The effect of atomic hydrogen on the growth of gallium nitride by molecular beam epitaxy

Zhonghai Yu, S. L. Buczkowski, N. C. Giles, and T. H. Myers[a)]
Department of Physics, West Virginia University, Morgantown, West Virginia 26506

M. R. Richards-Babb
Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

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GaN was grown by molecular beam epitaxy using an rf plasma source. Growth under gallium-rich conditions at 730 °C was required to produce high quality layers as indicated by photoluminescence, Hall effect, atomic force microscopy, and x-ray diffraction measurements. Atomic hydrogen has a significant effect for Ga-rich growth, increasing growth rates by as much as a factor of 2. © *1996 American Institute of Physics.* [S0003-6951(96)04344-6]

The potential of blue and ultraviolet optoelectronic devices has been recognized for many years.[1] Recent advances in epitaxial GaN growth by metalorganic chemical vapor deposition (MOCVD) have lead to the report of the first demonstration of a blue laser based on GaN.[2] Rapid progress in this direction is also being accomplished by molecular beam epitaxy (MBE) growth using active nitrogen species.[3,4] One aspect of the MBE growth of GaN commonly cited as a disadvantage is the low growth rate. A recent study[5] has reported the use of ammonia for the MBE growth of GaN, leading to growth rates comparable to that found in MOCVD growth.

Most studies have either ignored the effect of hydrogen on the growth, or have only considered its effects in compensating *p*-type dopants such as Mg.[6] For example, the intent of using ammonia for MBE growth in the previously mentioned study was to obtain a larger flux of active nitrogen through catalytic decomposition on the GaN surface[7] with hydrogen considered an undesirable by-product. Hydrogen may, however, be altering the growth kinetics as well. In this letter, we present evidence that atomic hydrogen can have a significant effect on the growth kinetics of GaN when the growth is limited by the amount of active nitrogen present.

The GaN layers for this study were grown at West Virginia University by MBE. A standard MBE source (EPI-40M) provided the Ga flux. A cryogenically cooled rf plasma source (Oxford Applied Research CARS-25) operating at either 500 or 600 W was used to produce the active nitrogen flux. All layers reported here were grown with a nitrogen flow rate of 6 sccm, resulting in a system background pressure of 6×10^{-5} Torr. Our growth rates were limited to less than 1 Å/s by the maximum flux of active nitrogen available from our source configuration. The distance between our nitrogen source and the growing layer was about 30 cm, nearly double that found in most MBE systems.

Atomic hydrogen was produced using a thermal cracker (EPI). Typically, 1×10^{-6} Torr beam equivalent pressure (BEP) of hydrogen was passed through the thermal source operating at 9.5 A, giving a dissociation efficiency of about 5% for this operating condition. Photoluminescence (PL) measurements were performed using the 325 nm He-Cd laser line focused to a power density of 5 W/cm^2, a grating monochromator, and standard detection electronics. Hall, x-ray diffraction, and atomic force microscopy (AFM) (Digital Instruments Nanoscope II) measurements were also made.

Determination of substrate temperature and growth rate are important in this study. A calibrated spring-loaded type *K* thermocouple was in intimate contact with the back of the molybdenum sample block with the substrate mounted with indium. This calibration was routinely checked by using the melting points of various metals, oxide desorption from GaAs, and the use of an optical pyrometer for the higher temperatures. Temperature determination was reproducible to ±5 °C.

Growth rate was determined using total sample thickness and the growth time. The 1 cm^2 sapphire substrates were held by a retaining mask which provided a step allowing measurement with a stylus surface profilometer. In addition, the thickness at the sample's center was determined from interference fringes in optical transmittance measured using a Cary-14 spectrophotometer. The edge and center thicknesses agreed to within 10%.

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 80 °C. Based on our earlier study,[8] 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 a Ga flux of 5.0×10^{-7} Torr (BEP) with a 6 sccm nitrogen flow at 500 W. Buffer layer growth was initiated by simultaneous exposure to the Ga and N flux. This nucleation layer was then annealed at 730 °C for 20 min under nitrogen flux, cooled to the growth temperature, and growth was resumed. As discussed later, these conditions represent buffer layer growth under highly Ga-rich conditions. However, after the 730 °C anneal, examination of the buffer layers by AFM indicated continuous films with no evidence of Ga condensation.

GaN layers were grown under a variety of conditions, with the resulting growth rates indicated in Fig. 1. In Fig. 1, the growth rate is plotted as a function of Ga beam equivalent pressure. For an active nitrogen flux in excess or equal to the Ga flux, one would expect a linear increasing growth

a)Electronic mail: thmyers@wvu.edu

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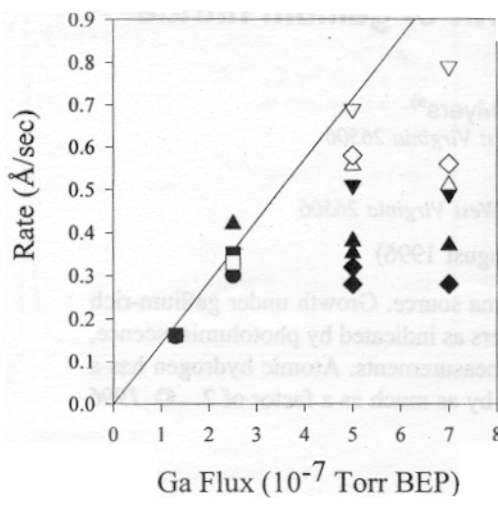

FIG. 1. Growth rate of GaN as a function of Ga flux. Substrate temperatures and rf power are: (●) 600 °C and 500 W; (■) 630 °C and 500 W; (▲) 660 °C and 500 W; (▼) 660 °C and 600 W; (◆) 730 °C and 600 W; (□) 630 °C and 500 W with H; (△) 660 °C and 500 W with H; (▽) 660 °C and 600 W with H; and (◇) 730 °C and 600 W with H.

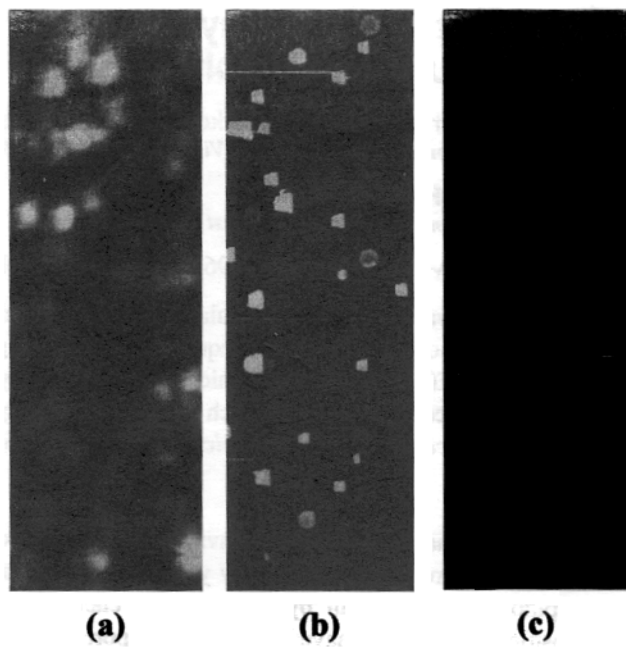

FIG. 2. AFM micrographs (5 μm×15 μm) illustrating the typical surface morphologies for: (a) nearly equal gallium and active nitrogen flux, (b) intermediate gallium flux, and (c) gallium-rich conditions. The height scale is 135, 200, and 35 nm, respectively, for the micrographs.

rate with increasing Ga flux. When the surface ratio of Ga to active nitrogen is increased beyond unity, then either Ga condensation will occur if the desorption rate for excess Ga is low or the growth rate will become fairly constant with increasing Ga flux if the excess Ga desorption rate is high. A linear increase in growth rate was observed in going between 1.3 and 2.5×10^{-7} Torr BEP Ga. At growth temperatures of 600 (●) and 630 °C (■) with 500 W rf power, Ga-droplet condensation occurred for growths with a Ga flux above 2.5×10^{-7} Torr BEP Ga. In contrast, Ga condensation did not occur until beyond 7.0×10^{-7} Torr BEP upon raising the substrate temperature to 660 °C (▲), also at 500 W. The growth rate remained fairly constant for a Ga flux between 2.5 and 7.0×10^{-7} Torr BEP, indicating that the growth was limited by the amount of active nitrogen available.

Increasing the power into the nitrogen rf source increases the amount of active nitrogen.[9] The concomitant increase in growth rate observed in going from 500 (▲) to 600 W (▼) power at 660 °C thus supports the assertion that the growth rate is limited by the amount of active nitrogen present. Our study is also in agreement with others,[10] that temperatures above 700 °C are necessary to obtain high quality material, as detailed below. Unfortunately, the GaN growth rate was observed to decrease significantly in going from 660 °C (▼) to 730 °C (◆) at 600 W rf power, from about 0.5 to about 0.3 Å/s. The increase in temperature has apparently either reduced the residence time of unreacted N on the surface or increased the GA desorption rate, thereby reducing the growth rate. Prior studies of Ga desorption for GaN growth using ammonia[11] indicate that the Ga desorption rate increases rapidly above 700 °C.

The surface morphology was distinctly different for layers grown under Ga-rich conditions as compared to layers grown closer to equal Ga and active nitrogen flux. Nitrogen sufficient conditions gave a highly textured, three-dimensional surface, as shown by the micrograph in Fig. 2(a). Such morphology is similar to that reported earlier[12] for the growth of GaN by MBE using an identical rf nitrogen source. Increasing the Ga flux resulted in isolated structures interspersed on flat regions of the surface, as can be seen in Fig. 2(b). The measured rms. surface roughness between the structures ranged between 0.6 and 1.5 nm. As we reported earlier,[8] Ga-rich growth close to, but below the Ga condensation point resulted in smooth, featureless surfaces indicative of two-dimensional growth with an rms surface roughness of 1.5 nm over a 15 μm span, similar to that reported for high quality MOCVD growth.[13] This can be seen in Fig. 2(c). Subnanometer tall terraces representing atomic steps were present on the top of the "flat" regions of the sample.

This change in surface morphology is very similar to that reported earlier[14] for growth of GaN using an electron cyclotron resonance microwave (ECR) plasma source. In the ECR study, the amount of active nitrogen was changed by controlling the plasma density. Lower power led to smooth surfaces, while high powers resulted in textured surfaces. It is known that, in addition to increasing the active nitrogen flux, high-power operation of an ECR source can lead to a significant amount of high-energy ions in the nitrogen flux[15] which could influence the growth morphology. In our study, the nitrogen source parameters were unchanged for the samples shown in Fig. 2 (600 W, 6 sccm) while the Ga flux was altered. Thus, the agreement between the two studies suggests that the change from smooth to textured growth is a universal phenomenon related to the ratio of active nitrogen to gallium at the growth front.

Introduction of atomic hydrogen resulted in a dramatic increase in the growth rate of the GaN under Ga-rich conditions as also summarized in Fig. 1. The samples whose growth rates are indicated by the open symbols in Fig. 1 were grown under a total (atomic and molecular) hydrogen flux of 1×10^{-6} Torr BEP. The other growth parameters remained the same. Note that the growth rate was essentially

doubled for each case of Ga-rich growth. In contrast, a sample grown under nitrogen-sufficient conditions at 630 °C did not exhibit an enhanced growth rate. The increase in growth rate for the Ga-rich cases did not appear to be very sensitive to the overall hydrogen flux. Changing the hydrogen flux from 0.5 to 2.0×10^{-6} Torr BEP gave the same value for the increase in the growth rate. To see if the increased growth rate originated with molecular hydrogen, samples were grown under hydrogen flux with the cracker turned off. The resulting samples exhibited identical growth rates to the GaN grown without hydrogen, indicating that molecular hydrogen is not significantly affecting the growth kinetics. Also, to see if the atomic hydrogen was possibly forming active species with molecular nitrogen, an attempt was made to grow under an atomic hydrogen flux with the rf power turned off on the nitrogen source. The resulting GaN growth rate, if nonzero, was too small to be detected.

The increase in growth rate for Ga-rich conditions is apparently related to the presence of atomic hydrogen. We propose that the atomic hydrogen becomes loosely bonded to the growing GaN surface. Nitrogen atoms adsorbed on the surface are then attracted by this hydrogen layer, resulting in an increased nitrogen residence time. The longer residence time increases the probability that a Ga atom will diffuse to within an interaction distance of the nitrogen, and thus enhance the growth rate of GaN. Thus, the atomic hydrogen could be increasing the effective active nitrogen concentration. In addition, the surface morphology for samples grown under atomic hydrogen more nearly resembled that shown as Fig. 2(a). This, along with the increased growth rate, is consistent with shifting the growth kinetics towards a more nitrogen-sufficient case.

PL measurements were made at both room and liquid helium temperatures on the samples. At room temperature, samples investigated exhibited band-edge emission at about 365 nm (3.39 eV). All samples grown at or below 660 °C also exhibited significant luminescence centered at about 560 nm (2.2 eV). Layers grown at 730 °C did not exhibit detectable yellow luminescence. We take this as direct evidence that the higher growth temperatures are necessary to produce high quality material. In low-temperature PL measurements, the layers grown at 730 °C exhibited primarily near-band-edge luminescence related to excitonic transitions, again indicating high quality layers. The PL obtained from a GaN layer grown at 730 °C under an atomic hydrogen flux is shown in Fig. 3. There is a single bound-exciton peak at about 3.47 eV and no evidence of PL related to deep levels, indicating that growth under hydrogen does not degrade layer quality.

The best GaN samples grown without atomic hydrogen were grown under Ga-rich conditions at 730 °C and exhibited x-ray diffraction rocking curve full widths at half maximum (FWHM) between 4 and 5 arcmin. Hall measurements made on these layers indicated *n*-type carrier concentrations as low as 4×10^{17} cm^{-3} with room-temperature mobilities as high as 120 cm^2/V s. The x-ray FWHM of the samples grown with atomic hydrogen were indistinguishable from those grown without atomic hydrogen under the same conditions. However, the background *n*-type carrier concentration was about a factor of 2 larger, at the low 10^{18} cm^{-3} level also with a mobility of about 120 cm^2/V s. Although hydrogen may introduce donor levels in GaN,[16] we have no direct evidence that this is the case here. As shown in Fig. 3, we did not observe the 3.35 eV PL feature which has been associated with the hydrogen-related donor.[16] It may be that the higher carrier concentration is related to the three-dimensional growth indicated by the textured surface.

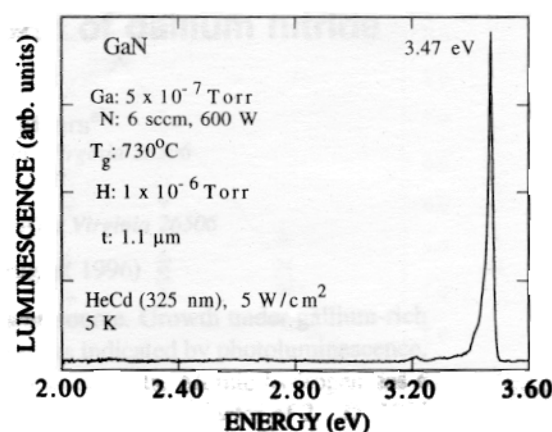

FIG. 3. Photoluminescence of GaN.

In conclusion, we have demonstrated that the presence of atomic hydrogen can have a significant effect on the growth rate of GaN under Ga-rich conditions. PL and Hall measurements indicate that layer quality is not degraded by growth under atomic hydrogen. The increased growth rate and change to a textured surface morphology are suggestive that the atomic hydrogen increases the effective surface concentration of nitrogen. In addition, we have presented evidence that Ga-rich growth promotes a smoother growth surface.

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