第20卷第11期 半 导 体 学 报 Vol. 20, No. 11
1999年11月 CHINESE JOURNAL OF SEMICONDUCTORS Nov., 1999

Quasi-Thermodynamic Model for MOVPE of AlGaN*

Lu Dacheng(陆大成)[1], Duan Shukun(段树坤)[2]

(1 Laboratory of Semiconductor Materials of Sciences, Institute of Semiconductors, The Chinese Academy of Sciences, Beijing 100083)

(2 National Integrated Optoelectronic Laboratory, Institute of Semiconductors, The Chinese Academy of Sciences, Beijing 100083)

Abstract A quasi-thermodynamic model of MOVPE growth of $Al_xGa_{1-x}N$ alloy using TMGa, TMAl and ammonia as sources has been proposed. In this improved model, number of moles is used to express the mass conservation constraints of element N, H, Al and Ga. The equilibrium partial pressures over $Al_xGa_{1-x}N$ have been calculated. The effect of varying growth conditions (growth temperature, reactor pressure, input V/III ratio, hydrogen fraction in the carrier gas and the decomposed fraction of ammonia) on the distribution coefficient of Al has been calculated. In the case of $Al_xGa_{1-x}N$, preferential incorporation of Al is predicted. The calculated relationship between input vapor and deposited solid composition has been compared with data in the literature. A good agreement between the calculated and the experimental composition shows that our improved model is suitable for applying to the $Al_xGa_{1-x}N$ alloy grown by MOVPE.

PACC: 4460, 6855

1 Introduction

Thermodynamic analysis for the growth process always plays an important role in better understanding of any crystal growth technologies, including MOVPE. Although MOVPE is an open flow process, a vapor-solid equilibrium can be established at the growing interface when growth temperature is high enough. Thermodynamic analysis of many III-V and II-VI alloys has been developed[1~11]. These models provide us with useful information on the control of alloy composition, the phase diagram of MOVPE and doping processes. Although the growth temperature for the MOVPE of III-nitrides is higher than

* This work was supported by Jointly High Technology Research Project of the State Science and Technology Commission of China and Hewlett-Packard Company and by the National Natural Science Foundation of P. R. CHINA under contract No. 69789601.

Lu Dacheng(陆大成) male, was born in 1937, Professor. His research interests are in the areas of semiconductor materials sciences.

Duan Shukun(段树坤) female, was born in 1938, Professor. Her research interests are in the areas of semiconductor materials and optoelectronic devices.

Received 24 May 1999, revised manuscript received 12 July 1999

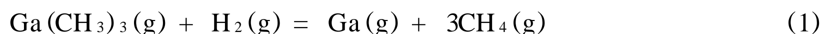
that of common III-V and II-VI semiconductors, a normal thermodynamic analysis may lead to wrong conclusions which cannot explain experimental results, if the slow decomposition rate of NH_3 and the inert behaviour of N_2 are neglected. In our previous paper a new quasi-thermodynamic model has been proposed to calculate the phase diagram for the MOVPE growth of GaN [8]. In that model, rather calculating the equilibrium decomposition pressure of ammonia, we introduced a fraction of ammonia decomposition (η) instead. The reaction of $2Ga+N_2=2GaN$ was also been neglected. To our knowledge until now few thermodynamic analysis of MOVPE growth of $Al_xGa_{1-x}N$ has been reported, although only one vapor-solid distribution curve has been showed in reference[9]. In this paper we have developed a new model to analyze the MOVPE growth of $Al_xGa_{1-x}N$ in detail, which exists in almost all optoelectronic and electronic GaN-based devices. It is very important to establish boundary conditions to control alloy $Al_xGa_{1-x}N$ composition, such as growth temperature, reactor pressure, hydrogen fraction of a mixture carrier gas, decomposition fraction of ammonia and V/III ratios, using the quasi-thermodynamic growth model.

2 Model

To analyse $Al_xGa_{1-x}N$, the following assumptions are used.

1. All gaseous species is ideal.

2. TMGa and TMAl are decomposed irreversibly near the vapor-solid interface above susceptor at usual growth temperature of $Al_xGa_{1-x}N$. Thus, we have



$$Ga(CH_3)_3(g) + H_2(g) = Ga(g) + 3CH_4(g) \quad (1)$$

$$Al(CH_3)_3(g) + H_2(g) = Al(g) + 3CH_4(g) \quad (2)$$

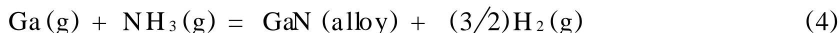
3. Based on thermodynamic calculations, NH_3 is almost fully decomposed to N_2 and H_2 when temperature is higher than 300℃. However without catalyst, the decomposition rate of ammonia is very low. In order to calculate the influence of decomposition of ammonia, we introduce a decomposed fraction of NH_3, η,

$$NH_3(g) = (1-\eta)NH_3(g) + (\eta/2)N_2(g) + (3\eta/2)H_2(g) \quad (3)$$

4. The reactions between N_2 and the group III elements have been ignored, since N_2 molecule has a strong inert behaviour.

Assumptions 3 and 4 make this model a quasi-equilibrium model.

5. The chemical reactions, taking place at the substrate surface to form $Al_xGa_{1-x}N$ alloy, are



$$Ga(g) + NH_3(g) = GaN(alloy) + (3/2)H_2(g) \quad (4)$$

$$Al(g) + NH_3(g) = AlN(alloy) + (3/2)H_2(g) \quad (5)$$

where GaN (alloy) and AlN (alloy) stand for the binary compounds in the $Al_xGa_{1-x}N$ alloy, respectively. A thermodynamic equilibrium of the reactions has been established at the vapor-solid interface of the substrate.

The following species are chosen as the necessary vapor species in analysing the growth of $Al_xGa_{1-x}N$: Al, Ga, NH_3, H_2, CH_4, N_2 and inert gas.

The equations of mass action for reaction (4) and (5) are as follows:

$$\alpha_{GaN} P_{H_2}^{1/2} / (P_{Ga} P_{NH_3} P_{tot}^{1/2}) = K_1 \quad (6)$$

$$\alpha_{AlN} P_{H_2}^{1/2} / (P_{Al} P_{NH_3} P_{tot}^{1/2}) = K_2 \quad (7)$$

where P_i is the equilibrium partial pressure of species i, P_{tot} is the total pressure, and K_i is the equilibrium constant of the reaction i[10]. α_{GaN} and α_{AlN} are the activities of the solid GaN and AlN in the $Al_xGa_{1-x}N$ alloy and are determined from the regular solution model as follows:

$$\alpha_{GaN} = (1 - x)\exp[x^2 \Omega / RT] \quad (8)$$

$$\alpha_{AlN} = x\exp[(1 - x^2)\Omega / RT] \quad (9)$$

where Ω is the interaction parameter of $Al_xGa_{1-x}N$ and is taken as 672cal/mol[13], and x is the mole fraction of Al in $Al_xGa_{1-x}N$ alloy.

Usually partial pressures are used to express the mass conservation constraints of the elements[1~5], since the change of the total number of molecules created by the reactions is very small. However, in the MOVPE growth of Ⅲ-nitrides, the partial pressure of NH_3 is very high and the change of the total number of molecules created by the reactions (mainly by the decomposition of ammonia) should not be neglected. In our improved model, instead of using partial pressures to describe the MOVPE growth of Ⅲ-nitrides[9,10], we use number of moles to express the mass conservation constraints of element N, H, Al and Ga:

$$n_{NH_3}^0 + n_{N_2}^0 = n_{GaN}^{alloy} + n_{AlN}^{alloy} + n_{NH_3} + 2n_{N_2} \quad (10)$$

where n_i^0 is input number of moles of species i, n_{GaN}^{alloy} and n_{AlN}^{alloy} are number of moles of GaN and AlN in the alloy, respectively.

$$2n_{H_2}^0 + 3n_{NH_3}^0 = 3n_{NH_3} + 2n_{H_2} + 3n_{RH} \quad (11)$$

$$n_{TMAl}^0 = n_{AlN}^{alloy} + n_{Al} \quad (12)$$

$$n_{TMGa}^0 = n_{GaN}^{alloy} + n_{Ga} \quad (13)$$

where n_{Al}, n_{Ga}, n_{RH} and n_{NH_3} are number of moles of aluminium, gallium, methane and ammonia in the gas phase, respectively.

The partial pressure of species i can be obtained by:

$$P_i = n_i (P_{tot} / n_{tot}) \quad (14)$$

where n_{tot} is the total number of moles in the gas phase,

$$n_{tot} = n_{NH_3} + n_{N_2} + n_{H_2} + n_{Ga} + n_{Al} + n_{CH_4} + n_{IG} \quad (15)$$

where n_{IG} is the number of modes of inert gas.

The total pressure in the reactor is expressed as follows:

$$P_{tot} = P_{NH_3} + P_{N_2} + P_{H_2} + P_{Al} + P_{Ga} + P_{RH} + P_{IG} \quad (16)$$

where P_{IG} is the partial pressure of inert gas, $P_{RH} = 3(n_{TMAl} + n_{TMGa})P_{tot}$.

In order to describe the effect of hydrogen in carrier gaseous composition, a parameter f is introduced:

$$f = n^0_{H_2} / (n^0_{H2} + n^0_{IG}) \tag{17}$$

which is the mole fraction of H_2 relative to the inert gas in the carrier gas

The x value can be expressed as (on stoichiometry conservation constrains):

$$x = n^{alloy}_{Al} / (n^{alloy}_{Al} + n^{alloy}_{Ga}) \tag{18}$$

In addition, the input V/III ratio, R, has been introduced:

$$R = n^0_{NH_3} / (n^0_{TMAl} + n^0_{TMGa}) \tag{19}$$

By solving eqs (6)~(19), the equilibrium partial pressures in the gas phase and the distribution coefficient can be obtained for a given set of growth temperature, reactor pressure, R, f, x and n^0_i.

3 Results and discussions

Figure 1 shows that the calculated activities of AlN and GaN in $Al_xGa_{1-x}N$ deviate slightly from the ideal solution, because the lattice constant of AlN is close to that of GaN. Therefore, the $Al_xGa_{1-x}N$ alloy can form a solid solution over the entire composition. Furthermore, the deviation changes weakly with temperature.

Figure 2 shows the equilibrium partial pressure of gaseous species over $Al_xGa_{1-x}N$ alloys The equilibrium partial pressures of Ga and Al change with the solid composition.

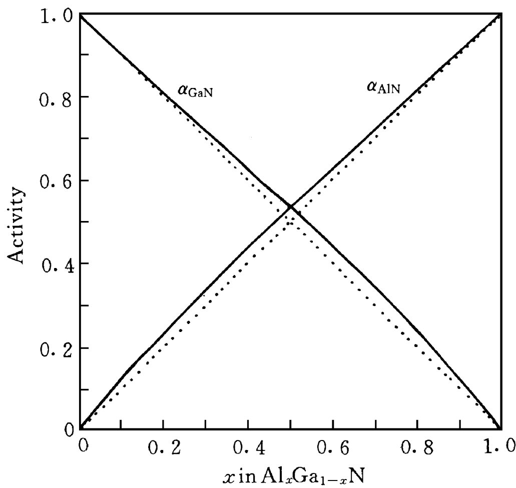


FIG. 1 The activities of AlN and GaN for 1000℃ as a function of the solid composition

The doted lines show those in the case of ideal solid solution. For the calculation, Ω= 672cal/mole.

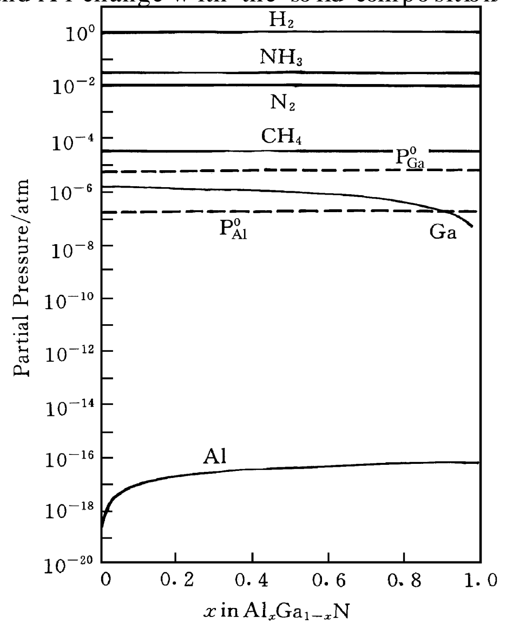


FIG. 2 The equilibrium partial pressures as a function of the solid composition, x, in $Al_xGa_{1-x}N$ alloy

The dotted lines show the vapor pressure of pure Al and Ga metal, P^0_{Al} and P^0_{Ga}; T_g= 1000℃, P_{III}= 1×10^{-5}atm. P_{tot}= 1atm, η= 0.4, f = 1 and R = 5000.

The dotted lines show the vapor pressure of pure metal Al and Ga, P^0_{Al} and P^0_{Ga}, respectively. It can be seen that the equilibrium partial pressure of Al is significantly lower than that of Ga. The equilibrium constant of reaction (6) is smaller than of reaction (7), which leads to the preferential Al incorporation into the $Al_xGa_{1-x}N$ alloy. It is worth while to point out that the equilibrium partial pressures of Ga or Al are smaller than the vapor pressure of Ga or Al. So that there is no Ga or Al droplets deposited on the substrate under most commonly used growth conditions.

For the growth of $Al_xGa_{1-x}N$ epilayer, control of the composition of the alloy is most important. Figure 3 shows the theoretical curves of $Al_xGa_{1-x}N$ solid composition at different growth temperatures as a function of the input mole ratio of [TMAl]/[TMAl+TMGa]. At higher temperature (> 1000℃), Al shows a stranger tendency of incorporating into the solid phase than that of Ga. This result is also confirmed by a much higher partial pressure of Ga than that of Al in the gaseous phase at elevated temperature shown in Fig.2. The equilibrium partial pressure of Ga decreases with the growth temperature. At 900℃ the partial pressure of Ga is low enough that the calculated solid composition shows an almost linear dependence on the input mole ratio of the group III metalorganic sources.

Figure 4～7 show the theoretical curves of alloy $Al_xGa_{1-x}N$ as a function of reactor pressure, input V/III ratio, decomposed fraction of ammonia and hydrogen fraction in the carrier gas. In all the cases, preferential Al incorporation is predicted. Figure 4 shows the theoretical curves of the $Al_xGa_{1-x}N$ as a function of input mole ratio of the group III metalorganic compounds. The reactor pressure varies from 0.1 to 2 atm. A linear function of

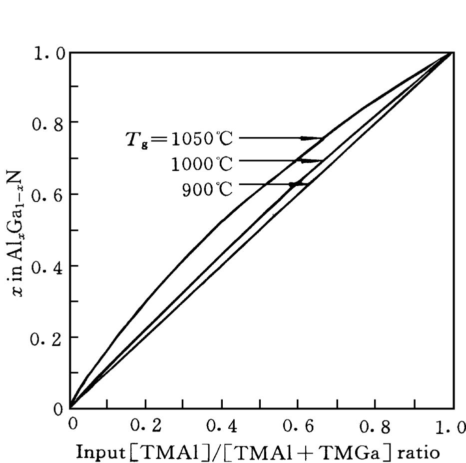


FIG.3 Calculating composition of $Al_xGa_{1-x}N$ layers as a function of the input metalorganic compound gas phase ratio [TMAl]/[TMAl+TMGa]

The growth temperature varies from 900 to 1050℃. For the calculation, P_{tot}= 1atm, P_{III}= 1×10^{-5}atm, R= 5000, f= 1 and η= 0.4.

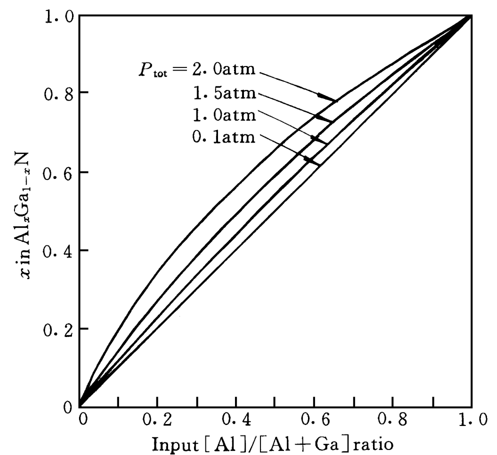


FIG.4 Theoretical curves of the $Al_xGa_{1-x}N$ solid composition as a function of the input mole ratio of the group III metalorganic compound

The reactor pressure varies from 0.1 to 2atm. For the calculation, T_g= 1000℃, P_{III}= 1×10^{-5}atm, R= 5000, f= 1 and η= 0.4.

solid composition with the input [TMAl]/[TMAl+ TMGa] ratio can be obtained when the reactor pressure is equal to or less than 0.1 atm.

Figure 5 shows the theoretical curves of $Al_xGa_{1-x}N$ as a function of input mole ratio of the group III metalorganic compounds. Input V/III ratio varies from 1000 to 10000. The input V/III ratio, as seen in Fig. 5, plays an important role for the deviation of the alloy composition. An essential linear function of distribution coefficient can be obtained when input V/III ratio is higher than 5000.

In Fig. 6, the solid composition deviates from the linear function if η increases, since we assume that III-nitrides are synthesised by the reactions between III elements and undecomposed ammonia. The influence of η on the $Al_xGa_{1-x}N$ system, however, is smaller as compared with the InGaN system[9].

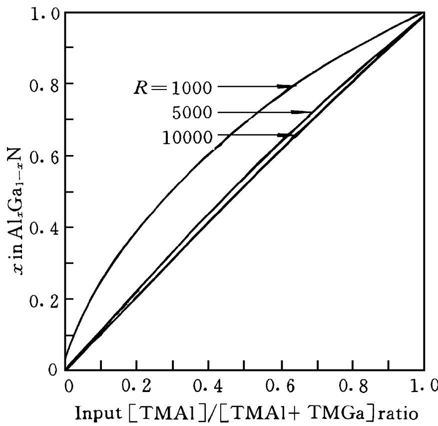


FIG. 5 Theoretical curves of $Al_xGa_{1-x}N$ as a function of input mole ratio of the group III metalorganic compounds. The input V/III ratio varies from 1000 to 10000
For the calculation, T_g= 1000°C, P_{tot}= 1atm, P_{III}= 1×10^{-5}atm, f = 1 and η= 0.4.

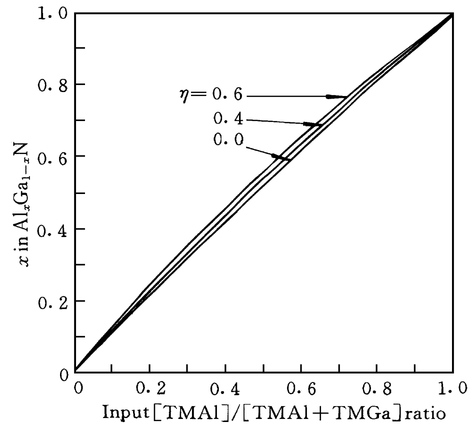


FIG. 6 The theoretical curves of the $Al_xGa_{1-x}N$ solid composition as a function of the input mole ratio of the group III metalorganic compounds for η= 0, 0.4, 0.6
For the calculation, T_g= 1000°C, P_{tot}= 1atm, P_{III}= 1×10^{-5}atm, R = 5000 and f = 1.

Figure 7 shows the theoretical curves of $Al_xGa_{1-x}N$ as a function of the input mole ratio of group III metalorganic compounds. The hydrogen fraction in a H_2-IG mixture carrier gas varies from 0.01 and 1. The predicted solid composition deviates slightly from the linear function if the hydrogen fraction in carrier gas increases. The increase of partial pressure of H_2 drives Eqs. (4) and (5) to the left and therefore less gallium will be incorporated into the solid phase. However, the use of inert gas or nitrogen as a carrier gas is not important for the growth of AlGaN alloy.

Figure 8 shows the comparison between the theoretically predicted and the experimental composition of $Al_xGa_{1-x}N$ alloys. Growth conditions used in the calculation were the same as those used by Clur *et al.*[14] (i.e. the growth temperature, reactor pressure and

V/III ratio were 980°C, 0.1atm., 10000 respectively). The input pressure of column III and the value of η were estimated to be 1×10^{6}atm and 0.5, respectively. The agreement between the calculated and experimental compositions is quite good. It indicates that the synthesis of $Al_xGa_{1-x}N$ in MOVPE reactor can be described mainly by the reactions of ammonia and group III elements and the composition of $Al_xGa_{1-x}N$ alloys grown by MOVPE can be easily controlled.

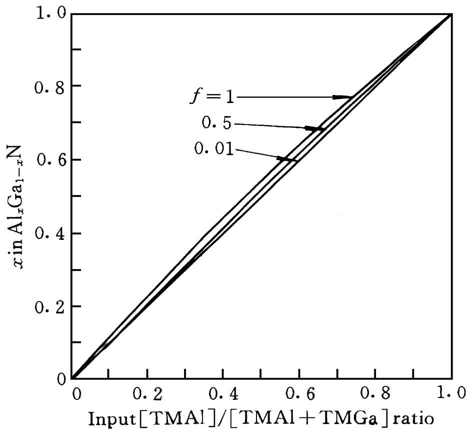


FIG. 7 The theoretical curves of the $Al_xGa_{1-x}N$ solid composition as a function of the input mole ratio of the group III metalorganic compounds

The the hydrogen fraction in carrier gas varies from 0.01 to 1. For the calculation, T_g= 1000°C, P_{tot}= 1atm, P_{III}= 1×10^{-5}atm, R= 5000 and η= 0.4.

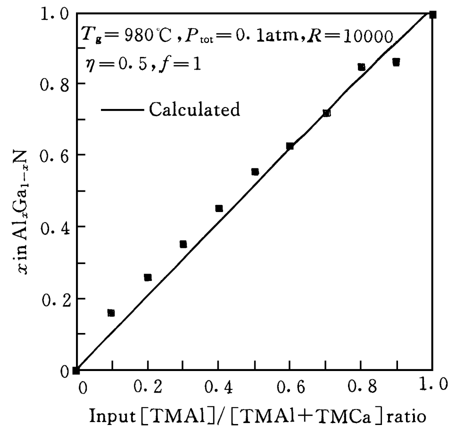


FIG. 8 The comparison between the theoretically predicated and the experimental composition of $Al_xGa_{1-x}N$ alloys

The calculated conditions were the same as those used by Clur *et al.* [15], i.e. the growth temperature, reactor pressure, V/III ratio were 980°C, 0.1atm., 10000, respectively. The input partial pressure of column III and the value of η were estimated to be 1×10^{6} atm and 0.5.

4 Conclusion

A quasi-thermodynamic model the MOVPE growth of $Al_xGa_{1-x}N$ alloy using TMGa, TMAl and ammonia as sources has been proposed. The equilibrium partial pressure above $Al_xGa_{1-x}N$ alloy surfaces has been calculated. The relationship between input vapor and deposited solid composition has been calculated with one adjustable parameter (η) for the $Al_xGa_{1-x}N$ alloy. A good agreement between the calculated and the experimental composition shows that our improved model is suitable to apply to the $Al_xGa_{1-x}N$ alloy grown by MOVPE and the solid composition grown by MOVPE is thermodynamic controlled by reactions (4) and (5). In the case of $Al_xGa_{1-x}N$, preferential incorporation of Al is predicted. However, a linear function of distribution coefficient can be achieved when using lower growth temperature, lower reactor pressure, higher input V/III ratio, lower hydrogen

pressure fraction in the carrier gas and reducing the decomposed fraction of ammonia.

References

[1] G. B. Stringfellow, Organometallic Vapor Epitaxy: Theory and Practice (Academic Press, San Diego, A, C 1989) ch. 3, p. 84.

[2] A. Koukitu and H. Seki, J. Cryst. Growth, 1986, **74**: 172.

[3] D. W. Kisker and A. G. Zawadzki, J. Cryst. Growth, 1988, **89**: 378.

[4] D-C Lu, X. Liu, D. Wang and L. Lin, J. Cryst. Growth, 1992, **124**: 383.

[5] D-C Lu, J. Cryst. Growth, 1993, **129**: 629.

[6] S-K Duan and D-C Lu, Proceedings of the international symposium on blue laser and light emitting diodes, Chiba, Japan, March 5-7, (1996) P. 332.

[7] S-K Duan and D-C Lu, J. Cryst. Growth, 1997, **170**: 514.

[8] S-K Duan and D-C Lu, Mat. Res. Soc. Symp. Proc., 1997, **468**: 81.

[9] A. Koukitu and H. Seki, Jpn. J. Appl. Phys., 1996, **35**: L1638.

[10] A. Koukitu, N. Takahashi, T. Taki and H. Seki, J. Cryst. Growth, 1997, **170**: 306.

[11] A. Koukitu and H. Seki, Proceedings of the second international conference on nitride semiconductors, Tokushima, Japan, 1997, p. 18.

[12] S. Nakamura, T. Mukai and M. S. Enoh, Appl. Phys. Lett., 1994, **64**: 1687.
S. Nakamura, M. Senoh, S-i Nagahama *et al.*, Jpn. J. Appl. Phys. Lett., 1996, **35**: L74.

[13] M. A. Khan, A. Bhattarai, J. N. Kuznia, D. T. Olsen, Appl. Phys. Lett., 1993, **63**: 1214.

[14] T. Matsuoka, Proceedings of the second international conference on nitride semiconductors, Tokushima, Japan, 1997, p. 20.

[15] S. Clur, O. Briot, J. L. Rouviere *et al.*, Mat. Res. Soc. Symp. Proc., 1997, **468**: 23.