ENHANCED GaN DECOMPOSITION AT MOVPE PRESSURES

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ABSTRACT

GaN decomposition was studied above 800 °C in flowing H_2 and N_2 for pressures ranging from 10 to 700 torr. From careful weighings of the GaN film on sapphire before and after annealing, the rates for GaN decomposition, Ga surface accumulation, and Ga desorption were obtained. An enhancement in the GaN decomposition rate was observed in H_2 pressures greater than 100 torr. Even with this enhanced GaN decomposition, the Ga desorption rate is nearly constant at higher pressures. As a result, Ga droplets accumulate on the surface. For N_2 pressures ranging from 76 to 400 torr no net enhancement in the GaN decomposition rate is observed and the GaN decomposition rate is reduced compared to identical annealing conditions in H_2. This suggests that H_2 is acting chemically to reduce the barrier for GaN decomposition. This may occur through a surface mediated dissociation of H_2 followed by the formation of more mobile and volatile hydrogenated N and Ga species. The significance of this study for GaN growth is that by increasing the GaN decomposition, the Ga atoms diffuse farther and subsequently re-incorporate into the growing lattice, increasing the GaN crystal quality. Connections between the enhanced GaN decomposition rate and the coalescing of nucleation layer during the ramp to high temperature and the consequences for the high temperature growth are discussed.

INTRODUCTION

GaN is of current interest for the fabrication of blue light emitting diodes [1], lasers [2] and for high power electronic devices [3]. It has been shown that the GaN quality plays a strong role in the device performance [1-3]. Typically, GaN is grown at high temperature (> 1000 °C) using MOVPE with N to Ga ratios larger than 1000 on sapphire or SiC substrates using a thin buffer layer. The high temperature is necessary for efficient catalytic dissociation of NH_3 and the large V/III ratio is needed to offset the N loss from the growing film [4]. The growth temperature is larger (i.e. 100-500 °C) than the threshold temperature for GaN decomposition, and it is not currently understood to what extent GaN decomposes during growth at MOVPE pressures.

Previously, we suggested that decomposition of the GaN film during growth enhances GaN ordering, by eliminating more weakly incorporated Ga and N atoms [4]. At equilibrium the growth rate is zero. For a positive growth rate close to equilibrium, the incorporation rate of atoms into the growing lattice is slightly larger than the decomposition rate [4-6]. Recently, we showed how the GaN decomposition rate is enhanced in flowing H_2 for pressures greater than 100 torr [7]. This result was explained by assuming chemical dissociation of H_2 on the GaN surface which then increases Ga surface mobility and enhances N_2 desorption. This paper reports a more detailed study of GaN decomposition in both H_2 and N_2 as a function of pressure and temperature, where the role of H_2 on the enhanced GaN decomposition rate is clarified.

EXPERIMENTAL DETAILS

Details of the GaN growth are discussed elsewhere [8]. The GaN films were grown at 76 torr using a close-spaced showerhead reactor design. This same reactor was also used to study the GaN decomposition. The growth process resulted in specular GaN growth over the 2” sapphire wafer, with excellent thickness uniformity. Temperature reproducibility of the susceptor was a major concern for the decomposition study. The temperature was calibrated by observing the melting point of 0.005” diameter Au wire and correlating it to a thermocouple in

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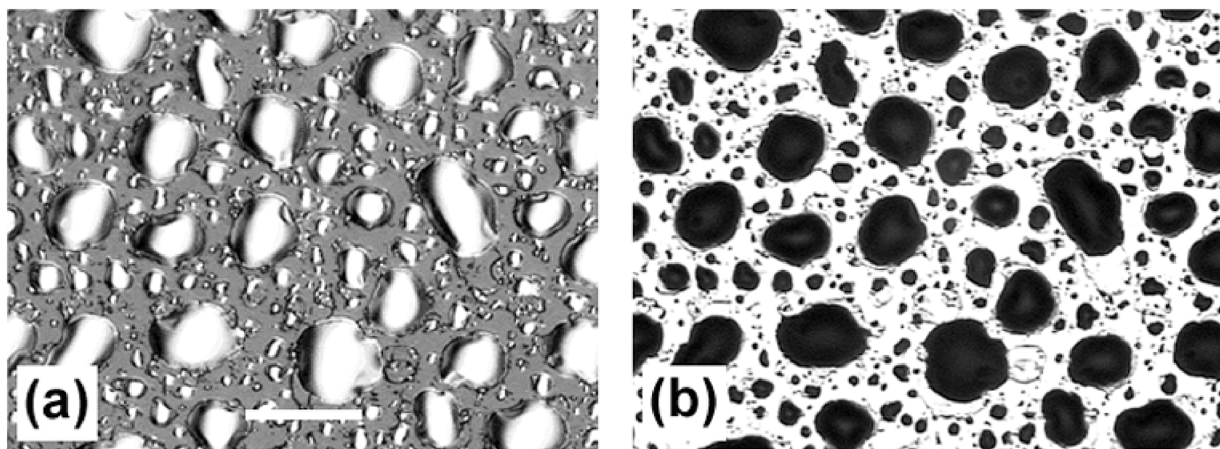

Figure 1. (a) Phase contrast and (b) transmission Normarski images of GaN surface heated for 20 minutes in H_2 at a pressure of 150 torr at a temperature of 811 °C. The bar on image (a) indicates a length of 20 μm.

close proximity to with the backside of the susceptor. Temperature measurement in the reactor was found to be reproducible to within 5 °C after 8 months of use.

For the decomposition study, pieces of the GaN on sapphire were cleaved and weighed to within 0.1 mg using an analytical balance [7]. Repeated weighing of the GaN on sapphire pieces were reproducible to within 0.1 mg. The pieces were reintroduced into the reactor and heated under varying conditions using either 6 SLM flow of H_2 or 3 SLM of N_2. Each piece was ramped at 25 °C per minute to the annealing temperature, which ranged from 800 to 1130 °C. After annealing for a set time and cooling, each piece was re-weighed in air to determine the mass loss. If Ga droplets were observed, they were removed by etching in dilute HNO_3 and rinsing with DI water. (On some samples which were not etched, the Ga droplets were found to be very stable in air even up to several months, suggesting minimal oxidation of the liquid Ga droplets.) Each piece was then weighed again to determine the weight of liquid Ga. Finally, the piece was annealed at 1080 °C until the remaining GaN was decomposed, leaving only the initial bare sapphire surface. The bare sapphire weight was used to calculate the sapphire area in order to convert the measured weights to kinetic rates (atoms/cm^2) [7].

RESULTS

After annealing GaN in the absence of NH_3, the most notable change in the GaN surface morphology is the appearance of Ga droplets as shown in Fig. 1. For Fig. 1, the GaN surface was annealed at a temperature of 811 °C for 20 minutes in H_2 at a pressure of 150 torr. The Ga droplets are observable as the lighter regions in the phase contrast image (Fig. 1(a)) and as the darker regions in the transmission image (Fig 1(b)). Because the GaN decomposition rate is larger than the Ga desorption rate, the liquid Ga droplets accumulate on the surface and coalesce into larger droplets, similar to the liquid droplet growth mechanism developed by Family and Meakin [9]. In flowing H_2 Ga droplets were observed for pressures greater than 22 torr [7] for anneals at 992 °C. Compared to the Ga droplets in flowing H_2, the Ga droplets in flowing N_2 were barely discernable even at the highest magnification of 1000x. The droplet size increased as both the anneal temperature and the pressure were increased in H_2 and in N_2 for temperature greater than 1000 °C.

For temperatures ranging from 800 - 1000 °C, the H_2 pressure had a strong influence on both the quantity of Ga and the Ga droplet size. This is shown in Fig. 2, where the kinetic rates for Ga accumulation (i.e. liquid Ga on the surface), GaN decomposition, and Ga desorption are plotted as a function of pressure. Figs. 2(a) through 2(c) show the rates at anneal temperatures of 992 °C, 902 °C, and 811 °C, respectively. It is clear from Fig. 2(a) that the GaN decomposition rate (filled circles) and the surface Ga accumulation rate (open squares) increase as the pressure is increased. The Ga desorption rate (filled diamonds) changes slightly as a function of pressure, peaking near 76 torr in Fig. 2(a), 100 torr in Fig. 2(b), and 120 torr in Fig. 2(c). The increase in the Ga desorption rate at these pressures is due to a maximum in the Ga surface area to volume ratio

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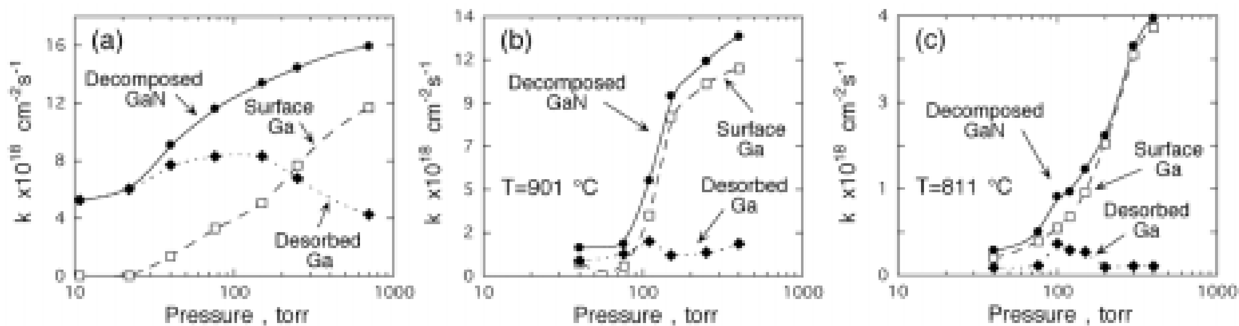

Figure 2. Plot of the GaN decomposition rate in H_2 (solid circles) at various pressures at (a) 992 °C, (b) 902 °C, and (c) 811 °C. The Ga desorption rate (solid diamonds) and the rate of Ga accumulation (open squares) on the surface during the anneal are also plotted.

which then decreases as the droplets coalesce. Clearly, as shown in Fig 2(b) and 2(c), the buildup of Ga on the surface directly coincides with the increase in the GaN decomposition rate.

Arrhenius plots of the GaN decomposition and Ga desorption rates in both H_2 and N_2 are plotted in Figs. 3 and 4, respectively. Because the GaN decomposition rates depend strongly on the H_2 pressure, the decomposition rates in H_2 (solid circles, solid line) are plotted only for 76 torr. From this data, the fit yields a pre-exponential of $(6.3\pm0.4)\times10^{30}$ $cm^{-2}s^{-1}$ and an activation energy, E_A, of 2.96 ± 0.06 eV. This is in close agreement with previous measurements of GaN decomposition in vacuum, where pre-exponentials of 4×10^{29} $cm^{-2}s^{-1}$ [10] and 5×10^{28} $cm^{-2}s^{-1}$ [11] and an E_A of 3.1 eV [10, 11] were measured. For comparison, values of the pre-exponentials and E_A for the GaN decomposition and Ga desorption kinetics are listed in Table 1. Arrhenius plots of the GaN decomposition at higher H_2 pressures gave slopes that were smaller than the slope measured at 76 torr, giving significantly smaller E_A at higher pressures. These values for E_A were not explicitly calculated because it is not clear if the GaN decomposition at these higher pressures is governed by a single, simple chemical mechanism. The GaN decomposition rates were also measured in N_2 at pressures of 76 (open diamonds) and 150 torr (open squares). At fixed temperature in N_2, the GaN decomposition rate was approximately constant for pressures up to 400 torr. In N_2, an exponential fit gives a larger pre-exponential of $(1.2\pm0.1)\times10^{32}$ $cm^{-2}s^{-1}$ and an substantially larger E_A of 3.62 ± 0.04 eV compared to the kinetic parameters measured in H_2. The

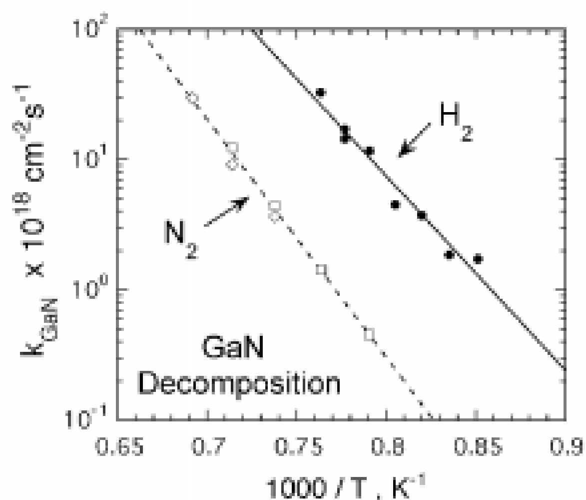

Figure 3. Arrhenius plot of the GaN decomposition rate vs. the reciprocal temperature under H_2 (filled circles, solid line) and N_2 (open diamonds and squares, dashed line). The pre-exponent and activation energy from the fit are listed in Table 1.

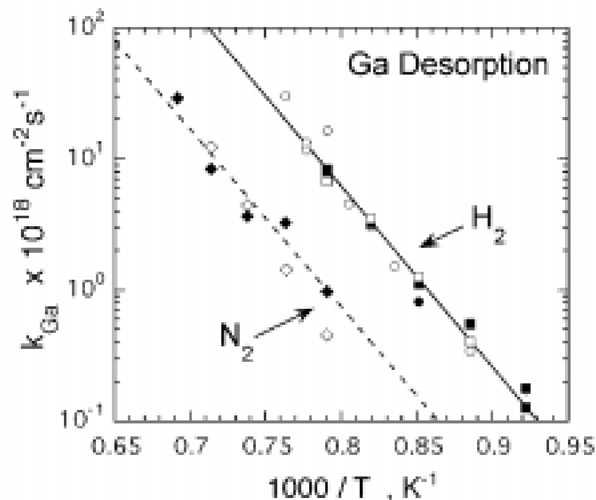

Figure 4. Arrhenius plot of the Ga desorption rate vs. the reciprocal temperature under H_2 (filled and open circles and squares, solid line) and N_2 (filled and open diamonds, dashed line). The pre-exponent and activation energy from the fit are listed in Table 1.

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TABLE I. Values for the kinetic parameters for GaN decomposition and Ga desorption. The first column lists the event, either GaN decomposition or Ga desorption and a brief description of the conditions for the study. The second column lists the measured pre-exponential and the third column lists the measured activation energy, E_A. The reference for the work listed in the table is shown in the fourth column.

Event	pre-exponent	E_A (eV)	Ref.
GaN Decomposition			
Thermogravimetry	$4x10^{29}$ $cm^{-2}s^{-1}$	3.1	10
Mass Spectroscopy	$5x10^{28}$ $cm^{-2}s^{-1}$	3.1	11
Mass Spectroscopy	$1.2x10^{31}$ $cm^{-2}s^{-1}$	3.93	12
H_2 at 76 torr	$(6.3±0.4)x10^{30}$ $cm^{-2}s^{-1}$	2.96±0.06	this work
N_2 at 76 and 150 torr	$(1.2±0.1)x10^{32}$ $cm^{-2}s^{-1}$	3.62±0.04	this work
Ga Desorption			
desorption from liquid Ga	-	2.8	14
RHEED study	$1.0x10^{28}$ $cm^{-2}s^{-1}$	2.69	15
H_2 at 40, 76, 150, 250 torr	$(6.6±0.5)x10^{29}$ $cm^{-2}s^{-1}$	2.74±0.06	this work
N_2 at 76 and 150 torr	$(5.3±0.4)x10^{28}$ $cm^{-2}s^{-1}$	2.69±0.08	this work

GaN decomposition kinetic parameters measured in N_2 are closer to the mass spectroscopy work of Ambacher and coworkers [12] as shown in Table I.

GaN decomposition was also studied as a function of time at a fixed pressure of 150 torr and temperature of 811 °C. Images of the surface after (a) 3, (b) 10, (c) 20, and (d) 80 minutes are shown in Fig. 5. As shown in Fig. 5, the average Ga droplet size increases as the surface is annealed as described by the model of Family and Meakin [9]. After an initial incubation time, the GaN decomposition rate, Ga surface accumulation rate, and the Ga desorption rate were relatively constant in time suggesting zeroth order kinetics. Also, for one experiment the GaN surface was predosed with trimethylgallium for 10 minutes at 600 °C prior to the high temperature anneal in H_2. In agreement with the work of Pisch and Schmid-Fetzer who observed enhanced GaN decomposition on Ga predosed surfaces [13], a 34% increase in the GaN decomposition rate was observed on the Ga predosed surface. While the increase in the GaN decomposition rate by Ga predosing the surface is significant, it is not as large as the increase observed in Fig. 2 when the H_2 pressure is increased from low (< 76 torr) to high pressure (> 150 torr). From this work it is apparent that the GaN decomposition rates depend strongly on the ambient gas (i.e. H_2 or N_2), the pressure, and the condition of the initial surface.

Contrary to the large range in the measured kinetic parameters for GaN decomposition, the measured E_A for Ga desorption were found to be both independent of pressure and ambient gas composition. The data shown in Fig. 4 for H_2 were measured at 40 (solid circles), 76 (open circles), 150 (solid squares), and 250 (open squares) torr. From a fit to all the data a pre-exponential of $(6.6±0.5)x10^{29}$ $cm^{-2}s^{-1}$ and an E_A of 2.74±0.06 eV were measured [7]. In N_2, the desorption rates were measured at 76 (solid diamonds) and 150 (open diamonds) torr, yielding a pre-exponential of $(5.3±0.4)x10^{28}$ $cm^{-2}s^{-1}$ and an E_A of 2.69±0.08 eV. Both measurements of the

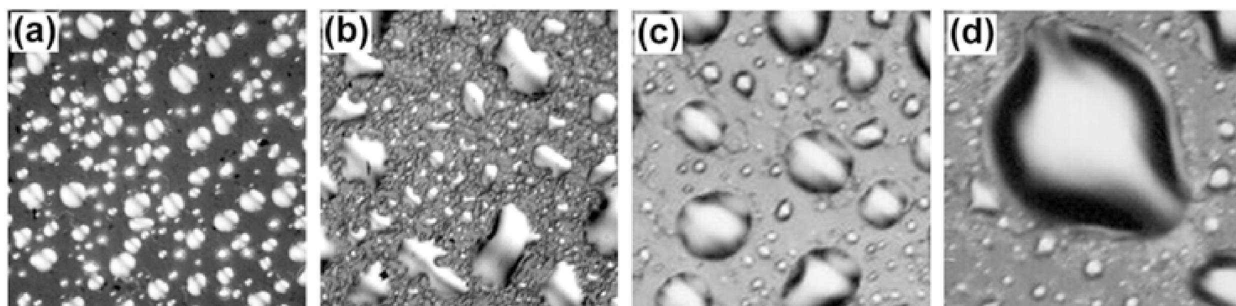

Figure 5: The growth in the Ga droplet size is shown for GaN surfaces anneal at 811 °C for (a) 3, (b) 10, (c) 20, and (d) 80 minutes in H_2 at a pressure of 150 torr.

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Ga desorption E_A are in excellent agreement with the value of 2.8 eV for Ga desorption from liquid Ga [14], and 2.69 eV for Ga desorption from GaN in vacuum [15]. The pre-exponential measured in H_2 is 12.5 larger than in N_2, which is close to the mass ratio of N_2 to H_2 of 14. The mechanism for Ga desorption suppression in N_2 and implications for GaN growth will be discussed in the next section.

DISCUSSION AND CONCLUSIONS

GaN thermal decomposition has been extensively studied in vacuum [10-12, 16-19]. From these previous studies activation energies, E_A, of 3.1 eV [10, 11] and 3.93 eV [12] were measured as listed in Table 1. In this study, we have shown how the measured kinetic parameters vary depending on the pressure and ambient gas. For example, in N_2 a larger E_A (3.62 eV) is measured compared to a lower E_A (2.96 eV) measured in H_2 at 76 torr. The E_A are even lower in H_2 when the pressure is increased above 100 torr. These differences in the E_A reflect a change in the GaN decomposition mechanism when GaN is heated in H_2 vs. heating in N_2.

The decomposition rate enhancement at high pressure coincides with an increase in liquid Ga coverage. Recently, Pisch and Schmid-Fetzer showed that liquid Ga can catalyze GaN decomposition for temperatures as low as 720 °C [13]. Although Ga droplet formation coincides with an increase in the GaN decomposition rate, it is not known if the liquid Ga accumulation is the cause or a result of the increased GaN decomposition rate. In Fig. 2, we show that the GaN decomposition rate is enhanced at higher pressure in H_2. However, no enhancement is observed in N_2. This implies that the GaN surface is chemically altered in H_2 and that N is preferentially removed from the lattice while the Ga desorption rate remains relatively constant.

To preferentially remove N from the lattice, the H_2 must first dissociate and adsorb on the surface. Ga metal is known to dissociate H_2 at high temperatures to form Ga hydrides [20]. The hydrogenated N and Ga species have the potential to be both more mobile and also more volatile. More mobile hydrogenated Ga species have been proposed to explain the increase in the Ga diffusion length when H_2 or atomic H is used in the MBE growth of GaAs [21]. In addition, Okamoto and coworkers have recently showed a suppression of 3D growth morphology when atomic H is used during MBE growth of GaN [22], implying an increase in the surface mobility for the hydrogenated Ga atoms. Increasing the Ga diffusion length would more rapidly uncover new areas of the GaN surface for N_2 desorption, which is 10-10^4 times faster than the Ga desorption rate for the temperature range of 800-1100 °C [4, 15]. Furthermore, the surface H can form more volatile NH_x species. Both an increased rate of NH_x desorption and an increased GaH mobility, will lead to the formation and growth of Ga droplets as shown in Figs. 1 and 5. When N_2 is substituted for H_2, the E_A for decomposition is larger because the chemical pathways for forming hydrogenated N and Ga species are absent. In N_2, the kinetic barrier to GaN decomposition is larger and may be limited by the formation and desorption rate of N_2.

Compared to the GaN decomposition kinetics, Ga desorption is simpler. The E_A listed in Table 1 all are in the range 2.69-2.8 eV, implying that the Ga desorption mechanism is similar under varying pressures and ambient gas flows. The agreement in the E_A for Ga desorption from liquid Ga [14] and the similarity of the measured E_A values in Table 1, suggest that the Ga atoms desorb from a Ga rich surface. As shown in Fig. 4, the measured pre-exponential factor in H_2 is 12.5 times the measured pre-exponential factor in N_2, which is close to the mass difference of 14 between N_2 and H_2. With the N_2 and H_2 molecules initially near room temperature (21 °C), their impact with the hot surface (near 800-1050 °C) would likely result in a general heat removal from the surface. The heat transfer between the N_2 and the hot surface is more efficient than between H_2 and the surface, because of its larger mass (more impulsive collision) and slower speed (mean speed of N_2 is 3.7 times slower than H_2) its collision time with the surface is longer. As a result of the increased collision time, heat transfer from the hotter surface Ga atoms to the cooler N_2 molecules is more efficient, resulting in a reduced population density of the Ga surface vibrations which lead to Ga desorption. The net effect of this is a reduction in attempt frequency (i.e. pre-exponential factor) for Ga desorption in N_2 compared to H_2.

This study of GaN decomposition has several consequences for the growth of GaN. We have found that the material quality is substantially improved when GaN growth is conducted above 100 torr. When the GaN epitaxial layer is grown above 100 torr, we find a near doubling of the electronic mobility ($\mu > 500\ cm^2/Vs$ for intentionally Si doped films with $n = 2$-$3 x 10^{17}\ cm^{-3}$) compared to films growth at 76 torr [7]. For films grown above 100 torr, the GaN grain size

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increased from < 1 μm to 2-5 μm, which may be directly responsible for the increased mobility [23]. Other groups using close-spaced or high speed rotating disk reactors have also reported improved electric properties when the pressure of the GaN growth is greater than 100 torr [24, 25]. Larger grains and narrower x-ray rocking curve widths have been reported for the growth of unnucleated GaN on sapphire in H_2 compared to N_2 [26], suggesting that the enhanced decomposition in H_2 aids in the breakup of smaller grains. Changes in the nucleation layer evolution during the ramp from low to high temperature have also been observed as a function of H_2 pressure [25, 27]. Enhanced GaN decomposition in H_2 may also increase the size and aid in the coalescence of the low temperature nucleation layers as shown by Han et al. [25]. If insufficient NH_3 is supplied, the GaN nucleation layer may be entirely decomposed [28], especially if the nucleation layer is annealed under higher H_2 pressure.

This study illustrates the significant differences between reduced and atmospheric pressure MOVPE GaN growth and the influence of carrier gas chemistry. We have demonstrated the direct influence of H_2 pressure on the GaN decomposition rate. A more thorough understanding of the GaN decomposition mechanism at the higher growth pressures currently used by many groups may serve to clarify the mechanisms contributing to GaN growth.

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REFERENCES

[1] S. Nakamura, M. Senoh, and T. Mukai, Appl. Phys. Lett. 64,1687 (1994).
[2] S. Nakamura, M. Senoh, S. Nagahama, N, Iwasa, T. Yamada, T. Matsushita, H, Kiyoku, Y. Sugimoto, Jpn. J. Appl. Phys. 35, L74 (1996).
[3] S.N. Mohammad, A.A. Salvador, and H. Morkoc, Proc. IEEE 83, 1306 (1995); S. Strite and H. Morkoc, J. Vac. Sci. Technol. B 10, 1237 (1992); R.F. Davis, Proc. IEEE 79, 702 (1991).
[4] D.D. Koleske, A.E. Wickenden, R.L. Henry, W.J. DeSisto, and R.J. Gorman, J. Appl. Phys. 84, 1998 (1998).
[5] S.Yu. Karpov and M.A. Maiorov, Surf. Sci. 393, 108 (1997).
[6] R. Heckingbottom in *Molecular Beam Epitaxy and Heterostructures*, eds. L.L. Chang and K. Ploog, (Martinus Nijhoff, Dordrecht, 1985). p. 71.
[7] D.D. Koleske, A.E. Wickenden, R.L. Henry, M.E. Twigg, J.C. Culbertson, and R.J. Gorman, Appl. Phys. Lett. 73, 2018 (1998).
[8]. M. Fatemi, A.E. Wickenden, D.D. Koleske, M.E. Twigg, J.A. Freitas, Jr., R.L. Henry, and R.J. Gorman, Appl. Phys. Lett. 73, 608 (1998).
[9]. F. Family and P. Meakin, Phys. Rev. Lett. 61, 428 (1988).
[10]. Z.A. Munir and A.W. Searcy, J. Chem. Phys. 42, 4223 (1965).
[11]. R. Groh, G. Gerey, L. Bartha, and J.I. Pankove, Phys. Stat. Sol. A 26, 353 (1974).
[12] O. Ambacher, M.S. Brandt, R. Dimitrov, T. Metzger, M. Stutzmann, R.A. Fischer, A. Miehr, A. Bergmaier, and G. Dollinger, J. Vac. Sci. Technol. B 14, 3532 (1996).
[13] A. Pisch and R. Schmid-Fetzer, J. Cryst. Growth 187, 329 (1998).
[14]. R.E. Honig and D.A. Kramer, RCA Rev. 30 , 285 (1969).
[15] O. Brandt, H. Yang, and K.H. Ploog, Phys. Rev. B 54, 4432 (1996).
[16] W.C. Johnson, J.B. Parsons, and M.C. Crew, J. Phys. Chem. 36, 2651 (1932).
[17] R.J. Sime and J.L. Margrave, J. Phys. Chem. 60, 810 (1956).
[18] R.C. Schoonmaker, A. Buhl, and J. Lemley, J. Phys. Chem. 69, 3455 (1965).
[19] A.S. Bolgar, S.P. Gordienko, E.A. Ryklis, and V.V. Fesenko, in: Chemistry and Physics of the Nitrides (ed. by G.V. Samsonov) [in Russian], (Naukova, Dumka, Kiev 1968), p. 151; also see I.G. Pichugin and D.A. Yas'kov, Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy 6, 1973 (1970).
[20] H. Remy, *Treatise on Inorganic Chemistry*, (Elsevier, New York, 1960), p. 18; W.R.S. Garton, Proc. Phys. Soc. A 64, 509 (1951).
[21] Y. Morishita, Y. Nomura, S. Goto, and Y. Katayama, Appl. Phys. Lett. 67, 2500 (1995).
[22] Y. Okamoto, S. Hashiguchi, Y. Okada, and M. Kawabe, Jpn. J. Appl. Phys. 37, L1109 (1998).
[23]. S.D. Hersee, J.C. Ramer, and K.J. Malloy, MRS Bulletin 22, 45 (1997).
https://doi.org/10.1557/S1092578300002763 Published online by Cambridge University Press

[24] B.T. McDermott, R. Pittman, E.R. Gertner, J. Krueger, C. Kisielowski, Z. Lilienthal-Weber, and E. Weber, Talk D2.2 at Fall Material Research Society Meeting, Boston, 1997.
[25] J. Han, and T.-B. Ng, R.M. Biefeld, M.H. Crawford, D.M. Follstaedt, Appl. Phys. Lett. 71, 3114 (1997).
[26] T.J. Kistenmacher, D.K. Wickenden, M.E. Hawley, and R.P. Leavitt, Mat. Res. Soc. Symp. Proc. 395, 261 (1996).
[27] J.C. Ramer, K. Zheng, C.F. Kranenberg, M. Banas, and S.D. Hersee, Mat. Res. Soc. Symp. Proc. 395, 225 (1996).
[28] Y. Kobayashi, T. Akasaka, and N. Kobayashi, Jpn. J. Appl. Phys. 37, L1208 (1998).

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