Influence of active nitrogen species on high temperature limitations for (000$\bar{1}$) GaN growth by rf plasma-assisted molecular beam epitaxy

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A reduced growth rate for plasma-assisted molecular beam epitaxy GaN growth often limits growth to temperatures less than 750 °C. The growth rate reduction is significantly larger than expected based on thermal decomposition. Characterization of various rf plasma source configurations indicated that a flux consisting predominantly of either atomic nitrogen or nitrogen metastables can be produced. The use of atomic nitrogen, possibly coupled with the presence of low energy ions, is associated with the premature decrease in growth rate. When the active nitrogen flux consists primarily of nitrogen metastables, the temperature dependence of the decrease is more consistent with decomposition rates. A significant improvement in electrical properties is observed for growth with molecular nitrogen metastables. In addition, atomic hydrogen stabilizes the growing surface of (000$\bar{1}$) GaN. © *1999 American Vacuum Society.* [S0734-211X(99)03304-1]

I. INTRODUCTION

Applications of blue and ultraviolet optoelectronic devices based on GaN have been recognized for many years. Recent advances in epitaxial GaN growth by metalorganic chemical vapor deposition (MOCVD) are leading to the rapid commercialization of this material system. Significant progress is also being accomplished by molecular beam epitaxy (MBE) growth using active nitrogen species.[1–5] Several issues remain to be resolved for MBE growth. While overall growth rate is no longer an issue, growth of GaN by plasma-assisted molecular beam epitaxy is typically limited to temperatures less than 750 °C due to a greatly reduced growth rate.[6–11] The temperature for the onset of decreased growth rate varies from group to group, but is typically lower than expected based on thermal decomposition rates for GaN. Recent results[12] also indicate that a significant increase in Ga flux can be required in order to obtain Ga-stabilized growth as the temperature is increased above 700 °C, suggesting a significant increase in Ga desorption. We present evidence that the observed decrease in growth rate and increase in Ga desorption are linked to the large reactivity of atomic nitrogen. Our results indicate that metastable molecular nitrogen may be the preferred active nitrogen specie for both growth at higher temperature and for improved electrical properties.

II. EXPERIMENTAL DETAILS

The GaN layers for this study were grown at West Virginia University by MBE in a custom system. A standard MBE source provided the Ga flux. Two rf plasma sources were used to produce active nitrogen, an Oxford Applied Research CARS-25 and an EPI Vacuum Products Unibulb source. The Oxford source featured a removable aperture plate allowing investigation of various hole configurations while maintaining the same overall conductance. The EPI source had a 400-hole aperture with an approximately 50% increase in conductance over the Oxford configuration. Characterization of these sources has been extensively reported elsewhere.[13] In brief, the sources were in direct line of sight to an Extrel quadrupole mass spectrometer whose repeller grid was biased separately to determine ion energies. An electrostatic plate could also be used to completely deflect ions out of the flux. The ionizer energy was set high enough to ionize both molecular and atomic nitrogen (typically >15 eV), but below the dissociation threshold of molecular nitrogen (<28 eV). During the EPI source characterization, considerable molecular nitrogen ions were produced with ionization energies approximately 6 eV lower than normally necessary to ionize molecular nitrogen. This energy corresponds to the $A\,^3\Sigma_u^+$ metastable state of the nitrogen molecule,[14] indicating the EPI source produces a significant flux of molecular nitrogen metastables. The observation of metastables in the EPI source flux is consistent with the previous spectroscopic study indicating that excited molecular nitrogen is generated in the plasma inside the source.[15]

Atomic hydrogen was produced using a thermal cracker (EPI-AHS). Typically, 1×10^{-6} Torr beam equivalent pressure (BEP) of hydrogen was passed through the thermal source operating at 9.5 A, although the hydrogen flux was varied for several samples. Literature supplied with the source indicated that dissociation efficiency was between 5% and 10% for this operating condition. Therefore, the sample was exposed to both atomic and molecular hydrogen during growth. Considering system pumping speed for hydrogen source-to-substrate distance, this gave an atomic hydrogen flux of one monolayer equivalent every 1–3 s.

Determination of relative sample growth rates were performed *in situ* by analyzing interference effects in reflectance measured from the growing layer using 680 nm light from a semiconductor laser. These measurements were converted to

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TABLE I. Typical flux of ions and atomic nitrogen, and the actual incorporation rate into GaN.

	Aperture				
Source	Hole diameter (mm)	Number of holes	Ion flux 10^{13} ions cm^{-2} s^{-1}	N atom flux 10^{15} atoms cm^{-2} s^{-1}	N incorporation in GaN 10^{15} atoms cm^{-2} s^{-1}
Oxford	1.0	9	7.6	4.5	0.58
CARS-25[a]	0.5	37	3.8	3.0	0.26
	0.2	255	2.3	2.3	0.19
EPI 600 W[b]	0.2	400	0.003	0.63	1.9
EPI 300 W[b]	0.2	400	0.001	0.28	1.1

[a]600 W, 6 sccm.
[b]2 sccm.

an absolute growth rate by using total sample thickness and the growth time. The total thickness was determined from interference fringes in *ex situ* optical transmittance measurements using a Cary-14 spectrophotometer. This method of determination of total thickness was found to agree with values determined by transmission electron microscopy.

Desorption mass spectroscopy (DMS) was also performed during growth, primarily to observe the desorbed Ga flux. A differentially pumped UTI Model 100C quadrupole mass spectrometer was placed in direct line of sight with the growing layer at normal incidence. The field of view was limited to the center of the samples using a series of apertures. All samples were grown on *c*-plane sapphire substrates (Union Carbide Crystal Products). Prior to growth, the substrates were degreased and etched in a phosphoric/sulfuric (1:3) acid mixture heated to 140 °C. Based on our earlier study,[6] buffer layers were grown by heating the substrate to 730 °C under an atomic hydrogen flux for 20 min and then cooling to 630 °C for the growth of a 200 Å thick GaN buffer layer under highly Ga-stable conditions. This procedure led exclusively to the nucleation and growth of $(0001\underline{1})$-oriented (or N-polarity) GaN as determined using the polarity-indicating etch described by Seelmann-Eggebert *et al.*[16]

III. DEPENDENCE OF GROWTH RATE ON ACTIVE NITROGEN SPECIES

Determining the effect of various active nitrogen species on layer growth is complicated when using rf plasma sources. These sources typically produce a complex mixture of active nitrogen superimposed on a background of presumed inert molecular nitrogen. This is illustrated by the source characterization data contained in Table I. The conditions shown are for those resulting in a maximum growth rate, plus one intermediate condition for the EPI source. The ion flux given is for the total ion flux (atomic plus molecular). The atomic ion flux was typically two to three times larger than that of the molecular ions. As reported previously,[17] the maximum ion energy for the Oxford source ranged from ~45 eV for the 9-hole aperture to 10 eV for the 255-hole aperture. The relatively insignificant ion flux from the EPI source had a maximum energy of about 3 eV.

Also included in Table I is the measured incorporation rate of nitrogen into the growing GaN (based on growth rates). Several observations can be made. Neither source produces enough ionic nitrogen to account for the observed growth rate, indicating that growth is due to other nitrogen species. The Oxford source configurations studied produced primarily atomic nitrogen, with little indication of the presence of molecular metastables based on the electron energies required for molecular ionization. Our study with this source indicates that atomic nitrogen is relatively inefficient for growing GaN, requiring about ten atoms in the flux for each one incorporated into the growing layer. In contrast, the EPI source configuration used produced significantly less atomic nitrogen and yet gave a factor of 3–5 increase in growth rate. These results, coupled with the ionization evidence for molecular metastables during source characterization, indicate that metastable molecular nitrogen is the dominant active nitrogen specie for our EPI source configuration.

Figure 1 illustrates the relative growth rate of GaN as a function of temperature for various configurations of the EPI and Oxford sources. Growth using a predominantly atomic nitrogen flux (the Oxford source) led to the early onset of decreased growth rate as reported previously.[18] Reported rates for Ga desorption from GaN surfaces indicate that Ga

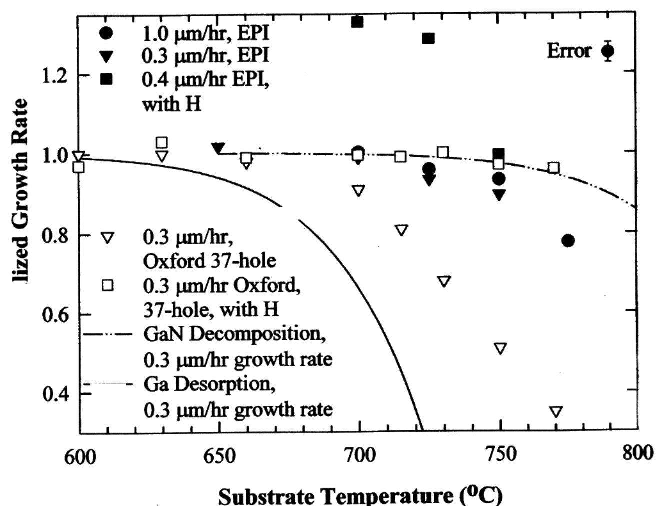

FIG. 1. Relative growth rates of GaN for various conditions. The growth rates were normalized to the low temperature rates. The rates for samples grown with atomic hydrogen were normalized to the low temperature rates of samples grown without atomic hydrogen but identical in other respects.

TABLE II. Mechanisms occurring during the growth of GaN.

Growth	Competition to growth
$Ga+\frac{1}{2}N_2^{+}+e^{-}\rightarrow GaN$	$GaN\rightarrow Ga\uparrow+\frac{1}{2}N_2\uparrow$ (Decomposition)
$Ga+\frac{1}{2}N_2^{*}\rightarrow GaN$	$Ga_{adsorbed}\rightarrow Ga\uparrow$
$Ga+N\rightarrow GaN$	$GaN+N\rightarrow Ga+N_2\uparrow$
$Ga+N^{+}+e^{-}\rightarrow GaN$	$GaN+N^{+}+e^{-}\rightarrow Ga+N_2\uparrow$

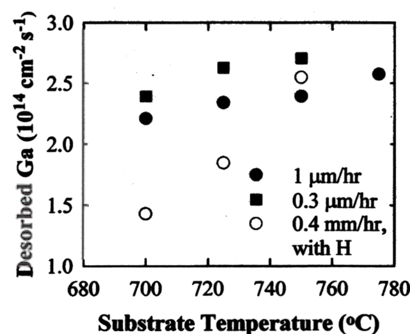

FIG. 2. Desorbed Ga flux vs temperature for two different growth rates and for growth under an atomic hydrogen flux.

desorption may play significant role over this temperature range.[19] To illustrate this, the temperature dependent growth rate decrease expected if the only contributing factor was the increased Ga-desorption rate is also shown in Fig. 1. This trend is also consistent with a recent study[12] using reflection high energy electron diffraction (RHEED) which indicated a rapidly increasing Ga flux is required to maintain Ga-stabilized conditions for rf plasma MBE growth above 700 °C. However, Ga-desorption alone is not the origin of the decreasing growth rate as increasing the Ga overpressure does not overcome the decreased growth rate for a given temperature.[6,18]

The relative growth rate versus temperature is shown for two operating conditions of the EPI source. For Ga-stable conditions and growth rates comparable to the Oxford source, the decrease in growth rate is now shifted to a higher temperature. A similar trend is observed for growth at 1 μm/h. Shown for comparison is the growth rate dependence on temperature expected if the only contributing factor was GaN decomposition.[19] The decrease in growth rate is now more comparable to the decomposition rate and is similar to that reported for ammonia-based MBE.[20,21] The results with the EPI source indicate that Ga desorption is not the dominant limiting factor, and that the role of active nitrogen species must be analyzed.

Table II contains a subset of possible reactions occurring during Ga-stable growth. The first column lists reactions leading to growth, while the second column details reactions in competition with growth. Of particular relevance is that ionic and neutral atomic nitrogen can participate both in the growth and in the decomposition of GaN. While rate constants for these reactions are not known there is a significant driving force based on free energy considerations.[14] This may explain the relatively poor efficiency for growth with atomic nitrogen indicated in Table I. Competition between growth, surface decomposition, and adsorbed nitrogen capture may limit the efficacy of atomic nitrogen. Such a situation would promote point defect formation, supported by the poor electrical properties discussed later. The decrease in growth rate observed at 775 °C for the EPI source may also be related to the residual atomic nitrogen flux.

Another interesting scenario[22] has been proposed suggesting a mechanism allowing improved growth using excited molecular nitrogen. Both atomic and metastable molecular nitrogen contain significantly more energy than required for GaN formation.[14] Incorporation of atomic nitrogen releases this energy into the lattice where it can drive unfavorable reactions. In contrast, the excited molecule can incorporate one atom into growing GaN while the other desorbs, carrying away the excess energy.

DMS was used to monitor reflected Ga flux during growth with the EPI source. Reduction of the desorbed Ga flux to values less than $0.3\times10^{14}\,cm^{-2}\,s^{-1}$ led to N-stable growth, as indicated by the RHEED pattern switching from a streaky, two-dimensional (2D) pattern to a spotty 3D pattern. In general, we maintained Ga-stable conditions during growth with a desorbed Ga flux between 0.5 and $1\times10^{14}\,cm^{-2}\,s^{-1}$. Figure 2 shows the temperature dependence of the desorbed Ga flux for different growth conditions measured with DMS. In obtaining the data shown in Fig. 2, the Ga- and nitrogen-source operating conditions were held constant. An approximate 20% increase in desorbing Ga flux was observed between 700 and 780 °C. While this correlates well with the observed decrease in growth rate, the observed increase in Ga desorption is significantly less than the rate indicated in Fig. 1. This gives further evidence that while Ga desorption plays a role in GaN growth, it is not a significant contributor for Ga-stable growth at these temperatures.

Figure 3 compares the electrical properties of samples grown with the various source configurations. As shown in Fig. 3(a), a significant increase in mobility occurred when using the EPI source, accompanied by a significant decrease in carrier concentration as indicated in Fig. 3(b). The results for the Oxford source are comparable to most values reported for rf plasma MBE, while the EPI results are consistent with improved electrical properties also observed by other groups[4,5,23] using a similar source configuration. Further indication of improvement in material quality is the observation of free excitonic transitions in preliminary photoluminescence measurements made on our GaN grown with the EPI source. Our current study indicates that growth with predominantly atomic nitrogen may result in significant point defects limiting layer quality. Indeed, our highest mobility values with the Oxford source were obtained for growth under a hydrogen flux, which may stabilize the growing surface as discussed later. Although lower carrier concentrations could be obtained with the Oxford source for growth without hydrogen, the accompanying mobilities were also significantly smaller.

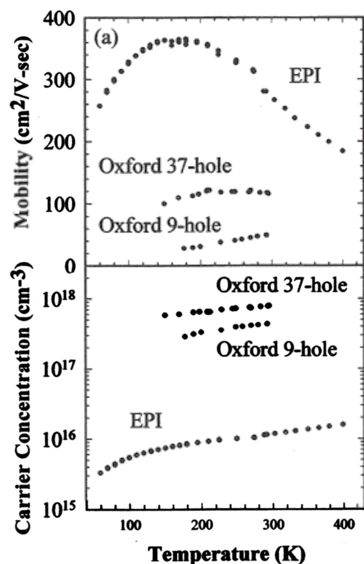

FIG. 3. (a) Mobility and (b) n-type carrier concentration for GaN grown using an EPI Unibulb source and an Oxford CARS-21 source. The results for the Oxford source are for samples grown under an atomic hydrogen flux.

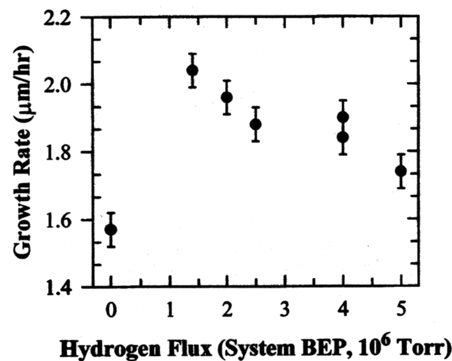

FIG. 4. Effect of atomic hydrogen on the growth rate of GaN when using the EPI source.

IV. EFFECTS OF ATOMIC HYDROGEN

The dramatic effect of atomic hydrogen on the growth of GaN by rf plasma MBE reported in previous studies[17,18] can now be better understood, at least for N-polarity growth. A bulk terminated surface would have a nitrogen dangling bond at the surface. This is normally accommodated by the formation of a surface Ga adlayer, as described by Smith *et al.*[24] The dangling bond, however, would make this surface more prone to decomposition through attack by atomic nitrogen. The rapid decrease in growth rate with increasing temperature may be related to the thermal activation of this reaction. If atomic hydrogen is available, it can also attach to the dangling bond thereby passivating the surface. The presence of a N–H bond would prevent the enhanced decomposition due to attack by atomic nitrogen. This scenario is supported by the recovery of the growth rate for the Oxford source when using atomic hydrogen as shown in Fig. 1. At the highest temperature investigated, growth with atomic hydrogen results in a growth rate about a factor of 3 larger than growth without atomic hydrogen. Growth under atomic hydrogen using the Oxford source appeared to be N stable as indicated by a spotty 3D RHEED pattern, the growth characteristics of inversion domains, and Ga-limited growth rates.[6,18] The recovery to the 0.3 μm growth rate indicated in Fig. 1 is reflective of the Ga-limited nature coupled with the fact that the Ga flux was kept constant for this comparison. Increasing the Ga flux led to steadily increasing growth rates until Ga condensation occurred at the temperatures investigated, to a maximum growth rate of 0.5 μm/h in our study. However, the relatively poor electrical properties of these growths resulted in our efforts being focused elsewhere.

The effect of atomic hydrogen on growth with the EPI source was significantly different, possibly reflecting the difference in the predominant active nitrogen specie. Rather than recovering the growth rate for a fixed Ga flux, an increase in the growth rate was observed for the same growth conditions as the 0.3 μm case, as indicated by relative growth rates larger than unity in Fig. 1. Interestingly, the increase at the lower temperature was approximately the same magnitude as the measured atomic nitrogen flux. The effect of the atomic hydrogen on growth rate became less for higher temperatures, with the growth rates being comparable with and without atomic hydrogen at the highest temperature investigated. Figure 2 also contains the desorbed Ga flux observed for growth under atomic hydrogen. Since the same source conditions were used as the 0.3 μm case, the reduced Ga desorption reflects the increase in growth rate. Increasing the substrate temperature led to a larger increase in desorption rate than for growth without atomic H.

The effect of increasing the atomic hydrogen flux for fixed growth conditions is shown in Fig. 4. Here, the base conditions lead to a GaN growth rate of about 1.6 μm/h. Addition of an atomic hydrogen flux increased the rate to more than 2 μm/h. Further increase in the atomic hydrogen flux then led to a steadily decreasing growth rate. The BEP shown reflect the total hydrogen flux. Based on published cracking efficiencies for this type of source along with relative ion gauge sensitivities, we estimate that 1×10^{-6} Torr BEP corresponds to approximately 0.5–1 monolayer/s equivalent of atomic H. The temperature is large enough for N–H bond breaking coupled with hydrogen desorption, and so any ''passivation'' effect must be dynamic. It is conceivable that the interaction of atomic hydrogen with the growing GaN surface is a complex situation. A relatively low concentration may protect the growing surface from attack by atomic nitrogen, while at higher concentrations the atomic hydrogen begins to compete with Ga for nitrogen bonds, resulting in a higher probability for Ga desorption. In addition, there is some evidence that hydrogen may even enhance the surface decomposition of GaN at higher temperatures, such as those used for MOCVD growth.[25,26] Since hydrogen is used in most successful growth approaches for GaN, further study is warranted.

V. CONCLUSIONS

The flux from rf plasma sources is a complex mixture of ionic and neutral atomic and molecular nitrogen. Studies of

growth rate as a function of temperature suggest the GaN surface is prone to "attack" by neutral and ionic atomic nitrogen above 700 °C, promoting decomposition. Growth using neutral metastable molecular nitrogen results in a temperature-dependent growth rate similar to that of growth with ammonia. Hydrogen can be used to stabilize the growing surface, at least for N-polarity growth. Too much hydrogen may promote Ga desorption, possibly due to competition for N bonds. Growth with predominantly metastable nitrogen also resulted in improved electrical quality. Metastable or low energy ionic molecular nitrogen may be preferable to neutral or ionic atomic nitrogen for MBE growth.

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