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Growth Rate Reduction of GaN Due to Ga Surface Accumulation

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Abstract

GaN(0001) has been grown on Al_2O_3 (0001) by molecular beam epitaxy where NH_3 was used as the nitrogen precursor. Desorption mass spectroscopy and reflection high energy electron diffraction (RHEED) were used to monitor the relationship between growth rate and the incident fluxes during growth. Excess surface Ga decreases the GaN formation rate when the substrate temperature is too low or the Ga flux is too high. A simple rate equation is used to describe the observed behavior.

1. Introduction

A number of issues related to growth kinetics of GaN must be addressed. Historically, the n-type conductivity commonly exhibited by GaN was attributed to N vacancies [1]. This problem was thought to arise from a kinetic barrier to N incorporation during growth. Recent results by Lee *et. al* [2] and also by Jones *et. al* [3] using NH_3 as the nitrogen precursor during molecular beam epitaxy (MBE) indicate that the GaN growth rate is strongly temperature dependent, exhibiting a maximum between 750°C and 800°C. The high temperature decrease in growth rate is typical of GaN, and has been attributed to Ga desorption at elevated substrate temperature [2] [3] as well as to the decomposition of GaN [4]. At lower substrate temperature the common belief is that reduced N incorporation efficiency limits the growth rate [2].

In this paper we will address the low temperature issues related to GaN MBE where the GaN decomposition rate is much less than the growth rate . In section 3.1 we examine the transient response of the GaN surface composition and chemistry to a step-function of Ga flux. The time dependence of the Ga desorption after exposure of the surface to incident Ga indicates that Ga adsorbs to the surface in two states. The first deposited layer of Ga sticks to the surface in a strongly bound state, whereas subsequent desorption occurs at a higher rate. The more tightly bound of these layers is observed only when the surface has been previously exposed to NH_3.

In section 3.2 we examine the relationship between growth rate, substrate temperature and the incident fluxes. We show how desorption mass spectroscopy (DMS) can be used to determine whether the GaN formation rate is limited by the available N (Ga rich) or by the available Ga (N rich) and present a single rate equation to explain a decrease in the GaN formation rate with increasing Ga flux.

2. Experimental

Growth was carried out in a cryopumped Gen II MBE system which is shown schematically in Figure 1. A quadrupole mass spectrometer mounted in one of the source ports enabled detection of the type and intensity of desorbed species from the substrate surface. The specular RHEED intensity was monitored using a photomultiplier tube. The NH_3 flux was held constant during growth using a capacitance manometer in conjunction with a closed loop PID controller and solenoid control valve to maintain constant pressure in the NH_3 gas line behind a manually regulated precision leak valve. A flux monitor located on the back of the sample manipulator was used to determine the incident beam equivalent pressure by rotating the sample manipulator. Absolute calibraiton of the incident Ga flux is achieved by monitoring RHEED intensity oscillations during growth of GaAs(001) in a separate experiment. Samples were prepared by successively cleaning in acetone and methanol, which was followed by a 5 minute etch at 70°C in 3:1 H_3PO_4:H_2SO_4. The substrates were then rinsed in deionized water and blown dry with N_2. This process

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3:1 H_3PO_4:H_2SO_4. The substrates were then rinsed in deionized water and blown dry with N_2. This process resulted in atomically smooth surfaces that exhibited ≈1000 Å terraces as indicated by atomic force microscopy (AFM). Without the etch, AFM showed polish marks on the substrate surface, and no atomic steps could be seen.

The samples were loosely mounted via mechanical support in order to reduce thermal stress during growth. Consequently, thermal contact between the substrate heater and the sample was reduced, and a 0.2 µm layer of Ti was deposited on the back of the wafers to efficiently couple radiative energy from the heater to the substrate.

3. Results

3.1. Transient Response of the Surface Composition

The transient response of the specular RHEED intensity observed along the $<01 1 \bar{2}>$ azimuth as well as the response of the desorbed Ga and H_2 fluxes to a step-function of incident Ga on the GaN surface are shown in Figure 2. These data were measured after growth had been terminated and the background NH_3 pressure had been reduced to $<10^{-9}$ Torr while maintaining a constant substrate temperature of 760°C. A number of important features are observed after opening the Ga shutter. The initially low Ga desorption flux seen in Figure 2 indicates that Ga adsorbs in a strongly bound site that is characterized by a long residence time. We also see in Figure 2 that H_2 is a byproduct of this adsorption process. After deposition of roughly one monolayer, the Ga desorption increases and the H_2 desorption decreases, indicating the presence of a second, weakly bound state. These results are consistent with the findings of Jones *et. al* [3] and Lee *et. al* [5] who both proposed that Ga exists in two adsorption sites during growth. After this initial Ga pulse, we close the Ga shutter and allow the excess Ga to desorb from the surface. Subsequent exposure to incident Ga results in only the higher Ga desorption flux, with no detectable change in the H_2 desorption, and no reduced desorption flux indicative of the strongly bound Ga. We can again prepare a surface that will adsorb Ga in the strongly bound sites by exposing the surface to NH_3. The procedure outlined above can be used to detect the presence of these sites. Measurement of the RHEED intensity as shown in Figure 2 and Figure 3 reveals that two slope maxima occur during the initial transient RHEED decrease. Quantitative information can be extracted from this RHEED intensity variation by definition of the time interval, Δt, as shown in Figure 3. We find that the time dependence of the transient Ga and H_2 desorption track this RHEED intensity variation as indicated in Figure 2. Based on this observation we believe that Δt gives an estimate of the time required for saturation of the strongly bound Ga sites. The quantity $1/\Delta t$ decreases linearly with increasing NH_3 beam equivalent pressure (BEP), while it increases linearly with incident Ga flux. Furthermore, this behavior is observed only when the incident Ga exceeds the available N provided by the incident NH_3.

Based on these transient data, we have identified two Ga adsorption sites. We will present evidence in the next section that the more tightly bound Ga site contributes to growth, whereas the weakly bound Ga acts to inhibit growth by blocking the strongly bound Ga, and inhibiting the incorporation of N from NH_3.

3.2. Steady State Growth Behavior

RHEED indicates that high Ga flux and high substrate temperature are necessary to achieve atomically smooth surface morphology. The objective of this section is to examine the growth kinetics when the incident Ga exceeds the available N provided by NH_3.

In Figure 4 and Figure 5 we see the desorbed H_2, N_2, and Ga fluxes resulting from exposure of the GaN surface to a 15 second pulse of Ga while the NH_3 BEP is held constant. Changes in other detected species such as NH_x complexes or atomic N were too small to measure. For the data shown in Figure 4 the Ga flux was 4.2×10^{14} $cm^{-2}s^{-1}$ whereas in Figure 5 it was increased to 1.4×10^{15} $cm^{-2}s^{-1}$. All other growth parameters were the same for both plots. The increased H_2 desorption during growth is attributed to the forward reaction

$$2\,Ga + 2\,NH_3 \rightarrow 2\,GaN + 3\,H_2 \qquad (1)$$

In the absence of incident Ga we find that contributions from the reaction

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \qquad (2)$$

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become significant at substrate temperatures exceeding 800°C, and we have not yet determined the relative contributions of the two reactions during and prior to growth at elevated temperatures. At temperatures below 800°C, however, we believe that ΔH_2 yields a reliable estimate of the growth rate. The accuracy of this technique is currently being investigated using post growth film thickness measurements. In Figure 5 we see that initiation of growth causes a transient pulse of H_2 to desorb from the surface, whereas in Figure 4 the desorbed H_2 flux reaches its maximum value at steady-state. In general, we find that the desorbed H_2 flux during steady-state growth increases linearly with increasing Ga flux, but then decreases as the Ga flux exceeds a saturation value. This relationship is shown in Figure 6, where we see the dependence of ΔH_2 on the incident Ga flux at three different substrate temperatures. In Figure 6 we see that high Ga flux causes a reduction in the growth rate, but that increasing the substrate temperature minimizes this effect. A temperature gradient of about 30°C exists across the substrate [6] which introduces unertainty to the data shown in Figure 6. This uncertainty arises from the fact that DMS measurements integrate the desorbed flux over the whole sample. This effect is particularly pronounced at high incident Ga flux, where the growth rate is strongly temperature dependent. This temperature gradient also makes verification of the DMS data difficult, since film thickness measurments are dependent on the location on the sample where the film thickness is measrued. These difficulties can be overcome by conducting the same measurements on samples that are known to be isothermal, and work is currently underway to achieve this goal.

In spite of the problems introduced by the temperature gradient, we are confident that the data in Figure 6 yield an accurate picture of the general relationship between growth rate, fluxes, and substrate temperature. The reduced growth rate at high Ga flux can be accounted for by consideration of the following simple kinetic model. We start by making a number of assumptions about the atomistic behavior of adsorbed Ga which will be justified by agreement with measured data. First, based on the DMS measurements presented in section 3.1 we consider Ga in the weakly bound state. The fractional area of the surface covered by weakly bound Ga is σ_{Ga}. The second assumption is that Ga desorption occurs only from this weakly bound state, which results in a Ga desorption term that is proportional to σ_{Ga}. We assume that for complete coverage (σ_{Ga} = 1), the desorption flux is equal to the evaporation rate of Ga from liquid Ga as developed in ref. [6], and therefore we approximate the Ga desorption rate as $\sigma_{Ga}F_0(T_{sub})$, where $F_0(T_{sub})$ is the desorption flux of Ga vapor leaving liquid Ga. This assumption is consistent with the temperature dependence of the Ga desorption data as measured using DMS. This model does not require that Ga completely wet the GaN surface, since the shadowing effect of droplets could account for the observed behavior as well. In the limit of complete wetting, σ_{Ga} is the Ga surface coverage. Direct measurement of σ_{Ga} is complicated by the temperature gradient discussed earlier [6], and we have been unable to obtain a reliable measure of σ_{Ga} due to the strong temperature dependence of the coverage.

The DMS measurements shown in Figure 6 indicate that excess Ga reduces the growth rate. We assume that NH_3 reacts only with the strongly bound Ga, and that the excess Ga in the weakly bound sites reduces the growth rate by blocking the underlying reactive Ga sites. Further motivation for such a growth mechanism can be found in the work of Liu and Stevenson [7], who found that the coexistence of Ga and GaN enhanced the decomposition of NH_3 relative to Ga alone.

We let the growth rate be proportional to the fraction of strongly bound Ga sites that are exposed to the incident NH_3, $(1-\sigma_{Ga})$. We now consider the following quantities:

F_N= total available incident N flux provided by the NH_3

F_{Ga}= total available Ga flux

$\sigma_{Ga}F_0(T_{sub})$= Ga desorption flux where all temperature dependence will be included in the Ga desorption term, $\sigma_{Ga}F_0(T_{sub})$. DMS measurements of both the H_2 and Ga desorption fluxes show that the NH_3 reactivity does not depend on substrate temperature over the range (700°C-820°C), and we therefore let F_N be independent of substrate temperature. We wish to determine the steady-state growth rate when $F_{Ga}>F_N$. The time derivative of the Ga coverage is given by

$$\frac{1}{A}\frac{dN_{Ga}}{dt} = F_{Ga} - F_N(1-\sigma_{Ga}) - \sigma_{Ga}F_0(T_{sub}) \qquad (3)$$

where the growth rate is $F_N(1-\sigma_{Ga})$, and N_{Ga} is the number of free Ga atoms on the surface. The substrate surface area is A. Solving equation 3 for σ_{Ga} at steady-state gives the growth rate

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$$F_N(1-\sigma_{Ga}) = F_N \frac{F_{Ga} - F_0(T)}{F_N - F_0(T)} \tag{4}$$

The results of this model are shown as solid lines in Figure 6. As stated earlier, we estimate the desorption term $F_0(T_{sub})$ from the equilibrium vapor pressure of Ga over liquid Ga given in ref. [8]. We see from Figure 6 that the measured data is in reasonable agreement with the steady-state solution given in equation 4. The only parameter used to fit the predictions of equation 4 to the measured data was F_N, which is equated to the known Ga flux for which ΔH_2 is maximum. The main points to be extracted from this discussion are that excess Ga reduces the formation rate of GaN, and that this effect can be minimized by increasing the substrate temperature. Additionally, we see that a drastic reduction in growth rate occurs when $F_{Ga}=F_0(T_{sub})$, where $\sigma_{Ga}=1$ and growth is inhibited. We can also explain the increase in H_2 desorption observed after closing the Ga shutter as seen in Figure 5 as follows. During growth, excess Ga resides on the surface and reduces the growth rate by blocking the reactive sites. After closing the Ga shutter, the excess Ga is depleted either by evaporation or by reaction with the GaN surface. As more surface area is exposed, the growth rate increases for a short time while the remaining surface Ga reacts with NH_3 on the exposed GaN surface, resulting in the short pulse of H_2 desorption from the surface.

3.3. Conclusions

Analysis of the transient H_2 and Ga desorption, along with the specular RHEED intensity show that Ga resides on the surface in both weakly bound and a strongly bound sites. After saturation of the strongly bound Ga sites, the Ga desorption flux increases, indicating the presence of the more weakly bound Ga. The adsorption process of Ga into the strongly bound sites produces H_2 as a byproduct.

Analysis of the steady-state growth rate using DMS shows that excess Ga reduces the growth rate. A rate equation giving the steady-state value of the Ga coverage in the weakly bound state was described. The key feature of this model is the blocking of reactive sites by the weakly bound Ga. The model shows that by increasing the substrate temperature, the growth rate can be increased due to reduced coverage of this excess Ga.

Acknowledgments

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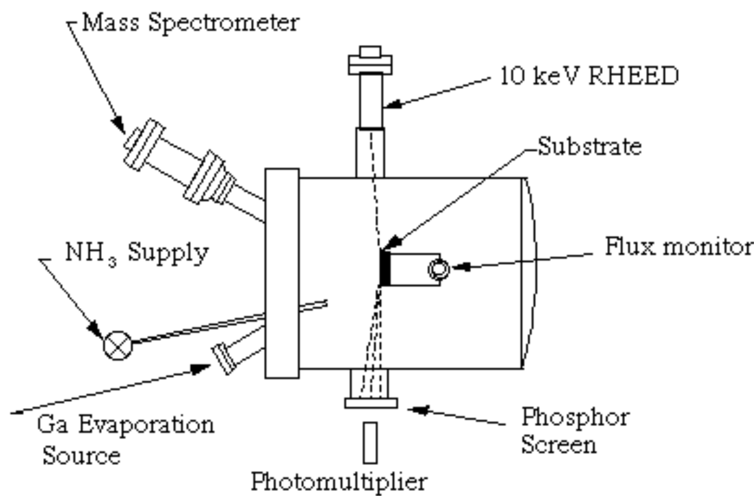

Figure 1. Schematic diagram of the Gen II MBE system used for growth.

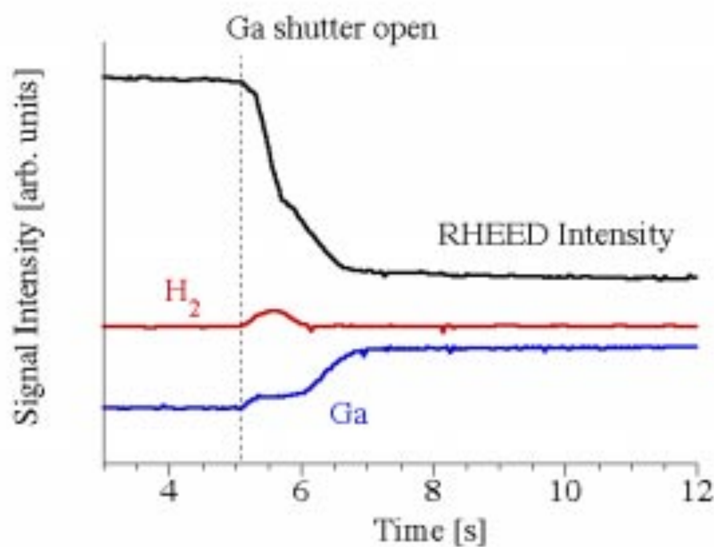

Figure 2. The transient response of the Ga and H_2 desorption to a step-function of incident Ga is shown in the absence of incident NH_3. The response of the specular RHEED intensity observed along the <$011\bar{2}$> azimuth is also shown. ($F_{Ga}=1.6\text{x}10^{15}$ $cm^{-2}s^{-1}$, T_{sub}=760°C).

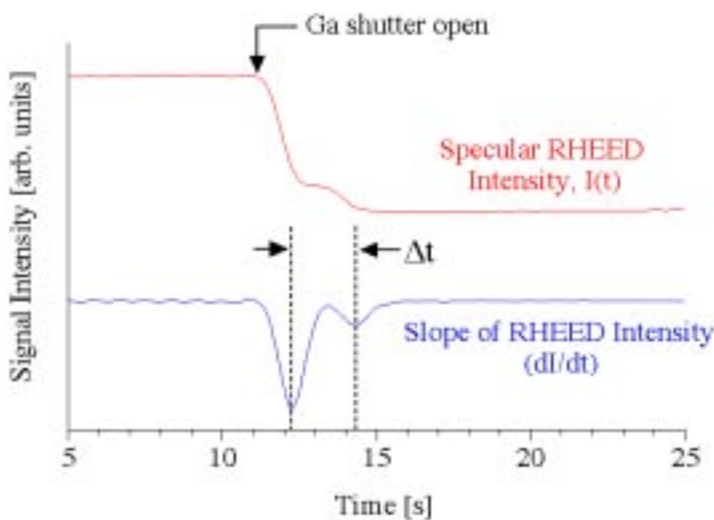

Figure 3. Specular RHEED intensity and its first derivative. Differentiation of the signal allows quantitative analysis of the transient signal. Experimental conditions for the data shown here are T_{sub}=780°C, NH_3 BEP=$1.1\text{x}10^{-5}$ Torr. F_{Ga} = 1.45ML/s.

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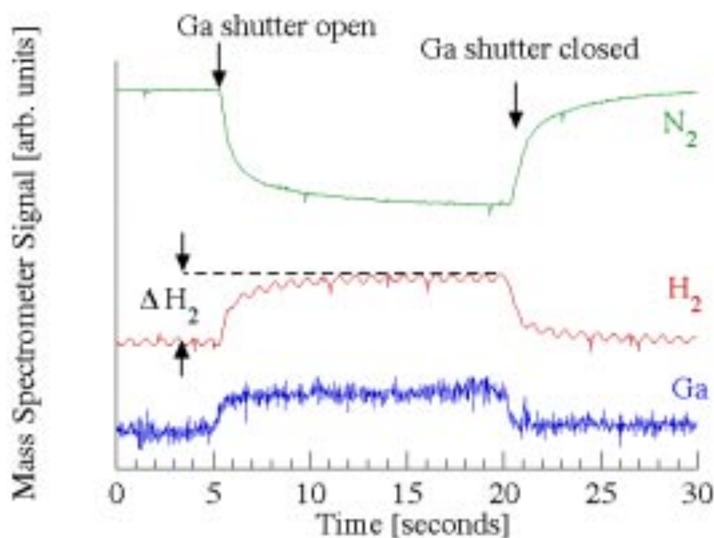
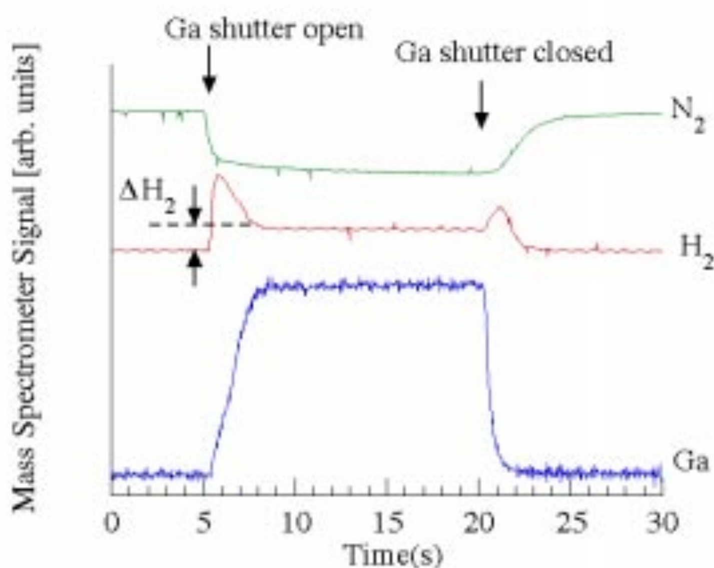


Figure 4. Changes in the N_2, H_2 and Ga desorption are caused by exposing a smooth GaN sample to a 15 second pulse of incident Ga under N rich growth conditions. Substrate temperature=820°C, NH_3 beam equivalent pressure = 7x10^{-6} Torr, Ga flux =4.2x10^{14} cm^{-2}s^{-1}. The high frequency H_2 signal oscillations arise from fluctuations in H_2 background pressure caused by temperature cycling of the cryopumps.



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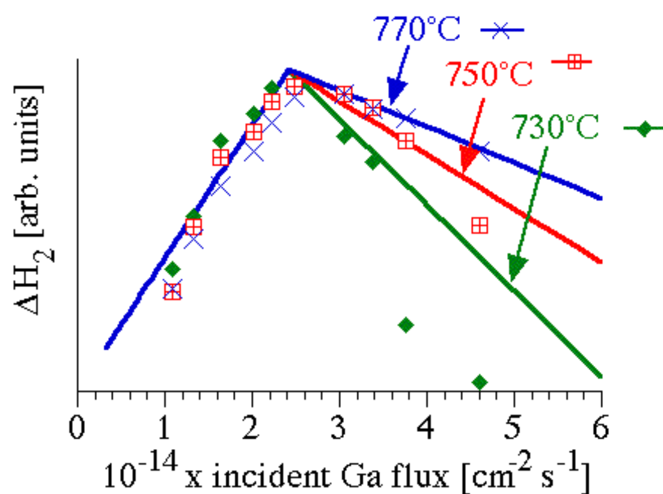

Figure 6. Dependence of ΔH_2 on the incident Ga flux. The lines show the theoretical incorporation rate based on the simple kinetic model presented in this paper.

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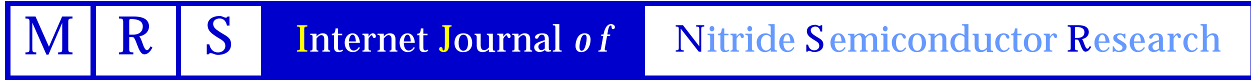

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