

GaN Decomposition in Ammonia

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ABSTRACT

GaN decomposition is studied as a function of pressure and temperature in mixed NH_3 and H_2 flows more characteristic of the MOVPE growth environment. As NH_3 is substituted for the 6 SLM H_2 flow, the GaN decomposition rate at 1000 °C is reduced from $1 \times 10^{16} \text{ cm}^2 \text{ s}^{-1}$ (i.e. 9 monolayers/s) in pure H_2 to a minimum of $1 \times 10^{14} \text{ cm}^2 \text{ s}^{-1}$ at an NH_3 density of $1 \times 10^{19} \text{ cm}^{-3}$. Further increases of the NH_3 density above $1 \times 10^{19} \text{ cm}^{-3}$ result in an increase in the GaN decomposition rate. The measured activation energy, E_A , for GaN decomposition in mixed H_2 and NH_3 flows is less than the E_A measured in vacuum and in N_2 environments. As the growth pressure is increased under the same H_2 and NH_3 flow conditions, the decomposition rate increases and the growth rate decreases with the addition of trimethylgallium to the flow. The decomposition in mixed NH_3 and H_2 and in pure H_2 flows behave similarly, suggesting that surface H plays a similar role in the decomposition and growth of GaN in NH_3 .

INTRODUCTION

Metallorganic vapor phase epitaxy (MOVPE) is currently being used to grow GaN for the fabrication of blue light emitting diodes [1], lasers [2] and for high power electronic devices [3]. For MOVPE growth, NH_3 is typically used as the N source and high temperatures (> 1000 °C) are required to efficiently dissociate (i.e. 40-50 %) the NH_3 [4], because of the large N-H bond strength [5]. As a result, MOVPE growth temperatures are 100-500 degrees Celsius larger than the threshold temperature for GaN decomposition in vacuum [6,7] and in H_2 and N_2 [8,9]. The high rate of N_2 desorption is compensated by using large flows of NH_3 [10], however the extent of GaN decomposition that occurs during growth has not been measured.

The recent studies of Grandjean *et al.* [7] and Rebey *et al.* [11] have shown dramatic decreases in the GaN decomposition rate when small NH_3 flows are dosed onto GaN surface. For example, Grandjean *et al.* measure a GaN decomposition rate of 5 \AA/s at 875 °C in vacuum, while under an NH_3 flux of $1.7 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$, the decomposition rate drops to 0.03 \AA/s [7]. To explain the decrease in the GaN decomposition rate in NH_3 , a site-blocking model has been proposed where the adsorbed NH_3 blocks sites necessary for N_2 formation and desorption [7]. A similar site blocking mechanism has also been proposed to explain reduced GaN growth when the NH_3 flux is increased [12]. In this paper we suggest that H also blocks sites on the GaN surface and H surface coverage effects must be considered in order to properly describe the GaN decomposition and growth kinetics.

EXPERIMENTAL DETAILS

Details of the GaN growth [13] and decomposition [8,9] are discussed elsewhere. The GaN films used in this study were grown and decomposed in a close-spaced showerhead MOVPE reactor. The growth and decomposition rates were determined from weight loss using an analytical balance [8]. The GaN films were grown at 1030 °C using 32 μmoles of trimethylgallium (TMGa), 2 SLM NH_3 and 4 SLM of

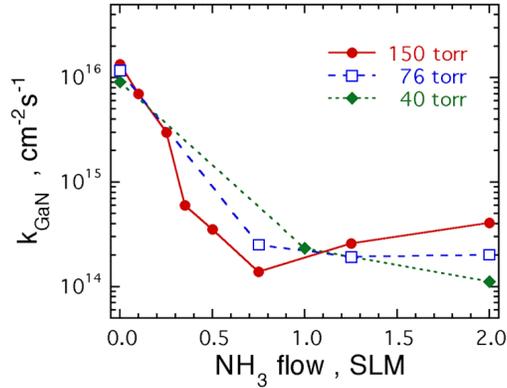


Fig 1. Plot of the GaN decomposition rate as a function of the NH₃ flow rate at three different pressures. For this plot the GaN was heated to a temperature of 992 °C using H₂ and NH₃ for a total flow of 6 SLM.

H₂ at pressures ranging from 40 to 300 torr. GaN decomposition was studied under similar flow conditions as the growth. The measured weights were converted to growth and decomposition rates per surface area (i.e. cm²s⁻¹) following Ref. 10. Expressed this way, a rate of 1.14 × 10¹⁵ cm²s⁻¹ corresponds to a thickness of 1 μm per hour. Temperature was calibrated by observing the melting point of 0.005" diameter Au wire on sapphire and correlating it to a thermocouple in direct contact with the susceptor underside [8]. After 2 years of use the set point temperature needed to melt the Au wire was reproducible to within 10 °C.

RESULTS

The change in the GaN decomposition rate, k_{GaN} , at a temperature of 992 °C as NH₃ is substituted for the H₂ flow is shown in Fig. 1. In Fig. 1, k_{GaN} is plotted as the NH₃ flow is increased from 0 to 2 SLM for pressures of 40, 76, and 150 torr. The total flow rate was kept constant at 6 SLM with the balance being H₂. Note that k_{GaN} decreases from $\approx 1 \times 10^{16}$ cm²s⁻¹ to $\approx 1 \times 10^{14}$ cm²s⁻¹ as the NH₃ flow increases. At 150 torr, the minimum k_{GaN} occurs at a flow of 0.75 SLM of NH₃. At 76 torr, the k_{GaN} minimum occurs between 1.25 and 2.0 SLM of NH₃. At 40 torr no minimum in k_{GaN} is observed. At 150 torr and a flow of 2 SLM of NH₃, k_{GaN} is $\approx 4 \times 10^{14}$ cm²s⁻¹.

In Fig. 2, the data from Fig. 1 are replotted as a function of the NH₃ gas density, which depends on pressure. In Fig. 2, it appears that the k_{GaN} measured at different pressures have a common minimum at a NH₃ density of $\approx 1 \times 10^{19}$ cm⁻³. This NH₃ density is the same order of magnitude as the calculated N desorption rate from GaN, which should be 9×10^{19} cm⁻²s⁻¹ at 992 °C [10]. Two different dependencies of k_{GaN} on the NH₃ density are evident in Fig. 2. At lower NH₃ density, the k_{GaN} drops steeply as the NH₃ density increases from 3×10^{17} cm⁻³ to a value of near 1×10^{19} cm⁻³. For NH₃ densities greater than 1×10^{19} cm⁻³, k_{GaN} increases. This differs from the behavior observed by Grandjean *et al.*, where k_{GaN} only decreased for increasing NH₃ flow [7].

To determine the dependence of k_{GaN} on the NH₃ density, [NH₃], separate fits were calculated for [NH₃] both less than and greater than 1×10^{19} cm⁻³. For [NH₃] < 1×10^{19} cm⁻³, a functional form of $k_{\text{GaN}} = c[\text{NH}_3]^n$ was used and the data were fit by

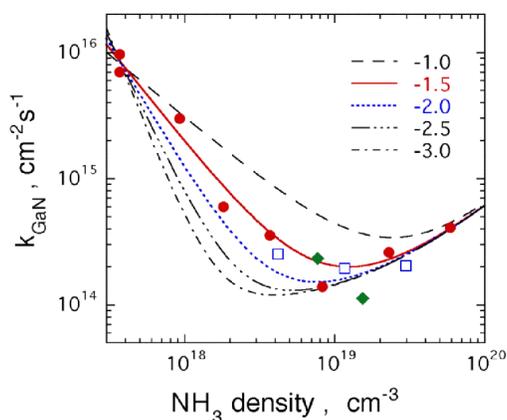


Fig. 2. Plot of the GaN decomposition rate measured as a function of the NH_3 density at 992 °C. The filled circles (red) were measured at 150 torr, the open squares (blue) were measured at 76 torr, and the filled diamonds (green) were measured at 40 torr. The lines are fits to the data using the expression $k_{\text{GaN}} = a + b[\text{NH}_3] + c[\text{NH}_3]^x$. For the fits the values of a and b are the same, while the value of x is fixed from -1.0 to -3.0 and c is varied for the best fit.

varying c , keeping x constant. For $[\text{NH}_3] > 1 \times 10^{19} \text{ cm}^{-3}$, a linear functional form, $k_{\text{GaN}} = a + b[\text{NH}_3]$, fit the data well. The series of lines shown in Fig. 2 are a combination of the two fits (i.e. $k_{\text{GaN}} = a + b[\text{NH}_3] + c[\text{NH}_3]^x$). For the combined fits, 5 curves were calculated for 5 values of x ranging from -1.0 to -3.0 , keeping the linear fit constant. Clearly, the data are best fit using with $x = -1.5$ to -2.0 .

Similar to NH_3 , the GaN decomposition rate in N_2 is lower when compared to the rates measured in H_2 [9], however, in mixed N_2 and H_2 flows the rate is substantially larger than in mixed NH_3 and H_2 flows. This is shown in Fig. 3, where k_{GaN} is

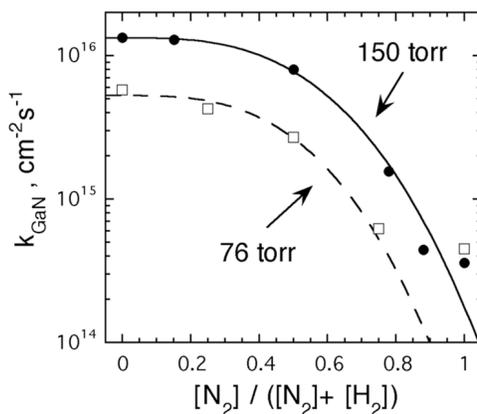


Fig. 3. Plot of the GaN decomposition rate vs. the ratio of the N_2 concentration to the total (i.e. $\text{N}_2 + \text{H}_2$) gas concentration. The GaN decomposition rate is shown at total pressures of 76 and 150 torr. The solid and dashed lines are cubic fits to the data.

plotted vs. the N_2 fraction of the total flow (i.e. $[N_2] + [H_2]$). For these measurements, the GaN films were annealed at 992 °C at pressures of 76 and 150 torr. In Fig. 3, k_{GaN} at 150 torr is reduced from $1.6 \times 10^{16} \text{ cm}^{-2}\text{s}^{-1}$ in pure H_2 to $3.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ in pure N_2 (factor of 45). For a 1:1 mixture of N_2 and H_2 at 150 torr, k_{GaN} decreases slightly to $8 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$, which is a factor of 2 compared to k_{GaN} in pure H_2 . This is a significantly smaller decrease when compared to the decrease in a 1:2 mixture of NH_3 and H_2 (factor of 120). Note that k_{GaN} in pure N_2 and in mixed H_2 and NH_3 flows can be similar. For example in pure N_2 , k_{GaN} is $3.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, while in mixed H_2 and NH_3 at 150 torr, k_{GaN} is $4 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, as shown in Fig. 1. The solid and dashed lines in Fig. 3 are cubic fits to the k_{GaN} vs. N_2 fraction. The cubic dependence is a result of the expected dependence of surface H coverage (i.e. $[H]^3$) for ammonia formation via the reaction $3H + N \rightarrow NH_3$. Previously, Thurmond and Logan also demonstrated NH_3 formation when GaN is heated in H_2 by titration of the basic exhaust gas [14].

In Fig. 4, the GaN decomposition and growth rates are plotted vs. pressure. In Fig. 4(a), k_{GaN} is plotted for GaN films annealed at 992 °C in H_2 [8]. Also in Fig. 4(b), the GaN growth rate at 1030 °C is plotted for conditions where 2 SLM NH_3 , 4 SLM H_2 , and 32 μmoles of TMGa were used. Finally, in Fig. 4(c) the GaN decomposition rate is plotted using the same conditions as (b) except no TMGa was used and hence decomposition was observed. Note that the decrease in the GaN growth rate as the pressure increases in Fig. 4(b) coincides with an increase in the GaN decomposition rate in Fig. 4(c). Also, the k_{GaN} shown in Figs. 4(a) and 4(c) have a similar shape as the pressure increases and these curves are nearly identical if the k_{GaN} in Fig 4(c) are multiplied by 30. This similarity in shape implies that surface H plays a similar role in the GaN decomposition for both pure H_2 and mixed NH_3 and H_2 gas environments.

DISCUSSION AND CONCLUSIONS

From the data presented in Fig. 1, the GaN decomposition rate is greater than $1 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ (i.e. $\approx 1/10 \mu\text{m}/\text{hour}$) even in mixed NH_3 and H_2 flows. This is important for GaN growth because it suggests that some level of decomposition occurs during

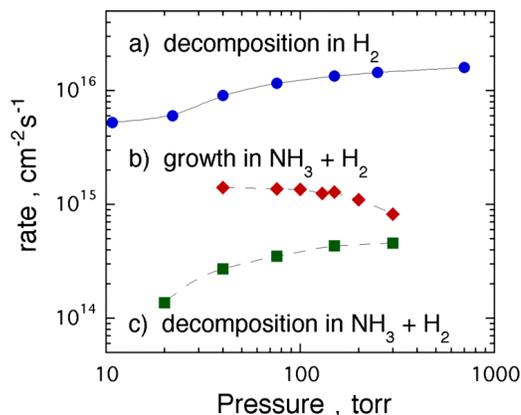


Fig. 4. Pressure dependence of the a) GaN decomposition rate in 6 SLM H_2 measured at $T = 992 \text{ }^\circ\text{C}$, b) GaN growth rate using, 32 μm TMGa, 2 SLM NH_3 and 4 SLM H_2 at $T = 1030 \text{ }^\circ\text{C}$, and c) GaN

decomposition rate using 2 SLM NH₃ and 4 SLM H₂ at T = 1030 °C. The only difference between b) and c) is the use of TMGa in b).

growth as previously speculated [10]. Currently, we are growing GaN at a pressure of 130 torr and a temperature of 1030 °C [13]. Under these growth conditions, the rates for growth and decomposition are $1.2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ and $4 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ respectively as shown in Fig. 4. If the growth rate equals the incorporation rate minus the decomposition rate [10], this means that the incorporation rate is ≈ 4 times the decomposition rate under these growth conditions.

The decrease in k_{GaN} as the NH₃ density increases is due to NH₃ adsorption, which blocks sites needed for GaN decomposition. As shown in Fig. 2, the decrease in k_{GaN} depends on the -1.5 to -2.0 power of the NH₃ density. Since Ga desorption from GaN has been shown to be independent of H₂ pressure [8], reactions which remove N from the lattice probably influence the GaN decomposition rate more. This is clearly observed in the cubic dependence of k_{GaN} in Fig. 3 where NH₃ formation is favored at higher pressure. For N₂ formation and desorption one or both of the N atoms diffuse across the surface until they combine to form N₂. If open surface sites are necessary for N diffusion, blocking of these sites by NH₃ or H would decrease the hopping rate and as a consequence the N₂ formation rate would be decreased. If two (one) N must migrate for N₂ formation, the N₂ desorption kinetics would be second (first) order in the number of open surface sites. As the NH₃ density on the surface increases, the decrease in the GaN decomposition rate should be between first and second order, i.e. $k_{\text{GaN}} \propto [\text{NH}_3]^{-1}$ or $k_{\text{GaN}} \propto [\text{NH}_3]^{-2}$, depending on the details of N₂ formation and desorption. From Fig. 2, it is clear that the decrease in k_{GaN} vs. NH₃ density is closer to second order (power of -2) than first order.

At higher NH₃ densities ($> 1 \times 10^{19} \text{ cm}^{-3}$), the GaN decomposition rate increases linearly. This may be due to a decrease in the NH₃ site blocking suppression of N₂ desorption or a general increase in the H surface coverage. The increased H coverage could block sites necessary for NH₃ adsorption. Surface H has also been shown to aid in NH₃ adsorption and dissociation on GaN [15] and on Al [16]. In addition, large H coverage can favor NH₃ reformation and desorption by combining with adsorbed NH_x species as suggested by Fig. 3. In contrast to NH₃, site blocking with H should lead to an increase in the decomposition rate.

Several groups have observed decreases in growth rate when H₂ is used in place of N₂ [17, 18], when the growth pressure is increased [19], and when higher NH₃ fluxes are used for growth [20]. In Fig. 4(b), the GaN growth rate decreases as the growth pressure increases. It is clear from Fig. 4(c) that the reason the growth rate decreases is because the increased GaN decomposition at higher pressures. However, to fully explain the reduction in the growth rate, the full effect of gas phase depletion of the TMGa also needs to be considered.

GaN grown in H₂, where GaN decomposition is enhanced compared to N₂, appears to have better crystalline order compared to GaN growth in N₂. Kistenmacher *et al* have shown that the FWHM of the GaN films grown in H₂ had narrower x-ray rocking curve linewidths and were better aligned compared (i.e. smaller mosaic dispersion) to GaN films grown in only N₂ [21]. Better alignment is also observed in laterally overgrown GaN when H₂ is used instead of N₂ [22]. Schön and coworkers find smoother morphologies and better electrical properties when growth is conducted in H₂ compared to N₂ [23]. Better electrical properties are observed for GaN grown at higher pressures where GaN decomposition is enhanced [13, 24, 25]. Recently, we have observed a near doubling of electron mobility in films grown at 150 torr compared to 76 torr, keeping all other growth parameters the same [13]. In this study, growth at higher pressure led to increased GaN

grain size in the films [13], suggesting that the increased GaN decomposition at higher pressure plays a significant role in determining the grain size of the GaN film.

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