a) and (c). Pattern depicted in (a) was taken in the bulk while (c) was taken at the film/substrate interface.

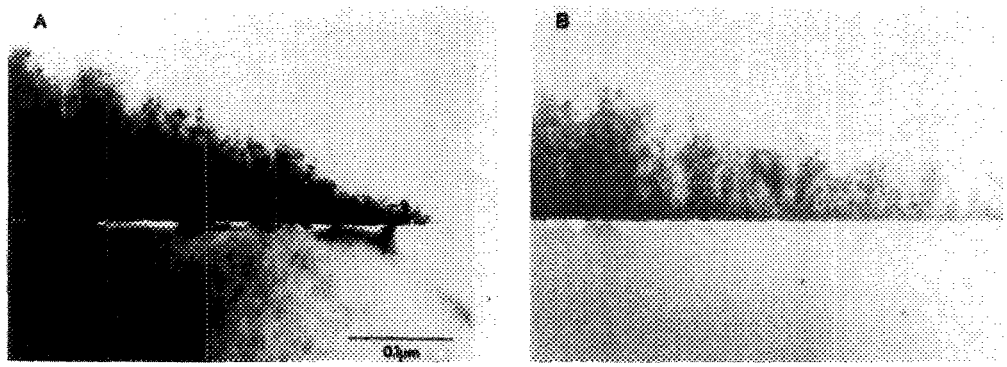

FIG. 5. TEM cross-section micrographs of GaN grown at 525 °C on GaAs (left) and GaP (right).

tions used for the nucleation if not the growth are adequate for deposition of cubic material.

One additional point should be noted regarding the use of surface nitridation for nucleation of cubic material. As shown in Fig. 5, significant dislocation generation is seen to occur at the surface of the GaAs or GaP buffer layers. On GaAs, these defects are rather shallow and elongated while on GaP they are triangular in shape. The origin of these defects is not clear, but may be related to the use of hydrogen to strike a plasma prior to introduction of the N_2 which could selectively leach group V atoms from the surface along the ⟨111⟩ planes. Later samples grown from plasmas struck by He rather than H_2 do not appear to suffer from the incorporation of these defects, although a more thorough investigation is needed to confirm the H_2 as the cause.

Given the improvement in the sharpness of the XRD peaks observed when the GaN on GaAs is grown at 700 °C rather than 525 °C, it was hoped that similar improvement would be observed in the morphology and crystallinity as well. However, as shown in Fig. 6, the surface of the layer deposited on GaAs appears to be quite rough. While the material deposited on GaP is smoother, it is also somewhat textured. The origin of this roughness can be identified quite clearly in the TEM, shown in Fig. 7, as very small diameter grains with a slight degree of misorientation with respect to one another. Similar behavior is observed for layers depos-

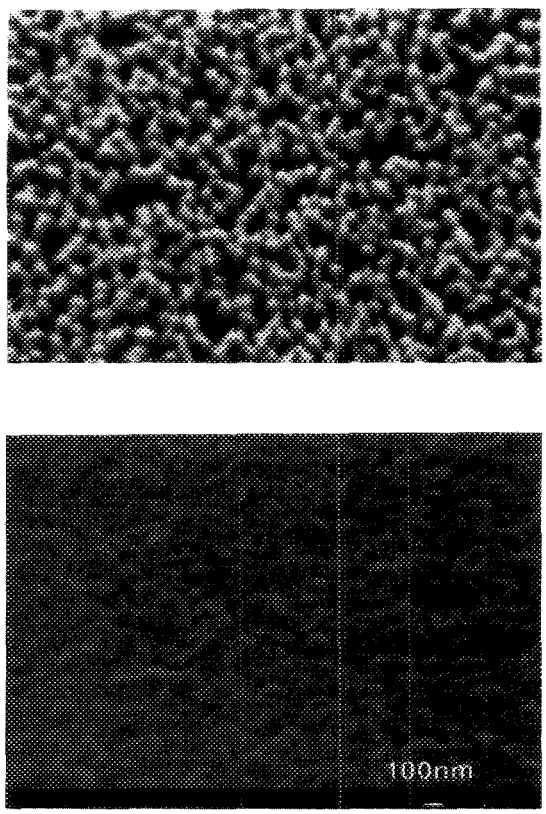

FIG. 6. SEM micrographs of GaN grown at 700 °C on GaAs (top) and GaP (bottom).

FIG. 7. TEM cross-section of GaN layer deposited on GaAs at 700 °C. Prior to growth of the thick layer, the substrate was annealed under a nitrogen plasma for 15 min at 700 °C and a 500 Å GaN buffer was deposited at 525 °C.

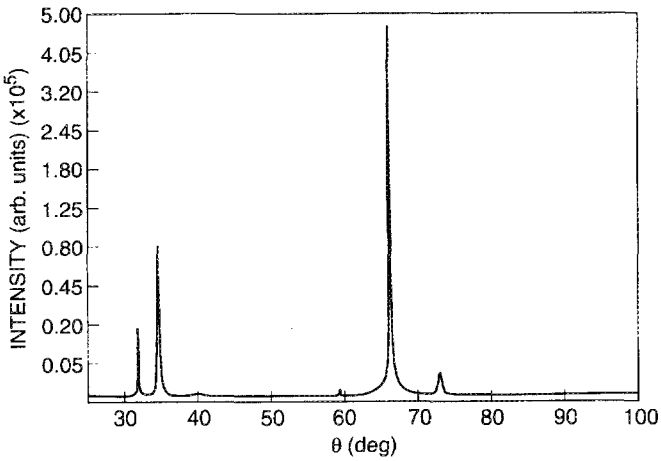

FIG. 8. XRD scan of GaN layer deposited at 700 °C at a growth rate of 70 Å/min on GaAs after the anneal and buffer layer sequence described in Fig. 7.

ited at 700 °C on GaP as well. Some improvement can be obtained by reducing the TEG flux, and hence the growth rate, by roughly a factor of two from 140 to 70 Å/min. As shown in Fig. 8, this produces a significant sharpening of the XRD peaks. The crystal planes associated with the various peaks are listed in Table I. Due to the overlap between some of the cubic and hexagonal peaks, it is difficult to unambiguously identify the layer as only cubic. However, the SADP confirms the existence of the cubic phase, exhibiting a *c*-GaN (110) pattern. TEM cross-section micrographs, however, show the same polycrystalline material, in this case with a grain size of ~600 Å, as observed at higher growth rates. Thus while reducing the growth rate is beneficial for obtaining the cubic phase, it is not clear if similar improvement in the crystallinity can be expected.

IV. CONCLUSIONS

The dependence of film quality as measured by surface morphology and crystallinity on substrate type and nucleation conditions has been investigated for growth of GaN by MOMBE. It was shown that GaP produces cubic GaN more readily than GaAs for similar growth conditions presumably due to its better lattice match with GaN. However, even with GaP, low growth temperatures induce a transition to the hexagonal phase even when the cubic phase is initially nucleated. Higher growth temperatures help to suppress this transition in both GaAs and GaP, as do low growth rates. The use of a thin graded Group V buffer layer prior to deposition of the GaN did not appear to improve the crystallinity or enhance the formation of the cubic phase. Cubic $GaAs_xN_{1-x}$ was, however, deposited on GaAs, suggesting that this material may be of some interest for future study. All of the samples examined appear to be fine-grained, 300–1000 Å grain size, highly oriented polycrystalline layers.

TABLE I. XRD peaks and their assignments for GaN grown on GaAs at 700 °C at a rate of 70 Å/min.

θ (deg)	d-spacing	I/I_{max}	Assignment
31.7250	2.8182	4.73	GaAs (200)
34.6050	2.5900	27.42	*c*-GaN (111) or *h*-GaN (002)
40.2450	2.2391	0.01	*c*-GaN (002)
59.0525	1.5630	0.07	
66.0875	1.4127	100.00	GaAs (400)
66.3250	1.4117	46.79	GaAs (400)
72.8850	1.2968	0.83	*c*-GaN (222) or *h*-GaN (004)
73.0750	1.2970	0.57	*c*-GaN (222) or *h*-GaN (004)

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