

Growth kinetics of AlGa_xN films by plasma-assisted molecular-beam epitaxy

E. Iliopoulos^{a)} and T. D. Moustakas^{b)}

Department of Electrical and Computer Engineering, Boston University, 8 St. Mary's Street, Boston, Massachusetts 02215

(Received 19 February 2002; accepted for publication 16 May 2002)

In this letter, we report on the kinetics of growth of aluminum gallium nitride films by rf plasma-assisted molecular-beam epitaxy on (0001) sapphire substrates at the temperature range of 750–800 °C. The determination of the incorporation probabilities of aluminum and gallium atoms was arrived at by measurements of the growth rate and composition of the films. We find that, in both the nitrogen-rich and group-III-rich growth regimes, the incorporation probability of aluminum is unity for the entire investigated temperature range. On the other hand, the incorporation probability of gallium is constant and equals 0.75 at a substrate temperature of 750 °C only in the nitrogen-rich growth regime. The temperature dependence of the incorporation probability in this regime has an activation energy of 2.88 eV which is consistent with gallium desorption from the surface. In the group-III-rich growth regime, the incorporation probability of gallium decreases monotonically with group-III fluxes due to the competition with aluminum for the available active nitrogen. In this regime, the GaN phase growth rate is determined by the capture probability of the available active nitrogen from the gallium surface adlayer. © 2002 American Institute of Physics. [DOI: 10.1063/1.1492853]

The kinetics of GaN growth by molecular-beam epitaxy (MBE), using either ammonia or plasma activated molecular nitrogen as group-V source, has been investigated by a number of groups.^{1–7} However, there are only a few studies addressing the kinetics of growth of AlGa_xN alloys by either MBE^{3,8,9} or metalorganic chemical vapor deposition.¹⁰ Kamp and co-workers³ have reported that, during growth of AlGa_xN alloys by MBE using ammonia, the Al incorporation is a nonlinear function of the Al/Ga flux ratio. Jenny and co-workers⁸ have reported on the impact of Al on Ga adsorption kinetics in AlGa_xN films grown by MBE also using ammonia as a nitrogen source. A study on the growth and structure of AlGa_xN films grown by electron cyclotron resonance assisted MBE was reported by Iliopoulos and co-workers.⁹ In the present letter, the results of a systematic study of the growth kinetics of AlGa_xN alloys by rf-plasma-assisted MBE is reported.

The Al_xGa_{1-x}N films were grown using an Eiko EV-500 MBE unit. Applied EPI Inc. SUMO effusion cells were used for the evaporation of group-III elements. For the activation of nitrogen, an Oxford Applied Research CAR-25 rf-plasma source, mounted in one of the effusion cell ports, was used. The films were grown on *c*-plane sapphire substrates back-coated with titanium for efficient radiative heating. Prior to growth, the substrates were subjected to plasma nitridation at 200 °C using an rf power of 500 W and a nitrogen flow rate of 2.5 sccm. Following this step, a 25 nm thick AlN buffer layer was grown at 800 °C. Finally, a series of AlGa_xN films, about 1 μm thick, were grown at 750 °C. In order to investigate the effect of substrate temperature, additional growths were carried out in the range of 750–800 °C. During the growth of all these films, the nitrogen plasma conditions

were kept constant (330 W rf power and 2.5 sccm N₂ flow). The growth was monitored *in situ* by reflection high-energy electron diffraction (RHEED).

The arrival rate of the group-III atoms was determined by measuring the beam equivalent pressures (BEP) prior to growth, using a nude ionization gauge placed at the substrate position. The arrival rate F_i of the i species (in cm⁻² s⁻¹), is given by¹¹

$$F_i = C_i \cdot \frac{P_i}{\sqrt{m_i \cdot k_B \cdot T_i}}, \quad (1)$$

where P_i is the measured BEP, m_i is the atomic mass, and T_i is the vapor temperature, which is taken to be approximately equal to the corresponding effusion cell absolute temperature. The constant C_i reflects the ionization gauge sensitivity factors for gallium and aluminum as well as geometrical factors related to placing the ion gauge in the exact position of the substrate. The determination of the proportionality constants, C_i , is accomplished by the following calibration experiments; for the case of aluminum, a thin metallic Al film was deposited at room temperature, while for the case of gallium, a GaN film was deposited at room temperature under high active nitrogen flux to make sure that all arriving Ga atoms were incorporated in the film. From the thickness of these films, the corresponding proportionality constants were determined using the value of the Al metal density (6.02×10^{22} atoms/cm³) and the density of GaN having the wurtzite structure (4.38×10^{22} Ga atoms/cm³).

The AlN mole fraction, x , of the grown Al_xGa_{1-x}N films was determined *ex situ* by energy dispersive x-ray spectroscopy, at beam energy of 5 keV. Using appropriate standards, we estimated the error in the AlN mole fraction to be less than 2%. The film thickness was measured *ex situ* by cross section scanning electron microscopy and optical reflection

^{a)}Electronic mail: lefter@bu.edu

^{b)}Electronic mail: tdm@bu.edu

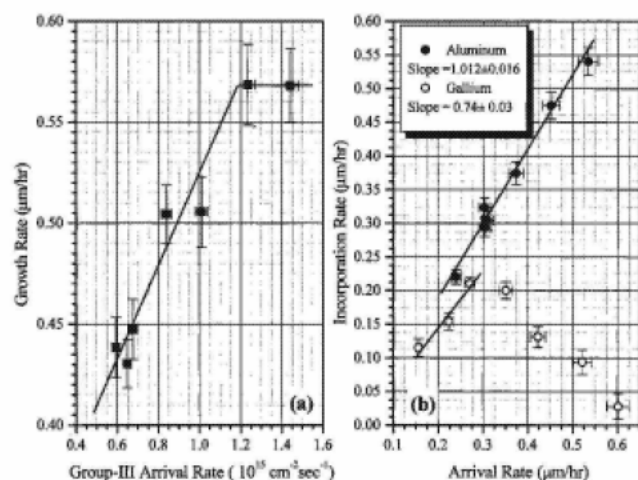


FIG. 1. (a) Growth rate of AlGaIn films vs arrival rate of group-III atoms for $T_{\text{growth}} = 750^\circ\text{C}$. (b) Incorporation rate of Al and Ga versus corresponding arrival rates.

measurements. The results of the two methods agreed to within $\Delta d = 35$ nm.

Figure 1(a) shows the growth rate of the investigated AlGaIn films versus the total arrival rate of the group-III atoms. The data show two distinct regimes: For lower group-III arrival rates, the growth rate increases monotonically with increasing total group-III flux, but saturates at a value of approximately $0.57 \mu\text{m/h}$. Thus, we can conclude that for the specific operating conditions of the plasma source and substrate temperature, the active nitrogen flux is equivalent to film growth rate equal to $0.57 \mu\text{m/h}$. Of course, this value should depend on the composition of the AlGaIn films, since the c -lattice constants of AlN and GaN differ by about 4%. However, our measurements of the growth rate have a higher experimental error.

Figure 1(b) describes the incorporation rate of Al and Ga in the films versus the corresponding incident fluxes. The Al incorporation rate, expressed as the growth rate of AlN in $\mu\text{m/h}$, is calculated from the product of the measured growth rate and AlN mole fraction of the AlGaIn films. The Al incorporation rate increases linearly with the incident Al arrival rate. From the linear regression through the experimental points, we conclude that the sticking probability of Al in the films is equal to one. Distinctively different behavior is observed for the Ga incorporation. While initially the Ga incorporation rate increases proportionally to the incident Ga flux, for higher Ga fluxes, it decreases monotonically. The initial increase of the incorporation rate of Ga atoms results from the fact that the incident active nitrogen flux is higher than the total group-III flux: $F_N > F_{\text{Al}} + F_{\text{Ga}}$ (nitrogen-rich growth regime). The decrease in Ga incorporation occurs when $F_N < F_{\text{Al}} + F_{\text{Ga}}$ (group-III-rich growth regime). In the case of pure GaN growth, we would expect that the incorporation rate of Ga will saturate at the group-III-rich growth regime. Thus, the observed decrease in Ga incorporation in this regime reflects the competition between Al and Ga to react with the available active nitrogen.

In Fig. 2, the incorporation probability of Ga and Al are plotted as a function of the total group-III incident flux ($F_{\text{III}} = F_{\text{Ga}} + F_{\text{Al}}$). The incorporation probabilities were calculated from the data of Fig. 1(b), as the ratio of the incor-

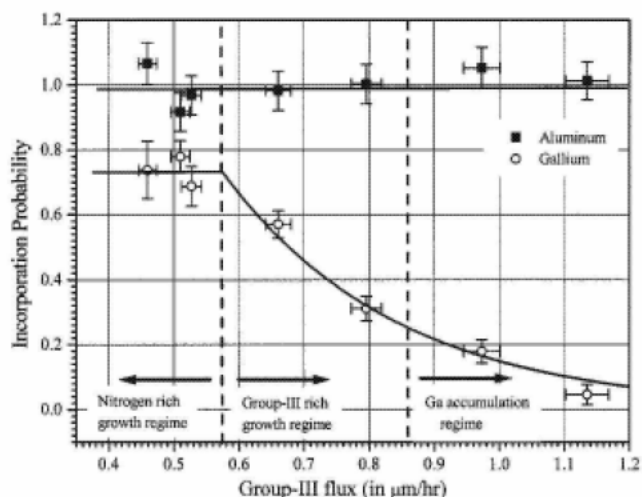


FIG. 2. Incorporation probabilities of Al and Ga atoms vs arrival rate of group-III atoms for AlGaIn films grown at 750°C .

poration rate of the atoms versus the corresponding incident rate. The data of Fig. 2 fall into three regimes of growth. The films grown at group-III flux less than approximately $0.6 \mu\text{m/hr}$ show a spotty RHEED pattern, resulting from a rough surface morphology.¹² Beyond this point, the RHEED pattern becomes streaky. This transition point coincides with the value of the active nitrogen flux deduced from the data of Fig. 1(a). For group-III flux higher than this transition point, the formation of a Ga adlayer at the growing surface is expected.¹³ For films grown with group-III flux higher than approximately $0.85 \mu\text{m/h}$, the RHEED pattern becomes dim and a postgrowth examination of the samples reveals the existence of Ga droplets on the surface.

From the data of Fig. 2, it is apparent that while all incident Al atoms incorporate in the AlGaIn films, the incorporation probability for Ga atoms is constant (about 0.75) only for the films grown under nitrogen-rich conditions of growth. Under group-III-rich conditions of growth, the Ga incorporation probability decreases monotonically. This difference reflects a competition in the incorporation of the Al and Ga atoms. The preferential incorporation of Al atoms is energetically favored due to the stronger Al—N bond. The cohesive energy per bond for Al—N is $E_{\text{cohesive}}^{\text{AlN}} = 2.88 \text{ eV}$, while the one for Ga—N is $E_{\text{cohesive}}^{\text{GaN}} = 2.20 \text{ eV}$.¹⁴ The difference of 680 meV is significantly higher than the value of $k_B \cdot T_{\text{growth}}$ (88 meV) at the growth temperature. Thus, exchange reactions of the type $\text{GaN} + \text{Al}_{\text{adatom}} \Rightarrow \text{AlN} + \text{Ga}_{\text{adatom}}$ are expected, resulting in complete incorporation of all arriving Al atoms. These reactions also result in an adlayer consisting solely of Ga atoms, as in the case of GaN growth.¹³ Therefore during growth of AlGaIn alloys by rf-plasma-assisted MBE under group-III rich conditions of growth, it appears that Ga behaves as a surfactant. In other words, it participates in the growth process but it does not incorporate in the films. Similar surfactant behavior has been reported for In on growing MBE GaN films and during the MBE growth of InGaIn alloys.¹⁵

From the previous discussion, it is apparent that the incorporation rate of Ga atoms, in the group-III-rich growth regime, is dictated by the difference between the active nitrogen flux minus the Al flux $\Delta F = F_N - F_{\text{Al}}$. In order to

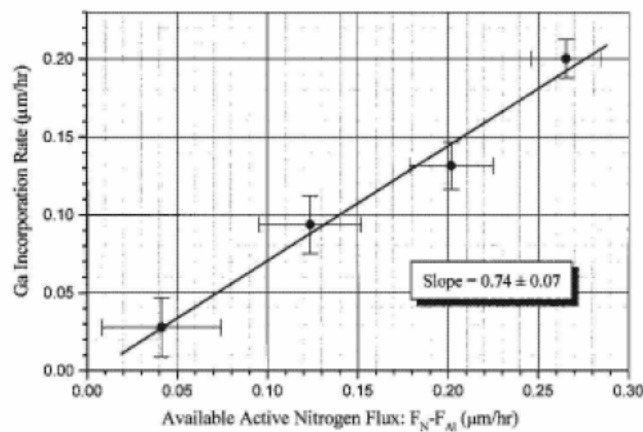


FIG. 3. Incorporation rate of Ga atoms vs ΔF , the net available nitrogen flux for the growth of the GaN phase for $T_{\text{growth}} = 750^\circ\text{C}$.

investigate the growth of the GaN phase, in this regime, we plot in Fig. 3 the Ga incorporation rate versus ΔF . The Ga incorporation rate is directly proportional to the net nitrogen flux ΔF with a proportionality constant, σ_N , equal to 0.74 ± 0.07 . Since in this regime, there is a continuous Ga adlayer on the surface, the observed slope of 0.74 should reflect the capture probability of available active nitrogen species from the Ga adlayer.

The temperature dependence of the incorporation probabilities of Ga and Al for films grown in the nitrogen-rich growth regime has also been investigated. The measured incorporation probability of Al in the temperature range of 750°C to 800°C was found equal to one. The incorporation probability of Ga versus $1/k_B T$ is plotted in Fig. 4 and an

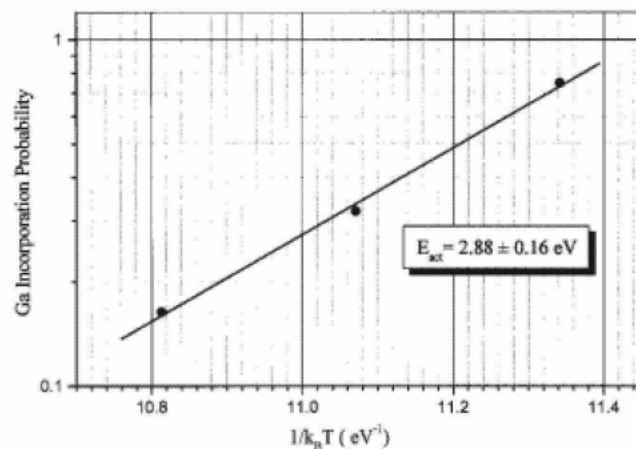


FIG. 4. Incorporation probability of Ga atoms for AlGaIn films grown under nitrogen-rich growth conditions vs $1/k_B T$.

activation energy equal to 2.88 ± 0.16 eV was deduced. This value is close to the values of 2.69 and 2.76 eV reported for the activation energy for the desorption of Ga atoms from the GaN surface.^{16,17}

In conclusion, we have investigated the kinetics of growth of AlGaIn films by rf-plasma-assisted MBE in the temperature range of 750°C – 800°C . We find that Al incorporates with unity incorporation probability in both the group-III and nitrogen-rich growth regimes. In contrast, the incorporation probability of Ga atoms is constant (but less than one) only under nitrogen-rich conditions of growth. Temperature dependent studies in this growth regime show that the incorporation probability of Ga is governed by desorption of Ga from the film surface with an activation energy of ~ 2.88 eV. In group-III-rich conditions of growth, there is a competition between the incorporation of Al and Ga atoms. As a result, the incorporation of Ga is controlled solely by the available nitrogen flux that is not consumed by the Al.

The authors would like to thank S. Iyer for assistance with the experiments. The work was funded by ONR under Grant No. N00014-98-1-0213 (monitored by Dr. C. E. C. Wood)

- ¹D. E. Crawford, R. Held, A. M. Johnson, A. M. Dabiran, and P. I. Cohen, *MRS Internet J. Nitride Semicond. Res.* **1**, 12 (1996).
- ²C. T. Foxon, T. S. Cheng, S. E. Hooper, L. C. Jenkins, J. W. Orton, D. E. Lacklison, S. V. Novikov, T. B. Popova, and V. V. Tret'yakov, *J. Vac. Sci. Technol. B* **14**, 2346 (1996).
- ³M. Kamp, M. Mayer, and A. Pelzmann, and K. J. Ebeling, *MRS Internet J. Nitride Semicond. Res.* **2**, 26 (1997).
- ⁴K. Evans, T. Lei, and C. R. Jones, *Solid-State Electron.* **41**, 339 (1997).
- ⁵J. R. Jenny, R. Kaspi, and K. R. Evans, *J. Cryst. Growth* **175**, 89 (1997).
- ⁶B. Heying, R. Averbeck, L. F. Chen, E. Haus, H. Riechert, and J. S. Speck, *J. Appl. Phys.* **88**, 1855 (2000).
- ⁷S. Y. Karpov, R. A. Talalaev, Y. N. Makarov, N. Grandjean, J. Massies, and B. Damilano, *Phys. Status Solidi A* **176**, 333 (1999).
- ⁸J. R. Jenny, J. E. Van Nostrand, and R. Kaspi, *Appl. Phys. Lett.* **72**, 85 (1998).
- ⁹E. Iliopoulos, K. F. Ludwig, T. D. Moustakas, P. Kominou, T. Karakostas, G. Nouet, and S. N. G. Chu, *Mater. Sci. Eng., B* **87**, 227 (2001).
- ¹⁰S. C. Choi, J. H. Kim, J. Y. Choi, K. J. Lee, K. Y. Lim, and G. M. Yang, *J. Appl. Phys.* **87**, 172 (2000).
- ¹¹D. L. Smith, *Thin-film Deposition* (McGraw-Hill, New York, 1995).
- ¹²T. D. Moustakas, in *Gallium Nitride (GaN) II*, Semiconductors and Semimetals Vol. 57, edited by J. I. Pankove and T. D. Moustakas (Academic, New York, 1998).
- ¹³J. E. Northrup, J. Neugebauer, R. M. Feenstra, and A. R. Smith, *Phys. Rev. B* **61**, 9932 (2000).
- ¹⁴W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1980).
- ¹⁵S. Kruece, S. Einfeldt, T. Böttcher, and D. Hommel, *Appl. Phys. Lett.* **79**, 3425 (2001), and references therein.
- ¹⁶O. Brandt, H. Yang, and K. H. Ploog, *Phys. Rev. B* **54**, 4432 (1996).
- ¹⁷P. Hacke, G. Feuillet, H. Okumura, and S. Yoshida, *Appl. Phys. Lett.* **69**, 2507 (1996).