ELSEVIER

Materials Science and Engineering B 136 (2007) 29–32

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Effect of growth conditions on the Al composition and quality of AlGaN film

G.S. Huang*, H.H. Yao, H.C. Kuo, S.C. Wang

Department of Photonics, Institute of Electro-Optical Engineering, National Chiao Tung University,
1001 TA Hsueh Road, Hsinchu, 300 Taiwan, ROC

Received 10 November 2004; received in revised form 26 January 2005; accepted 19 August 2006

Abstract

Effects of growth conditions on Al composition and quality of $Al_xGa_{1-x}N$ epilayer grown by low-pressure matelorganic vapor phase epitaxy (MOVPE) have been investigated. The dependences of Al composition, growth rate and quality on the NH_3 flow rate, TMAl flow rate and growth temperature were studied. The Al composition and quality of $Al_xGa_{1-x}N$ film depend not only on the TMAl flow rate, but also on the NH_3 flow rate and on the growth temperature. The Al composition of $Al_xGa_{1-x}N$ film becomes saturated when the gas-phase composition TMAl/(TMAl + TMGa) increases to 0.4, while quality of $Al_xGa_{1-x}N$ film becomes much worse. The Al composition of $Al_xGa_{1-x}N$ film increases with increase in the NH_3 flow rate. The quality of $Al_xGa_{1-x}N$ epilayer is improved when the growth temperature increases. Possible Al incorporation mechanism is discussed.

Keywords: MOVPE; AlGaN; Al composition

1. Introduction

The group-III-nitride semiconductors consisting of AlN, GaN, InN and their alloys are recognized as very promising materials for many optoelectronic device applications such as blue-green and UV light-emitting diodes (LEDs), laser diodes (LDs), UV solar blind detectors, and high-temperature/high-power electronic devices [1–3]. AlGaN with the Al composition in the range of 0.1–0.3 is one of the key materials for the optoelectronic devices operating in the UV spectral range. At the same time there are well-known difficulties in growing such layers by MOVPE, associated with low efficiency of aluminum incorporation in AlGaN, caused by parasitic gas-phase reaction. However, the parasitic reaction can be reduced by separating NH_3 and MO sources [4]. In addition, the growth conditions affect the Al incorporation and quality of $Al_xGa_{1-x}N$ epilayer. For these devices, one important thing is to obtain high-quality $Al_xGa_{1-x}N$ epilayer at an optimal growth conditions. However, the optimal growth conditions of $Al_xGa_{1-x}N$ have not been investigated in detail. The effects of growth conditions on Al composition, growth rate and crystal quality are needed to obtain high-quality $Al_xGa_{1-x}N$ thin films.

In this paper, the growth conditions for $Al_xGa_{1-x}N$ have been studied systematically by changing the growth parameters such as NH_3 flow rate, TMAl flow rate and growth temperature.

2. Experimental procedure

All the samples in this work were grown in a low-pressure vertical EMCORE D75 reactor with a gas foil rotation of the susceptor. The reagents were pure ammonia, trimethylgallium (TMGa) and trimethylaluminum (TMAl). Hydrogen and nitrogen purified by purifier were used as the carrier gas. The reactor pressure and rotating speed were 100 Torr and 900 rpm, respectively. C-plane sapphire epi-ready substrates were used for all the growth.

The group III and V precursors were separated in the manifold and mixed before they entered the reactor. Prior to material growth, the sapphire substrate was annealed to remove any residual impurities on the surface in H_2 ambient at 1100 °C for 5 min. For all samples, a nominal 30 nm thick GaN nucleation layer was deposited at 500 °C. Then before growing a 0.4 μm thick $Al_xGa_{1-x}N$ film, a 2 μm thick GaN bulk layer was grown on the substrate. All the growth conditions of GaN bulk layer are same.

---

* Corresponding author. Tel.: +886 3571 2121x56327; fax: +886 3571 6631.
E-mail address: gshuang@mail.nctu.edu.tw (G.S. Huang).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.08.064

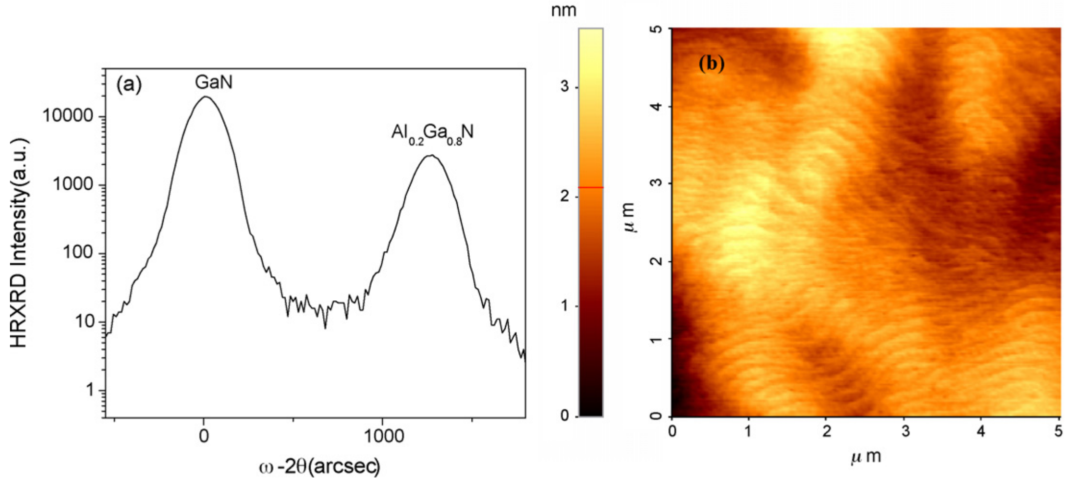

Fig. 1. (a) High-resolution X-ray diffraction rocking curve and (b) AFM image of the surface of $Al_{0.2}Ga_{0.8}N$ film with GaN buffer grown on sapphire.

The first group of samples was grown by varying the NH_3 flow rate from 0.3 to 1.2 slm with other parameters kept constant. The second group of samples was grown by varying the TMAl flow rate from 3 to 10 sccm with other parameters kept constant. The growth temperature was at 1110 °C for the first and second group of samples. The third group of samples was grown at different growth temperatures with other parameters kept constant. The growth process was in situ monitored by using filmetrics F-series thin-film measurement system. The composition and crystal quality of $Al_xGa_{1-x}N$ films on GaN were measured by using a Bede Scientific D1 double-rystal X-ray diffraction. The surface morphology was observed by atomic force microscope (AFM).

3. Results and discussion

Fig. 1(a) shows the high-resolution X-ray diffraction rocking curve (0 0 0 4) of AlGaN epilayer grown on the GaN buffer/sapphire substrate. The ratio of TMAl/(TMGa + TMAl) is 0.21. The Al composition is calculated to be 0.2. The NH_3 flow rate is 0.6 slm. The full width of high maximum (FWHM) of AlGaN and GaN are 164 and 157 arcsec, respectively. Fig. 1(b) shows an AFM image of the same $Al_{0.2}Ga_{0.8}N$ film. We clearly observe steps and terraces. The roughness average measured by AFM is less than 1 nm over a 5 μm × 5 μm surface area, which is comparable to that of high-quality GaN layers.

3.1. Dependence of Al incorporation and quality on the NH_3 flow rate

Fig. 2 shows dependence of Al composition in the solid on the NH_3 flow rate with all other parameters kept constants. Al composition in the solid increases with the NH_3 flow rate. The reactor pressure was 100 Torr with a total H_2 and N_2 flow of 4.3 slm. The TMGa and TMAl flow rates are fixed at 16.40 and 4.34 μmol/min, respectively. The ratio of TMAl/(TMGa + TMAl) is 0.21. The parasitic reaction between NH_3 and fixed TMAl is very weak because the lower metalorganic source flow rate of group III and lower pressure [4]. However, the Al incorporation in the solid increases with the NH_3 flow rate at our case. Even at lower NH_3 flow rate, the Al composition is solid kept at 0.2. In this experiment, the LT-buffer layer deposited under a high V/III (∼14,000) had N-face polarity [5]. For the high V/III growth conditions, there are a large number of nitrogen species at surface to pin the aluminum species in place thereby increasing the Al incorporation of $Al_xGa_{1-x}N$. It is different from the Al incorporation of $Al_xGa_{1-x}N$ grown on the GaN buffer/sapphire substrate, which shows decreasing Al composition in the solid because of the parasitic reaction [6]. Consider the case of a low V/III conditions, there are fewer nitrogen species at the surface to pin the Al species and Ga species. The Al incorporation is nearly same as the Ga incorporation, so the Al composition in solid remains at 0.2 which is nearly same as the ratio of TMAl/III. Fig. 2 also shows the growth rates of $Al_xGa_{1-x}N$ epilayers grown with increasing the NH_3 flow rate. Because the TMGa and TMAl concentrations in gas phase decrease when the NH_3 flow rate increases, the growth rates of $Al_xGa_{1-x}N$ epilayers decrease.

Structure defects such as strain, bending and dislocations can all contribute to the measured width of a rocking curve [7]. In

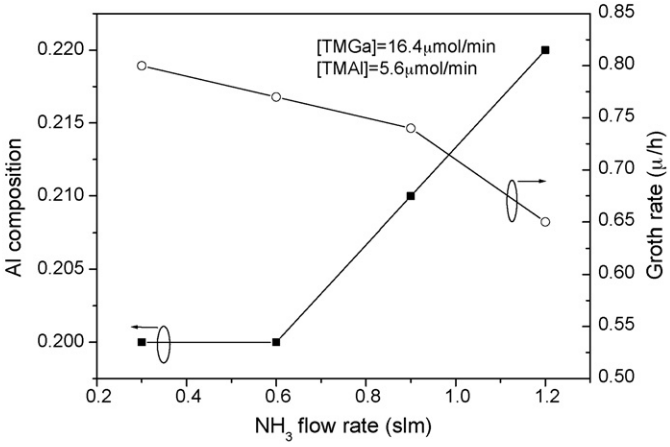

Fig. 2. Dependences of Al composition and growth rate on NH_3 flow rate with other parameters kept constant.

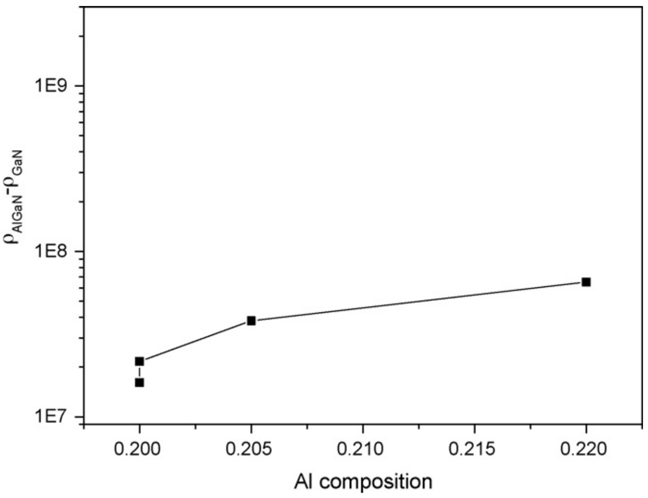

Fig. 3. The difference of dislocation density of AlGaN and underlying GaN on Al composition by changing the NH_3 flow rate with other parameters kept constant.

a first approximation the different contribution on the FWHM is assumed to be Gaussian shapes, so that the measured FWHM can be described as [8]:

$$W_{\mathrm{AlGaN}}^2 = w_{\mathrm{s}}^2 + w_{\mathrm{b}}^2 + w_{\mathrm{d}}^2 \qquad (1)$$

where w_{s}, w_{b} and w_{d} are contributions from strain, bending and dislocation, respectively. The residual strain is negligible, a result to be expected for layers exceeding the critical thickness, and no evidence of characteristic bending patterns was found [7,9]. Therefore, we assume that the dominant contribution to the width of the rocking curves observed here is due to lattice distortion caused by dislocation. The density of dislocations can then be calculated from the FWHM by using the formula [10] $\rho_{\mathrm{AlGaN}} = W_{\mathrm{AlGaN}}^2/4.35b^2$, where W_{AlGaN} is the FWHM and b is burgers vector which, for the $Al_xGa_{1-x}N$ alloy, is expected to be $a\sqrt{3}/2$ where a is the in-plane lattice parameter [11]. The dislocation densities of $Al_xGa_{1-x}N$ epilayer and underlying GaN can be calculated from their FWHMs, respectively. Fig. 3 shows the dependence of difference of dislocation density of $Al_xGa_{1-x}N$ epilayer and underlying GaN on Al composition by varying the NH_3 flow rate. As Al composition in $Al_xGa_{1-x}N$ increases from 0.2 to 0.22, the dislocation density increases lightly and quality of $Al_xGa_{1-x}N$ epilayer becomes worse. However, the dislocation density increases as the Al composition is same with increase in NH_3 flow rate from 0.3 to 0.6 slm, which may result from the desorption of III species. It agrees with that the growth rate also decreases with increasing NH_3 flow rate shown in Fig. 2.

3.2. Dependence of Al incorporation and quality on the TMAl flow rate

Because the Al solid composition of the film is nearly same as the ratio of TMAl to group III sources at NH_3 flow rate of 0.6 slm, we chose these growth conditions and changed the TMAl flow rate to check the dependence of Al incorporation on the TMAl flow rate. Fig. 4 shows that the Al solid compositions increase with increase in TMAl flow rate. The Al solid composition of 15.5% is more than the Al gas composition of 13.6%. This indicates that the Al incorporation is larger than Ga incorporation at lower TMAl flow rate. Then the Al solid composition of 20% is nearly same as the Al gas composition of 21%. Finally, the Al solid composition becomes saturated when the Al gas composition is 40%. This implies that the nitrogen species as the absorption centers of Al atoms are limited when the NH_3 and TMGa flow rates are fixed. If the high Al solid composition is achieved, the NH_3 flow rate must be increased. Fig. 4 also shows the dependence of growth rate on TMAl flow rate. Al species would depress Ga diffusion, so the grow rate of $Al_xGa_{1-x}N$ epilayer decreases.

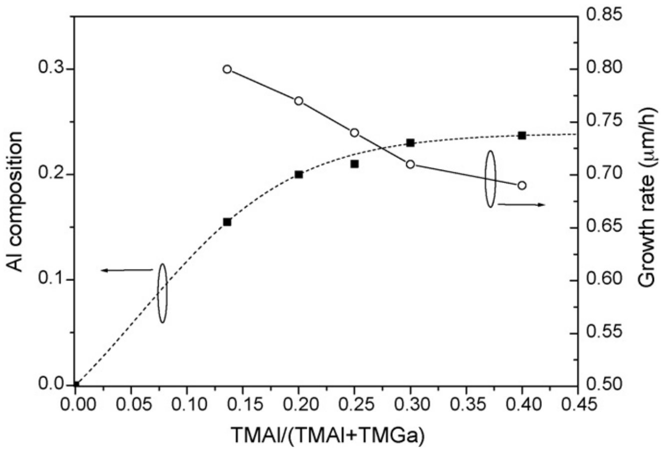

Fig. 4. The Al composition in the solid and growth rate vs. the TMAl source flow composition in a group III gas mixture.

Fig. 5 shows the dependence of the dislocation density of $Al_xGa_{1-x}N$ epilayer on the TMAl flow rate. When the Al solid composition increases from 0.155 to 0.21, the quality of $Al_xGa_{1-x}N$ becomes worse lightly. When the Al solid composition increases with increasing TMAl flow rate further, the quality becomes worse rapidly. The excess TMAl flow will increase the dislocation density of $Al_xGa_{1-x}N$ epilayer. The quality of $Al_xGa_{1-x}N$ becomes worse lightly with increase in both TMAl

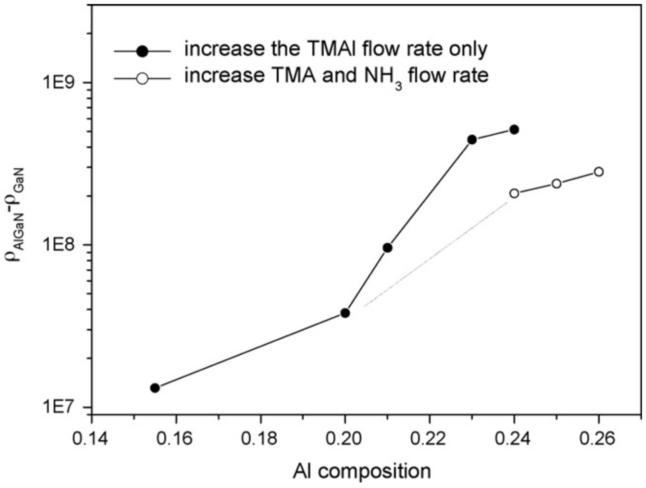

Fig. 5. The differences of dislocation density of AlGaN and underlying GaN on Al solid composition with increasing TMAl flow rate only or both TMAl and NH_3 flow rate, respectively.

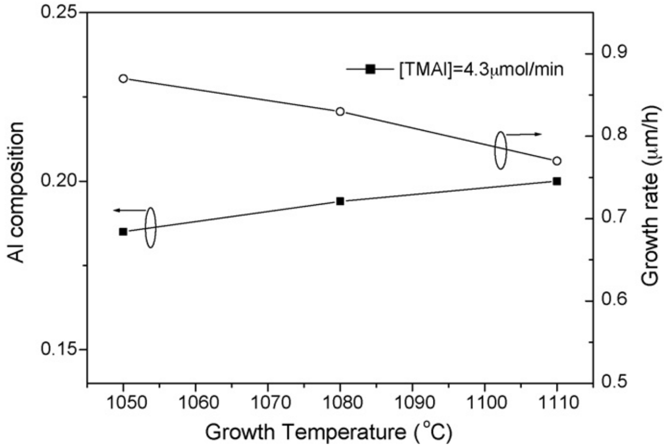

Fig. 6. Dependences of Al composition and growth rate of $Al_xGa_{1-x}N$ epilayer on the growth temperature with other conditions kept constant.

and NH_3 flow rate as shown in Fig. 5. The excess Al species would depress diffusion of the Ga species but the Ga species is dominant III species. Dislocations increase only with the increase of TMAl flow rate. However, the III species were diluted by increasing both TMAl and NH_3 flow rate. The depression of diffusion of the Ga species decreases, so the dislocations also decrease. AFM image also shows that the surface of the sample is improved by increasing both TMAl and NH_3 flow rate.

3.3. The influence of growth temperature at same source flow rates

Fig. 6 shows dependence of the Al solid composition on the growth temperature at same source flow rate. The Al solid composition increases with increasing the growth temperature, which shows that the thermal convection of TMAl is higher than that of TMGa during the growth of $Al_xGa_{1-x}N$ epilayers at certain growth conditions [12]. Meanwhile, Fig. 6 shows that growth rate decreases with increasing growth temperature. The pyrolysis efficiency of NH_3 is low when the growth temperature is low. Thus the growth rate increases with decreasing effective V/III ratio discussed in Section 3.1. Fig. 7 shows the difference of dislocation density between $Al_xGa_{1-x}N$ epilayers and GaN on Al solid composition with increasing growth temperature. The quality of $Al_xGa_{1-x}N$ increases with increasing growth temperature.

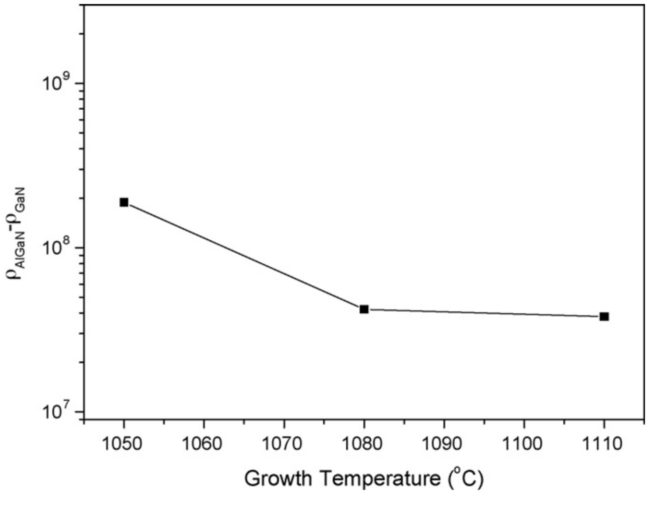

Fig. 7. The difference of dislocation density between $Al_xGa_{1-x}N$ epilayer and GaN on Al solid composition with increasing temperature.

4. Conclusions

Al composition and quality of $Al_xGa_{1-x}N$ epilayers grown by low-pressure MOVPE were studied. The dependences of Al composition, growth rate and quality of $Al_xGa_{1-x}N$ epilayers on the NH_3 flow rate, TMAl flow rate and growth temperature were investigated in detail. The Al solid composition increases with the NH_3 flow rate meanwhile the growth rate and quality of $Al_xGa_{1-x}N$ epilayers decreases. The Al composition in the solid increases with the TMAl flow rate and then becomes saturated when the TMAl flow rate reached at 40%. The growth rate decreases with increasing the TMAl flow rate. The quality of $Al_xGa_{1-x}N$ becomes worse lightly when the Al solid composition increases. Then it becomes worse rapidly when the Al composition becomes saturated. The Al composition also increases with increasing the growth temperature but the growth rate of $Al_xGa_{1-x}N$ epilayer decreases. The quality of $Al_xGa_{1-x}N$ epilayers increases with increasing the growth temperature.

Acknowledgements

One of authors (G.S. Huang) thanks Mr. Shyh-Horng Shore of Centre for Nano Science of Technology of National Chiao Tung University for XRD measurements. This work was supported in part by the National Science Council of Republic of China (ROC) in Taiwan under contract No. NSC93-2120-M-009-006 and by the Academic Excellence Program of the ROC Ministry of Education under the contract No. NSC93-2752-E-009-008-PAE.

References

[1] F. Omnes, N. Marenco, S. Haffouz, H. Lahreche, P. de Mierry, B. Beaumont, P. Hageman, E. Monroy, F. Calle, E. Munoz, Mater. Sci. Eng. B59 (1999) 401.
[2] J. Han, M.H. Crawford, R.J. Shul, J.J. Figiel, M. Banas, L. Zhang, Y.K. Song, H. Zhou, A.V. Nurmikko, Appl. Phys. Lett. 73 (1998) 1688.
[3] T. Someya, Y. Arakawa, Appl. Phys. Lett. 73 (1998) 3653.
[4] I.S. Seo, S.J. Lee, S.H. Jang, J.M. Yeon, J.Y. Leem, Y.J. Park, C.R. Lee, J. Crystal Growth 241 (2002) 297.
[5] M. Sumiya, N. Ogusu, Y. Yotsuda, M. Itoh, S. Fuke, T. Nakamura, S. Mochizuki, T. Sano, S. Kamiyama, H. Amano, I. Akasaki, J. Appl. Phys. 93 (2000) 1311.
[6] S.C. Choi, J.H. Kim, J.Y. Choi, K.J. Lee, K.Y. Lim, G.M. Yang, J. Appl. Phys. 87 (2000) 172.
[7] S.B. Qadri, E.F. Skelton, A.W. Webb, J. Kennedy, Appl. Phys. Lett. 46 (1985) 257.
[8] M.J. Hordon, B.L. Averback, Acta. Metall. 9 (1961) 237.
[9] C.L. Kuo, P.E. Vanier, J.C. Bilello, J. Appl. Phys. 55 (1984) 375.
[10] P. Gay, P.B. Hirsch, A. Kelly, Acta Mater. 1 (1953) 315.
[11] J.-M. Bethoux, P. Vennegues, F. Natali, E. Feltin, O. Tottereau, G. Nataf, P. De Mierry, F. Semond, J. Appl. Phys. 94 (2003) 6499.
[12] C.R. Lee, J. Crystal Growth 220 (2000) 62.