Metal-organic molecular-beam epitaxy of GaN with trimethylgallium and ammonia: Experiment and modeling

I. Gherasoiu,[a] S. Nikishin, and H. Temkin
Department of Electrical Engineering, Texas Tech University, Lubbock, Texas 79409

(Received 11 April 2005; accepted 29 July 2005; published online 13 September 2005)

Metal-organic molecular-beam epitaxy with trimethylgallium and ammonia is used to grow GaN on Si(111). Our analysis of the growth data shows an increase in the apparent formation energy E_{app} of epitaxial GaN, from 0.168 to 0.56 eV, with an increasing flux of ammonia. A rate-equation-based growth model is proposed and used to fit the growth data. Regarding the interaction potential, the model assumes the presence of an activated state, intermediate between physisorption and chemisorption, and includes second-order recombination-desorption processes important in the modeling of high-temperature growth. It is shown that the formation energy of epitaxial GaN, E_f, depends on the growth conditions as the activation energy and surface diffusion energy barriers increase or decrease with the change in the impinging fluxes and surface density of precursors. For such a particular set of growth conditions, the model allows us to determine the formation energy of epitaxial GaN as E_f=0.11 eV, ~35% smaller than the apparent activation energy obtained directly from the growth data. E_{app}=0.168 eV. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2039276]

I. INTRODUCTION

Gallium nitride is an important semiconductor material, used in a wide range of applications from optoelectronic devices to microwave transistors. It is therefore important to understand its epitaxial growth by methods such as metal-organic chemical-vapor deposition (MOCVD), plasma-assisted molecular-beam epitaxy (PAMBE), metal-organic molecular-beam epitaxy (MOMBE), gas source MBE (GSMBE), and hydride vapor-phase epitaxy (HVPE).

In parallel with experimental investigations, models for different growth methods of GaN have been proposed. Powell *et al.*[1] used rate equations to describe the PAMBE of GaN. Their model, as noted by the authors, was capable of reproducing trends but did not allow for fitting of experimental data. Brandt *et al.*[2] studied the relation between surface reconstruction transitions and surface kinetics in the PAMBE of cubic GaN, simulating observed reflection high-energy electron-diffraction (RHEED) transients. Held *et al.*[3] proposed a model for the GSMBE growth of GaN in the regime of stable morphology, where surface decomposition could be neglected. Fu and Venkat[4] proposed a model to describe GSMBE growth with a bilayer of Ga and N on top, resulting in the description of Ga and N layer coverages as a function of time. The model parameters were obtained by fitting the experimental data of Held *et al.*[5] Koleske *et al.*[6] suggested a kinetic model to describe MOCVD growth of GaN with ammonia. Their rate equation model was based on postgrowth characterization parameters such as surface roughness, x-ray-diffraction (XRD) linewidth, and photoluminescence (PL) intensity.

Growth of GaN by MOMBE with triethylgallium (TEGa) has been investigated in a number of studies. Abernathy and co-workers[7,8] reported the growth of GaN on GaAs and sapphire substrates using TEGa. The chemistry of MOMBE growth from TEGa with N plasma and ammonia has been studied by Li *et al.*[9] Trimethylgallium (TMGa) is a very attractive source for MOMBE because of high vapor pressure at room temperature, more than 200 Torr. The combination of TMGa with ammonia for the growth of nitride compounds could provide the basis for more economical growth systems than MOCVD, capable of producing high quality material. In spite of the potential advantages, the growth with TMGa and ammonia has not been discussed in the literature.

This work provides a quantitative description of MOMBE growth of GaN. The growth rate measured as a function of temperature and ammonia fluxes is analyzed in terms of an apparent activation energy determined from Arrhenius plots. In the presence of competing surface phenomena the energy determined directly from Arrhenius plots does not represent the actual formation energy of epitaxial GaN and does not have a constant value. A rate equation growth model is formulated that relies on the activation temperature and second-order reaction kinetics to account for observed growth regimes.

II. APPARENT FORMATION ENERGY IN MOMBE OF GAN

The growth of GaN was performed on AlN buffer layers, ~80-nm thick, on Si(111) substrates. An ammonia injector temperature of 470 °C, beam equivalent pressure (BEP) of TMGa of 2.1×10^{-6} Torr, and ammonia fluxes between 30 and 150 SCCM (standard cubic centimeter per minute) were used. For each of the ammonia fluxes the growth rate was determined as a function of temperature in the range of 765–865 °C. The results are presented in Fig. 1.

[a]Electronic mail: iulian.gherasoiu@ttu.edu

0021-8979/2005/98(5)/053518/5/$22.50 © 2005 American Institute of Physics

Downloaded 13 Sep 2005 to 129.118.86.57. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

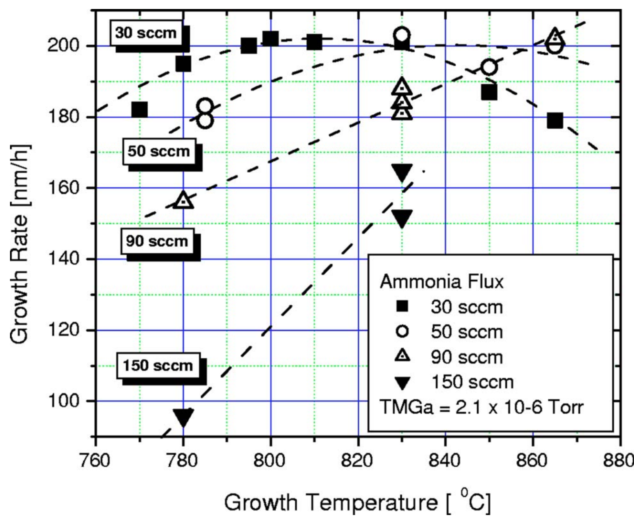
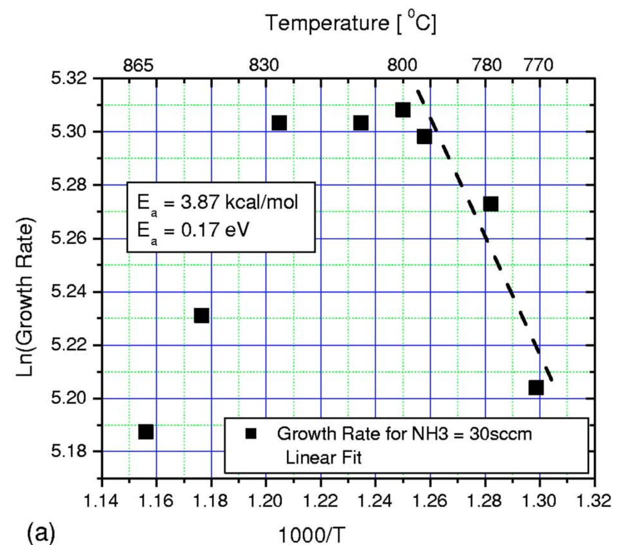


FIG. 1. (Color online) Growth rate dependence on growth temperature and ammonia flux. The lines are guides for the eye.

At a low ammonia flux of 30 SCCM we observe three regions in the growth rate dependence on temperature. A slight increase in the growth rate seen in the low-temperature range is followed by a saturation region and a decrease at the highest growth temperature. The growth behavior changes at higher fluxes of ammonia. Most notably, for a fixed growth temperature, the growth rate of GaN decreases with an increased flux of ammonia. Consequently, while the growth rates of GaN appear to reach similar maxima for 30, 50, and 90 SCCM of ammonia, the peak value shifts gradually toward higher temperatures with larger fluxes. Temperature limitations of the growth system and roughening of the surface restrict the growth temperature to 865 °C and the ammonia flux to 150 SCCM, respectively.

A similar behavior of the growth rate was found in the GSMBE of GaN by Kim *et al.*[10] Their analysis pointed out the importance of reaction-controlled growth at low temperatures and the importance of desorption reaction leading to reduced growth rates at high temperatures. The three growth regions seen in Fig. 1 for the ammonia flux of 30 SCCM can be described by different rate-limiting processes. The low-temperature (765–800 °C) region appears to be *reaction limited*. The surface residence time is considered long enough for adsorbed species to reach, through diffusion, an incorporation site. The growth rate is determined, to a large extent, by the *formation* rate of epitaxial GaN. In the intermediate temperature (800–830 °C) region formation and *desorption* appear to be largely balanced. The growth rate becomes weakly dependent on temperature and it reaches a maximum. At high temperatures (830–865 °C) the growth rate becomes desorption limited. The residence time starts to decrease and adsorbates can recombine before reaching an incorporation site.

Such growth phenomena are well documented for metal-organic vapor-phase epitaxy (MOVPE) (see for instance Briot[11] and Herman *et al.*[12]) In the MOCVD of GaN from TEGa and ammonia, Briot found two growth regimes, for low and high temperature, and used Arrhenius plots to determine an activation energy for a GaN formation of 0.165 eV(3.8 kcal/mol).



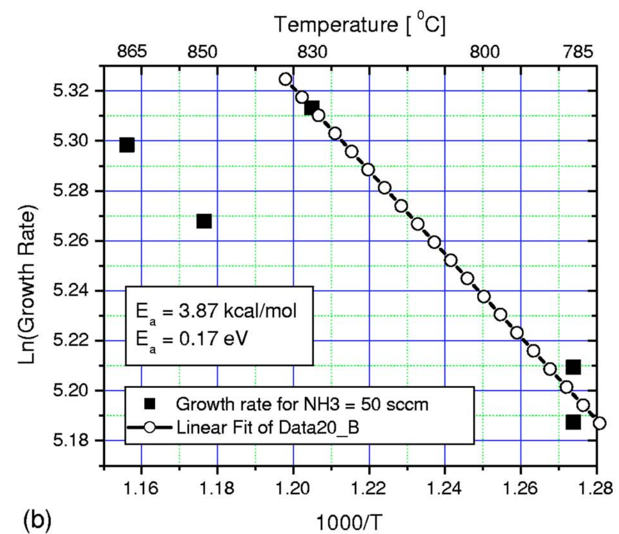
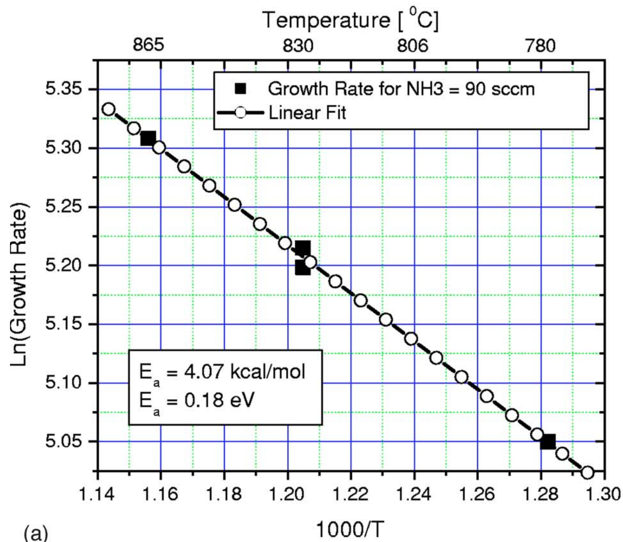


FIG. 2. (Color online) Arrhenius plots for ammonia fluxes of (a) 30 SCCM and (b) 50 SCCM.

In order to better understand the growth process it is useful to extract the activation energy (E_a) for the formation of epitaxial GaN from the growth data. In particular, the low-temperature growth regime that appears to be dominated by first-order reaction kinetics can be fitted by an Arrhenius rate equation $G_R=F\exp(-E_a/RT)$, where F is a preexponential factor and R and T have their usual meanings. At low growth temperature only one-step surface reactions need to be considered. These are of the first order and the growth rate is proportional to the fluxes impinging the surface.

The E_a of epitaxial GaN, for the four ammonia fluxes used, is extracted from the Arrhenius plots of Figs. 2 and 3. For ammonia fluxes of 30 and 50 SCCM we obtain $E_a \sim 0.17$ eV(3.9 kcal/mol). For an ammonia flux of 90 SCCM a slightly higher $E_a \sim 0.18$ eV(4.1 kcal/mol) is obtained. These energies are similar to those obtained previously by Briot.[11] The growth with an ammonia flux of 150 SCCM exhibits a significantly higher $E_a \sim 0.56$ eV(12.9 kcal/mol). A similar range of formation energies has been obtained by McGinnis *et al.*[13]

Downloaded 13 Sep 2005 to 129.118.86.57. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp



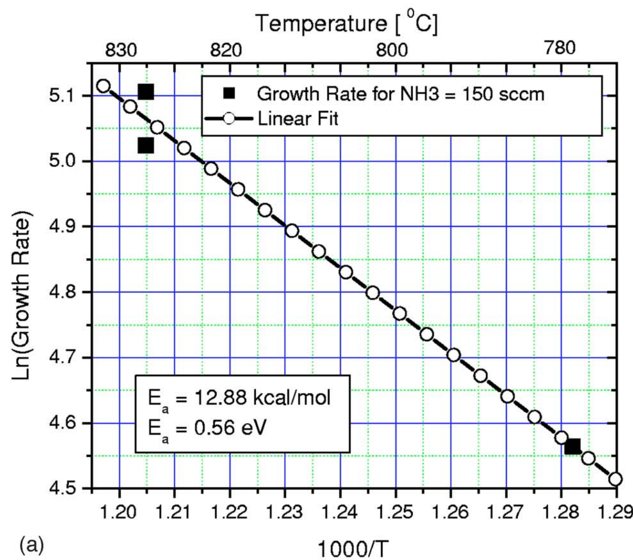


FIG. 3. (Color online) Arrhenius plots for ammonia fluxes of (a) 90 SCCM and (b) 150 SCCM.

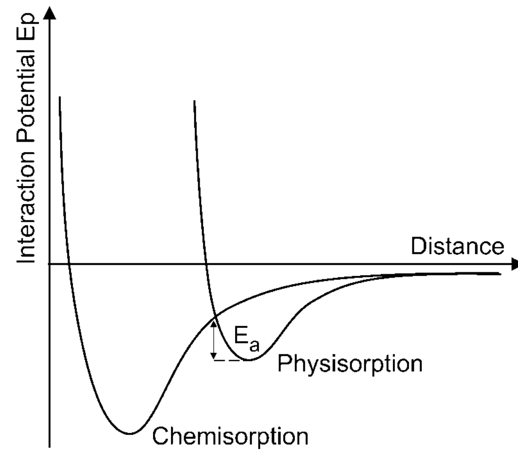


FIG. 4. Usual description of interaction energy between the incoming molecule and surface is limited to physisorption followed by chemisorption state.

Our analysis of the growth of GaN shows that the energy determined from Arrhenius plots varies by a factor of 3, from 0.17 to 0.56 eV, with an increased flux of ammonia. The activation energy has a well-defined meaning for processes, such as desorption from a surface, which are not accompanied by competing processes, such as adsorption. We attribute the change in the E_a determined from our growth data to the presence of competing processes. It is thus appropriate to use the term apparent activation energy for the energy determined from Arrhenius plots.

III. GROWTH RATE MODEL OF GAN

Most growth models of GaN assume that the desorption process limiting the growth rate at high temperatures is of first order (Brandt *et al.*[2] and Koleske *et al.*[6]). In other words, the desorption rate is proportional to the instantaneous surface coverage. This assumption is realistic for the case of vacuum desorption (no growth) when there are no interactions between surface species. In MOMBE or MOCVD the instantaneous impinging fluxes ($10^{16}-10^{22}$ at. cm^{-2}) are much larger than the surface site densities ($\sim 10^{15}$ at. cm^{-2}), making interactions between species possible. Molecular N_2, volatile species of Ga, and liquid Ga are likely to form through collisions with the probability that is proportional to the product of surface densities. This suggests that a second-order process, e.g., decomposition and desorption, may need to be considered in the description of the growth of epitaxial GaN.

The growth of epitaxial GaN is usually modeled in terms of two potential profiles corresponding to the processes of physisorption and chemisorption for incoming molecules. The activation energy E_a is then interpreted as the energy needed for transition from one state to the other, as shown in Fig. 4.

The variation in E_a implies the presence of competing processes with relative contributions that depend on the flux of precursor molecules. We take account of the changing relative contributions of different process by introducing an activated state, intermediate between the usual physisorption and chemisorption states. This allows us to include bond-breaking and recombination-desorption reactions. These processes are thermally activated but they have different onset temperatures and activation energies. The modified set of potential profiles is shown in Fig. 5. We consider three major steps, each represented by a potential well, resulting in the formation of epitaxial GaN. The first step is the physisorption of precursors, represented by the well labeled (1). The second well represents the activated state. The third potential well represents chemisorption. At this point the incoming radical becomes attached to the surface of GaN. The chemisorption process is completed when all the bonds of the radical are satisfied with either Ga or N, becoming a part of epitaxial GaN. We illustrate this further with an example of a TMGa molecule. The molecule of TMGa physisorbed in step (1) remains intact, only its charge distribution is altered by formation of a van der Waals bond with the underlying GaN. In step (2), pyrolysis of TMGa results in a loss of methyl radical, creating an activated molecule. The activated molecule diffuses on the surface and becomes chemisorbed in step (3), once a suitable site is encountered. The activation

Downloaded 13 Sep 2005 to 129.118.86.57. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

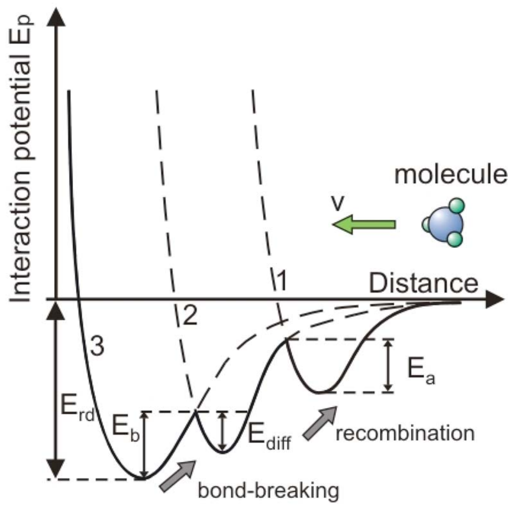


FIG. 5. (Color online) Interaction potential for MOMBE GaN growth. An activated state (2) is included between the physisorbed (1) and chemisorbed (3) states. The dashed potential corresponds to the apparent activation energy determined from the Arrhenius plots.

energy E_a represents the energetic cost of the removal of H or CH_3 for ammonia or TMGa, respectively. Energetically, the activated and chemisorbed species differ by surface diffusion energy E_{diff}. The sum of these two energies E_a+E_{diff} is the formation energy E_f of epitaxial GaN. In our model, the formation of GaN is hindered by thermally assisted bond breaking, requiring the energy E_b, and recombination processes in which the formation of liquid Ga or molecular nitrogen takes place. Other recombination processes may involve H or CH_3 to form primarily H_2 and methane.

Processes that allow transitions between adjacent potentials are usually described by first-order reaction kinetics where the reaction rate is given by the product of $A \exp(-E_a/RT)$. Here A is the prefactor representing the instantaneous surface density of molecular species. The rate of processes which involve transitions over one or more intermediate potential profiles, i.e., second-order kinetic processes, can be written as

$$\text{Rate} = AB \exp(-E_a/RT), \quad (1)$$

where A and B are the prefactors proportional to the surface densities of species A and B taking part in the process. An example of such a process, known as recombinative desorption,[14] would be $N-Ga(ad)+CH_3 \to N-Ga-CH_3(ad) \to GaCH_3(g)+1/2N_2(ad)$, where the nitrogen in the solid and the Ga surface adsorbate interacts with methyl, a byproduct of TMGa decomposition on the surface, forming an intermediate species of monomethyl adsorbate on the surface of GaN, eventually transforming into volatile monomethyl Ga and molecular nitrogen adsorbate. Other reactions of this type have been studied by Sakai *et al.*[15] In general, one can write $A(ad)+B(ad) \to AB(ad) \to AB(g)$ where A and B could be Ga, N, or other surface species.

Based on the model of Fig. 5 the growth of epitaxial GaN can be described by a number of processes of deposition and desorption, each having a specific rate. We write the rate of formation of GaN, R_F, as

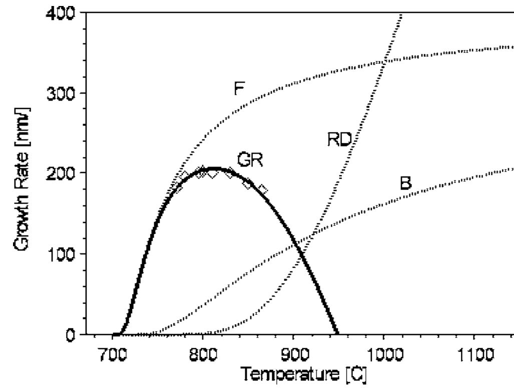


FIG. 6. Measured and calculated growth rates plotted as a function of temperature for an ammonia flux of 30 SCCM. The rates of specific processes contributing to the growth of GaN are also plotted; GR—growth rate, F—formation, B—bond-breaking, and RD—recombination-desorption. Open circles represent experimental data.

$$R_F = F \exp(-E_f/R(T-T_f)) , \quad (2)$$

where T_f is the onset temperature of the formation process and the energies $E_a+E_{diff}=E_f$ are illustrated in Fig. 5. The desorption includes two processes: a first-order process of bond breaking and a second-order process of recombination desorption. Their respective rates are written as

$$R_B = B \exp(-E_b/R(T-T_b)) , \quad (3)$$

$$R_{RD} = RD \exp(-E_{rd}/R(T-T_{rd})) . \quad (4)$$

The overall rate of growth of GaN, G_R, is then given by

$$G_R = R_F - R_B - R_{RD}. \quad (5)$$

Here, the prefactors F, B, and RD represent instantaneous densities of molecules participating in the particular process. Thus F represents the combined fluxes of ammonia and TMGa impinging on the surface. Similarly, B and RD represent densities of surface atoms participating in the bond-breaking and recombination-desorption processes, respectively. We assume here that physisorbed molecules (TMGa, NH_3) have a near unity sticking coefficient as argued by Koleske *et al.*[6] While F can be measured, other prefactors are determined by fitting the growth data. For the ammonia flux of 30 SCCM the low-temperature growth rate ranges from 2.3×10^{14} to 2.6×10^{14} at. $cm^{-2}\,s^{-1}$. The ammonia and TMGa fluxes are 0.7×10^{16} and 2.7×10^{14} molecule $cm^{-2}\,s^{-1}$, respectively. The prefactor F is taken to be equal to the sum of these two fluxes or $F=0.7\times10^{16}$ molecule $cm^{-2}\,s^{-1}$. The initial value of B is taken as $\sim10^{16}\,cm^{-2}\,s^{-1}$ and RD is estimated at $10^{32}\,cm^{-2}\,s^{-1}$.

The activation energy of the recombination-desorption process in epitaxial GaN was determined by Choi *et al.*[16] as $E_{rd}=2.61$ eV for temperatures over 900 °C. Koleske *et al.*[17] obtained a similar value of $E_{rd}=2.68$ eV and noted that the increase in ammonia flow partially suppresses the recombination-desorption process. Brandt *et al.*[2] determined $E_{rd}=2.69$ eV. It should be noted that higher values of 3.45 and 3.6 eV have been reported by Held *et al.*[18] and Grandjean *et al.*,[19] respectively.

The growth rate defined by Eq. (5) is plotted in Fig. 6 as

Downloaded 13 Sep 2005 to 129.118.86.57. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

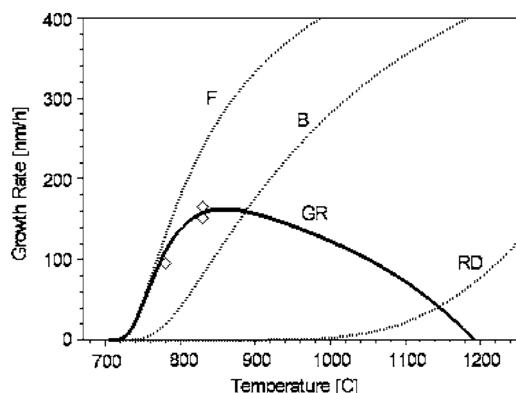


FIG. 7. Model of growth behavior at large ammonia flux. The open circles represent the experimental growth rate measured for an ammonia flux of 150 SCCM. GR—fitted growth rate, F—formation, B—bond-breaking, and RD—recombination-desorption.

a function of temperature and compared with experimental growth data obtained at the ammonia flux of 30 SCCM. The activation energy E_{rd} is fixed at 2.61 eV and the energies E_f and E_b are used as fitting parameters. The quality of the fit is judged by the coefficient of determination $R^2(0<R^2<1)$, the squared sum of deviations. The fit shown in Fig. 6 has $R^2 \sim 0.80$ confirming very good agreement with the experimental data points. The fit results in $E_f \sim 0.106$ eV(2.42 kcal/mol) and $E_b \sim 0.135$ eV(3.11kcal/mol). The formation energy E_f is thus smaller than the apparent activation energy of 0.168 eV(3.87 kcal/mol).

The growth rate increases with the temperature up to ~800 °C, saturates, and starts to decrease above ~850 °C. The growth terminates for temperatures above 900 °C, in good agreement with experimental observations of Grandjean *et al.*[19] At low temperatures the formation process is dominant. In the intermediate range, it is offset by the bond-breaking process. At high temperatures, the decrease in the growth rate is due to the recombination-desorption process.

Figure 7 illustrates the experimental data and the model fit for the ammonia flux of 150 SCCM, the highest flux used in our experiments. In this case, surface desorption is overwhelmed by the incident flux. The high-temperature decrease of the growth rate is less pronounced and the formation energy increases accordingly to $E_f \sim 0.21$ eV(4.92 kcal/mol). These estimates are less reliable than those obtained for 30 SCCM of ammonia, for which experimental data is more complete.

At high fluxes of ammonia the activation energy for recombination-desorption becomes very large, $E_{\mathrm{rd}} \sim 5.2$ eV (~119 kcal/mol), suggesting a suppression of the recombination-desorption process. A similar suppression of Ga desorption was observed by Held[20] who found an increase in the activation energy from 3.4 eV, under vacuum conditions, to 5.8 eV under the Ga flux of 0.61 ML/s (ML is monolayer). Apparently, a suppression of the decomposition of GaN, interpreted as decreased desorption, takes place under high fluxes of either Ga or ammonia.

IV. CONCLUSIONS

In summary, we have analyzed the MOMBE growth data to determine the apparent formation energy of epitaxial GaN. Our analysis shows an increase of the apparent formation energy from 0.168 to 0.56 eV with an increasing flux of ammonia. We propose a rate-equation-based growth model and show that it can be used to fit the growth data. The model relies on the presence of an activated state, intermediate between physisorption and chemisorption. We further show that the second-order recombination-desorption process is important in the modeling of high-temperature growth. The model allows us determine the formation energy of epitaxial GaN as $E_f = 0.11$ eV, smaller than the apparent activation energy obtained directly from the growth data $E_{\mathrm{app}} = 0.168$ eV. The modeled formation energy E_f depends on the growth conditions as the activation energy and surface diffusion energy barriers increase or decrease with the change in the impinging fluxes and surface density of precursors.

ACKNOWLEDGMENTS

This work was supported by grants from the National Science Foundation NSF (ECS-0323640 and ECS-0304224), RDECOM—US Army, NATO Science for Peace (974505), DARPA-SUVOS (monitored by Dr. J. Carrano), and J. F. Maddox Foundation.

[1] R. C. Powell, N. E. Lee, Y. W. Kim, and J. E. Greene, J. Appl. Phys. **73**, 189 (1993).
[2] O. Brandt, H. Yang, and K. H. Ploog, Phys. Rev. B **54**, 4432 (1996).
[3] R. Held, B. E. Ishaug, A. Parkhomovsky, A. M. Dabiran, and P. I. Cohen, J. Appl. Phys. **87**, 1219 (2000).
[4] W. Fu and R. Venkat, J. Vac. Sci. Technol. B **18**, 1467 (2000).
[5] R. Held, D. E. Crawford, A. M. Johnston, A. M. Dabiran, and P. I. Cohen, J. Electron. Mater. **26**, 272 (1997).
[6] D. D. Koleske, A. E. Wickenden, R. L. Henry, W. J. DeSisto, and R. J. Gorman, J. Appl. Phys. **84**, 1998 (1998).
[7] C. R. Abernathy, J. D. MacKenzie, and S. M. Donovan, J. Cryst. Growth **178**, 74 (1997).
[8] C. R. Abernathy, J. Vac. Sci. Technol. A **11**, 869 (1993).
[9] T. Li, R. P. Campion, C. T. Foxon, S. A. Rushworth, and L. M. Smith, J. Cryst. Growth **251**, 499 (2003).
[10] W. Kim, A. Salvador, A. E. Botchkarev, Ö. Aktas, S. N. Mohammad, and H. Morkoç, Appl. Phys. Lett. **69**, 559 (1996).
[11] O. Briot, in *Group III Nitride Semiconductor Compounds—Physics and Applications*, edited by B. Gil (Clarendon, Oxford, 1998).
[12] M. A. Herman, W. Richter, and H. Sitter, *Epitaxy—Physical Principles and Technical Implementation* (Springer, Berlin Heidelberg, 2004).
[13] A. J. McGinnis, D. Thomson, A. Banks, E. Preble, and H. H. Lamb, J. Vac. Sci. Technol. A **21**, 294 (2003).
[14] L. Pauling, *General Chemistry* (Dover, New York, 1988).
[15] S. Sakai, S. Kurai, K. Nishino, K. Wada, H. Sato, and Y. Naoi, Mater. Res. Soc. Symp. Proc. **449**, 15 (1997).
[16] H. W. Choi, M. G. Cheong, M. A. Rana, S. J. Chua, T. Osipowicz, and J. S. Pan, J. Vac. Sci. Technol. B **21**, 1080 (2003).
[17] D. D. Koleske, M. E. Coltrin, A. A. Allerman, K. C. Cross, C. C. Mitchell, and J. J. Figiel, Appl. Phys. Lett. **82**, 1170 (2003).
[18] R. Held, D. E. Crawford, A. M. Johnston, A. M. Dabiran, and P. I. Cohen, Surf. Rev. Lett. **5**, 913 (1998).
[19] N. Grandjean, J. Massies, F. Semond, S. Yu. Karpov, and R. A. Talalaev, Appl. Phys. Lett. **74**, 1854 (1999).
[20] R. Held, Ph.D. thesis, University of Minnesota, 1999.

Downloaded 13 Sep 2005 to 129.118.86.57. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp