THE EFFECT OF HYDROGEN ON THE MOLECULAR BEAM EPITAXY GROWTH OF GaN ON SAPPHIRE UNDER Ga-RICH CONDITIONS

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ABSTRACT

Nucleation and growth of GaN under Ga-rich conditions by molecular beam epitaxy using a nitrogen rf plasma source is shown to result in both a smoother GaN surface and a reduced inversion domain content. In addition, preliminary results of the dramatic effect of atomic hydrogen on growth kinetics for Ga-rich growth are presented.

INTRODUCTION

GaN typically nucleates and grows on sapphire by island formation. The use of low temperature buffer layers (450 - 600 °C) of AlN [1] or GaN [2,3] results in a dramatic improvement in layer morphology and electrical properties. Annealing prior to high temperature growth causes coalescence of the nucleation islands, resulting in low angle grain boundaries which create the observed dislocation arrays [4,5]. It appears that this subgrain structure is stable during growth under most conditions. Thus, subsequent crystal quality is strongly dependent on the nucleation layer. The predominant growth mode is a further factor in dislocation reduction with increasing layer thickness. Two dimensional growth results in the highest degree of structural perfection in epitaxial layer growth. Typical molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) growth conditions appear to promote three dimensional growth of GaN. [6,7] This may lead to individual growth of the low angle grains, preventing dislocation recombination and annihilation. A recent study has reported MOCVD growth conditions resulting in two-dimensional step-flow growth [8], with a concomitant reduction in dislocation density to about 2×10^8 cm^{-2}. It is desirable to achieve conditions for MBE growth to allow such a growth mode to occur.

One of the obvious differences between MOCVD and MBE growth of GaN is the presence of hydrogen, primarily as a component of the molecule supplying the nitrogen. Most studies have either ignored the effect of hydrogen, or have only considered its effects in compensating p-type dopants such as Mg. For example, the use of ammonia in MBE growth is primarily to obtain a larger flux of active nitrogen through catalytic decomposition on the GaN surface, again with the hydrogen considered only as a reaction by-product. In this paper, we present evidence that: nucleation under Ga-rich conditions results in reduced dislocation and inversion domain content; continued growth under Ga-rich conditions promotes a smoother, two-dimensional growth front; and hydrogen can have a significant effect on the growth kinetics of GaN when the growth is limited by the amount of active nitrogen present.

EXPERIMENT

The GaN layers for this study were grown at West Virginia University by MBE in a system described elsewhere. [9] A standard MBE source provided the Ga flux. A cryogenically-cooled rf plasma source (Oxford Applied Research CARS-25) operating at 600W was used to produce active nitrogen flux. Atomic hydrogen was produced using a commercial thermal

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cracker (EPI-AHS). Our source-to-substrate distance was large, about 14 inches, leading to a lower total active-nitrogen flux than typically obtained from an rf plasma source. When scaled by the differences in source-to-substrate distance ($1/r^2$), the active nitrogen flux was comparable to that reported by others. The layers were characterized by Hall measurements, photoluminescence, x-ray diffraction, and atomic force microscopy (AFM) (Digital Instruments Nanoscope II). High resolution transmission electron microscopy was performed at Xerox Palo Alto Research Center using techniques detailed elsewhere [10]

RESULTS

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,[11] buffer layers were grown by heating the substrate to 730 °C under an atomic hydrogen flux for 20 minutes 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 600 W. This procedure results in nucleation island sizes around 0.3 to 0.5 µm, giving dislocations due to domain-wall coalescence of order 10^9 cm^{-2}. Buffer layer growth was initiated by simultaneous exposure to the Ga and N flux. The 20 nm nucleation layer was then annealed at 730 °C for 20 minutes under active nitrogen flux, cooled (or heated) to the growth temperature, and growth was resumed. Our conditions represented highly Ga-rich growth for the buffer layer. However, after the 730 °C anneal, examination of buffer layers by AFM indicated continuous films with no evidence of Ga condensation.

GaN layers were grown on the annealed buffer layers. 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 (nitrogen sufficient), one would expect a linear increase in growth rate with increasing Ga flux. This is represented by the solid line in the figure. 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 large enough to prevent condensation. 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 [6] for the growth of GaN by MBE using an identical rf nitrogen source. Ga-rich growth close to, but

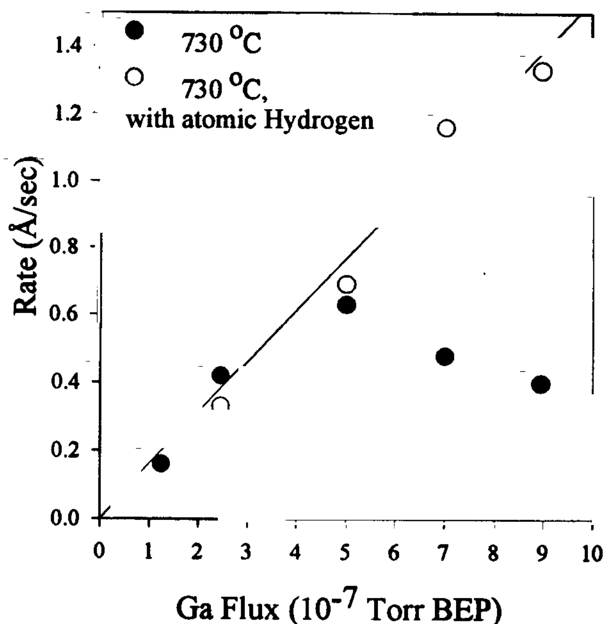
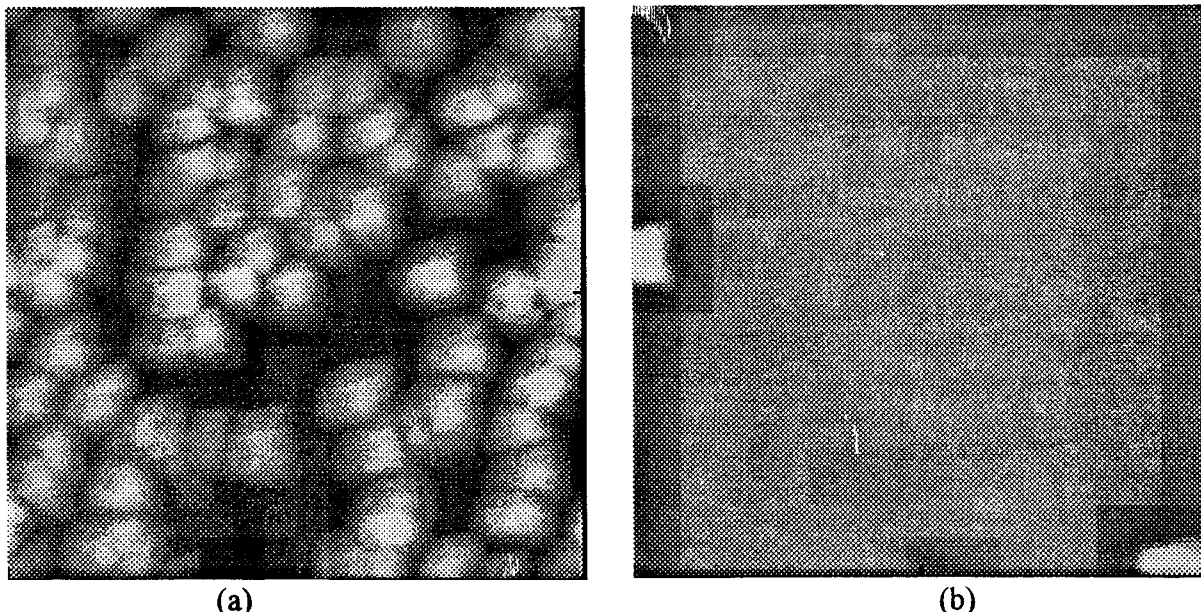


Figure 1. Growth rate v. Ga-flux.



(a) (b)

Figure 2. AFM micrographs of GaN grown under (a) nitrogen-sufficient and (b) Ga-rich conditions. The areas represented are 2 by 2 μm^2. The height scales are 135 nm in (a) and 50 nm in (b).

below the Ga condensation point resulted in much smoother surfaces indicative of two-dimensional growth with an rms. surface roughness of 1.5 nm over a 15 μm span. The smoother texture can be seen in the AFM micrograph in Fig. 2(b) for a 250 nm thick layer. Sub-nanometer 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 [12] 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 which could influence the growth morphology. In our study, the nitrogen source parameters were unchanged for the samples shown in Fig. 2 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.

The sample whose AFM micrograph is shown in Fig. 2(b) was also measured by high resolution TEM. As shown in Fig. 3, the microstructure is characterized by a high density of threading dislocations at the GaN-sapphire interface. These quickly annihilate resulting in a line defect density in the low 10^9 cm^{-2} after growth of only about 250 nm of GaN. By comparison, samples grown under nitrogen-sufficient conditions had line defect densities in the mid-10^{10} cm^{-2}. This decrease can be attributed to the layer-by-layer growth mode indicated by the smooth surface morphology measured by AFM. Thicker layers should result in commensurably fewer dislocations. Perhaps of more significance, the sample exhibited a low concentration of inversion domain boundaries, where the GaN crystal structure is inverted along the c-axis due to nucleation of the opposite phase at the substrate. As reported previously, inversion domain boundaries are a significant source of defects in GaN grown by any technique. [10] Our direct nucleation of GaN on sapphire under Ga-rich conditions appears to suppress the formation of such inversion domains, resulting in significantly less than 10 % by volume. This is comparable to most

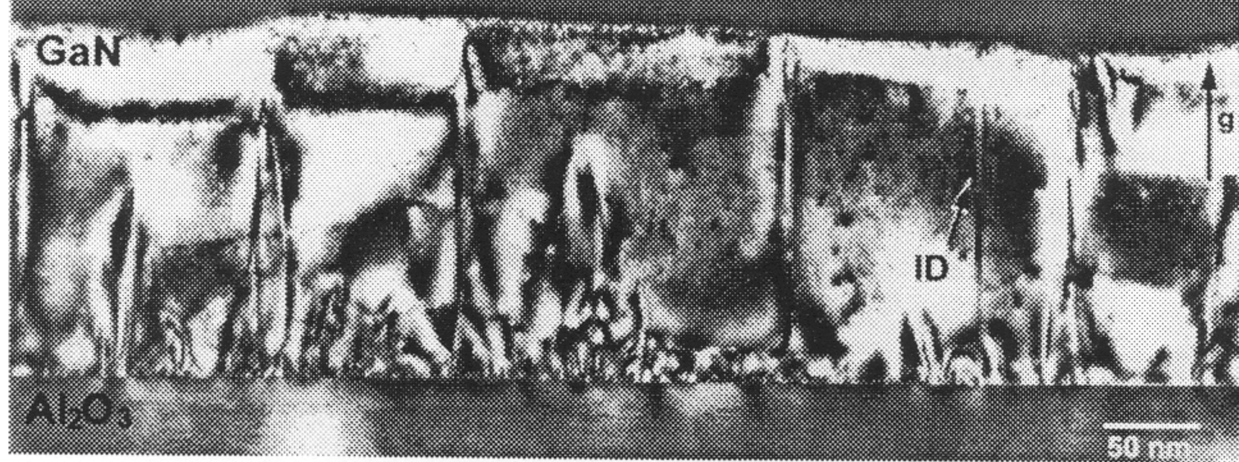


Figure 3. Dark Field TEM image taken with g = (0002) near the [11-20] zone axis of GaN. ID indicates the inversion domain in this micrograph. The remaining defects are nonedge-type dislocations.

MOCVD layers. In contrast, ECR-MBE layers grown on nitrided sapphire contain about an equal number of both orientations.[10]

Increasing the growth temperature should also increase the surface mobility of adatoms and promote better layer-by-layer growth, which may increase the rate of dislocation clean-up. Unfortunately, we [9] and others [13] have observed that the GaN growth rate decreases significantly at temperatures above about 730 ^{o}C. Further increase in temperature apparently either reduces the residence time of unreacted N on the surface or increases the Ga desorption rate, thereby reducing the growth rate. Prior studies of Ga desorption for GaN growth using ammonia [14] indicate that the Ga desorption rate increases rapidly above 730 ^{o}C. Thus, while this temperature can be increased somewhat by increasing the amount of active nitrogen, the regime between 750 and 800 ^{o}C may represent a practical limit to the growth temperature feasible by MBE using nitrogen plasma sources.

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 to 2 x 10^{-6} Torr BEP. The other growth parameters remained the same as for the corresponding filled-symbol case. Note that the growth rate was essentially brought up to the Ga-limit for each case of Ga-rich growth. In contrast, samples grown under nitrogen-sufficient conditions did not exhibit an enhanced 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 non-zero, was too small to be detected. Ammonia was not detected in an analysis of the background gases present during growth. This indicates that the enhanced growth rate is not due to the presence of ammonia formed due to gas-phase reactions.

The increase in growth rate for Ga-rich conditions is apparently related to the presence of atomic hydrogen at the surface of the growing layer. 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. Of practical importance, this shifting of the growth kinetics may allow much higher growth temperatures for MBE of GaN. We are continuing to investigate this phenomenon.

PL measurements were made at liquid helium temperatures on the samples. All samples grown at or below 660 ^{o}C exhibited significant luminescence centered at about 560 nm (2.2 eV). While the origin of this broad yellow luminescence band is still controversial, it is commonly attributed to deep states in the bandgap involving impurities or native defects. As reported earlier, [9] layers grown at 730 ^{o}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. The PL obtained from a GaN layer grown at 660°C under an atomic hydrogen flux is shown in Fig. 4. There is a single bound-exciton peak at about 3.48 eV and a small amount of yellow luminescence. As with the undoped layers, raising the growth temperature above 730 ^{o}C eliminated the yellow PL for samples grown under hydrogen, [9] 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 ^{o}C and exhibited x-ray diffraction rocking curve full widths at half maximum (FWHM) between 2 and 3 arc minutes for samples with thickness about 1 μm. Hall measurements indicated n-type carrier concentrations as low as 1×10^{17} cm^{-3} with room temperature mobilities of 120 $cm^2/V{\cdot}s$. The x-ray FWHM and Hall measurements of samples grown with atomic hydrogen were indistinguishable from those grown without atomic hydrogen. Although previously reported that hydrogen may introduce donor levels in GaN,[15] we have no direct evidence that this is the case here. As shown in Fig. 4 and in previously published spectra from samples grown at higher temperatures, we did not observe the 3.35 eV PL feature which has been associated with the hydrogen-related donor.[15] In addition, we did not see any significant difference in background doping between layers grown with and without hydrogen.

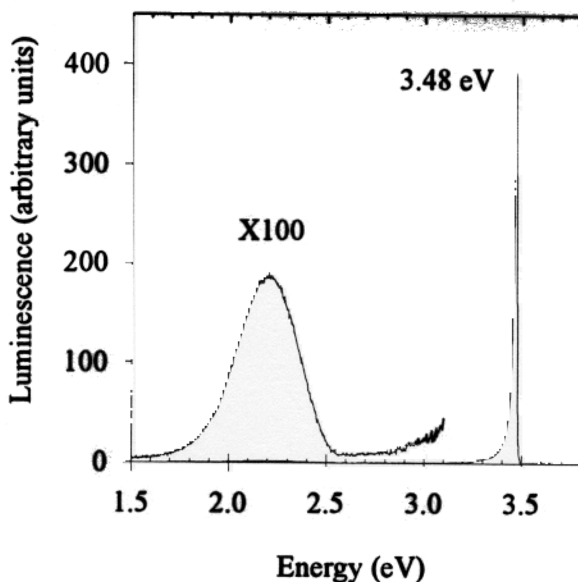


Figure 4. Photoluminescence of GaN grown at 660 °C under an atomic hydrogen flux.

CONCLUSIONS

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, resulting in an increase in growth rate limited by the total Ga flux. 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 to the hydrogen-related growth rate enhancement, we have presented evidence that Ga-rich nucleation and growth results in a significant reduction of inversion domain boundaries, promotes dislocation reduction and promotes a smoother growth surface.

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