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The relation of active nitrogen species to high-temperature limitations for $(000\bar{1})$ GaN growth by radio-frequency-plasma-assisted molecular beam epitaxy

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A reduced growth rate for plasma-assisted molecular beam epitaxy of GaN often limits growth to temperatures less than 750 °C. The growth rate reduction can be significantly larger than expected based on thermal decomposition. Conditions producing a flux consisting predominantly of either atomic nitrogen or nitrogen metastables have been established using various radio-frequency sources. 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. © *1999 American Institute of Physics.* [S0003-6951(99)01325-X]

Recent advances in epitaxial GaN growth by metal–organic 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] However, growth of GaN by plasma-assisted MBE is typically limited to temperatures less than 750 °C due to a greatly reduced growth rate[6–11] that is typically lower than expected based on thermal decomposition rates. Recent results[12] also indicate that a significant increase in Ga flux can be required in order to obtain Ga-stabilized growth above 700 °C. We present evidence that an enhanced decrease in growth rate with increasing temperature, along with an associated increase in Ga desorption, is 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.

The GaN layers for this study were grown at West Virginia University by MBE in a custom system.[6] A standard MBE source provided the Ga flux. Two rf-plasma sources, an Oxford Applied Research CARS-25 and an EPI Vacuum Products Unibulb, were used to produce active nitrogen. 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. Extensive characterization of these sources has been reported elsewhere.[13,14] During the EPI source characterization using a mass spectroscopy system,[14] a considerable fraction of the molecular nitrogen flux was ionized at electron energies approximately 6 eV lower than normally necessary. This energy corresponds to the $A^3\Sigma_u^+$ metastable state of the nitrogen molecule,[15] indicating the EPI source produces a significant flux of molecular nitrogen metastables. This observation is consistent with the previous spectroscopic study indicating that excited molecular nitrogen is generated by this source.[16]

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. In order to obtain an absolute growth rate, the total thickness was determined from interference fringes in *ex situ* optical transmittance measurements using a Cary-14 spectrophotometer. This method was found to agree with thickness 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), with *ex situ* substrate preparation as reported elsewhere.[14] Based on our earlier study,[6] buffer layers were grown by heating the substrate to 730 °C under an atomic hydrogen flux (EPI-AHS, EPI Vacuum Products, St. Paul, MN) for 20 min and then cooling to 680 °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 $(000\bar{1})$-oriented (or *N*-polarity) GaN as determined using the polarity-indicating etch described by Seelmann-Eggebert *et al.*[17]

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, as illustrated by Table I. The

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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 CARS-25[a]	1.0		7.6	4.5	0.58
	0.5		3.8	3.0	0.26
	0.2		2.3	2.3	0.19
EPI 600 W[b]	0.2		.003	0.63	1.9
EPI 300 W[b]	0.2		.001	0.28	1.1

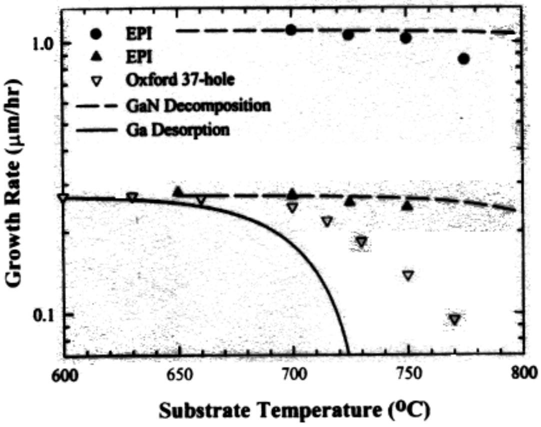
[a] 600 W; 6 sccm.

[b] 2 sccm.

conditions shown are for those resulting in a maximum growth rate, plus one intermediate condition for the EPI source. The atomic ion flux was typically two to three times larger than that of the molecular ions. As reported previously,[14] 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). It can be seen that 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 during characterization. Atomic nitrogen appears to be 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, indicating that metastable molecular nitrogen is the dominant active nitrogen specie in this source.

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) always led to the early onset of decreased growth rate as reported previously.[18] Since Ga desorption may play a significant role,[19] also shown is the temperature-dependent growth rate decrease expected if the only contributing factor was the increased Ga desorption. 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 cannot be the only effect as increasing the Ga overpressure does not overcome the decreased growth rate for a given temperature.[6,18,21]



For the EPI source, using Ga-stable conditions and growth rates comparable to the Oxford source, the decrease in growth rate is 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 indicate that Ga desorption is not the dominant limiting factor.

There are several possible reactions, both for growth and in competition with growth, occurring during Ga-stable conditions. Of particular relevance is that ionic and neutral atomic nitrogen can participate both in the growth and in the decomposition of GaN, which may explain the relatively poor efficiency for atomic nitrogen growth indicated in Table I. Possible reactions are the formation of GaN by bonding a Ga atom to a nitrogen atom, or to a nitrogen ion that needs an extra electron to maintain charge balance. Ionic and atomic nitrogen can also "attack" the growing GaN layer to form molecular nitrogen, which would then desorb, thereby enhancing decomposition. While rate constants for these reactions are not known, there is a significant driving force based on free-energy considerations.[15] Competition between growth, surface decomposition, and adsorbed nitrogen capture may limit the efficacy of atomic nitrogen. Such a situation would promote point defect formation and is 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.

Both atomic and metastable molecular nitrogen contain significantly more energy than required for GaN formation.[15] Another interesting scenario[22] proposes that incorporation of atomic nitrogen releases this energy into the lattice where it can drive unfavorable reactions, whereas 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

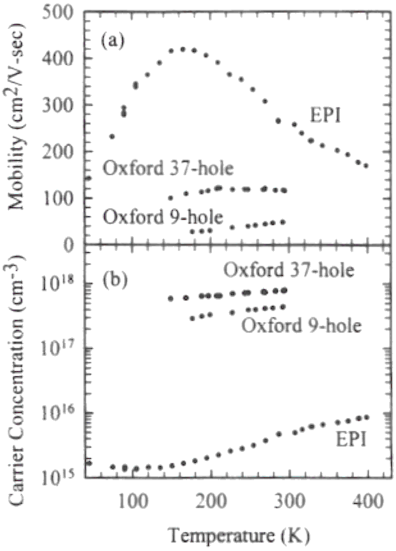


FIG. 2. Mobility (a) and *n*-type carrier concentration (b) for GaN grown using an EPI Unibulb source and an Oxford CARS-25 source. The results for the Oxford source are for samples grown under an atomic hydrogen flux.

growth with nitrogen metastables using the EPI source. Reduction of the desorbed Ga flux to values less than 0.3 $\times 10^{14}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ led to a switch from Ga-stable to N-stable growth, as indicated by the RHEED pattern switching from a streaky, two-dimensional pattern to a spotty pattern characteristic of three-dimensional growth. In general, we maintained Ga-stable conditions during growth with a desorbed Ga flux between 0.5 and $1\times 10^{14}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$. For a constant flux of both N and Ga, an approximate 20% increase in the 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 expected from 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 using nitrogen metastables.

As shown in Fig. 2(a), a comparison of the electrical properties measured for GaN grown using the various source configurations indicates that a significant increase in mobility occurred when using the EPI source. A significant decrease in the associated carrier concentration is shown in Fig. 2(b) for the metastable molecular nitrogen flux. The electrical 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.[18] Although lower carrier concentrations could be obtained with the Oxford source for growth without hydrogen, the accompanying mobilities were also significantly smaller.

In conclusion, 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 enhanced decomposition. Growth using neutral metastable molecular nitrogen results in a temperature-dependent growth rate similar to that of growth with ammonia. 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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