Key Engineering Materials
ISSN: 1662-9795, Vol. 508, pp 193-198
doi:10.4028/www.scientific.net/KEM.508.193

Effect of Nitridation on Indium-composition of InGaN Films

Jung-Hun Choi[1,2,*], Suresh Kumar[2], Shi-Yang Ji[3], Shojiki Kanako[1,2], Takashi Hanada[1,2], Ryuji Katayama[1,2] and Takashi Matsuoka[1,2]

[1]Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

[2]Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

[3]Advanced Power Electronics Research Center, National Institute of Advenced Industrial Science and Technology, Ibaraki 305-8568, Japan

[*]j.choi@imr.tohoku.ac.jp

Keywords: InGaN; In-composition; Reciprocal space mapping; Nitridation.

Abstract. The present study aims to understand the relation between the nitridation and indium-composition of InGaN grown on sapphire substrate using the metalorganic vapor phase epitaxy through X-ray diffraction reciprocal space mapping measurements. In-composition of InGaN on nitrided sapphire substrate increased to 13% which is higher than the sample without nitridation with 7%. Also, flat surface was observed in the nitrided sample. Two times larger in-plane strain was induced at the nitired sample. InGaN grown on low-temperature GaN buffer, however, did not show clear effect of nitridation. The two investigated samples showed similar Indium composition, surface flatness, and in-plane strain with and without nitridation. Differences of indium incorporation and relaxation of in-plane strain were attributed to the effect of AlN formed by nitridation process.

Introduction

III-nitride based devices, such as laser diodes, light emitting diodes, high electron mobility transistors, and solar cells have been intensely studied [1]. Especially, The InGaN alloy system has attracted much research interests over the last few decades due to its wide applications in the optoelectronic devices [2]. However, the differences in lattice constants, thermal stability, and equilibrium vapor pressure between InN and GaN interrupt the growth of InGaN films [3]. In the case of the high indium (In)-composition of InGaN for green emission, a severe challenge still remains. One of the critical issues is the formation of non-uniform InGaN alloys, which originated from the occurrence of phase separation (PS). Under equilibrium condition, homogeneous InGaN alloys at high In concentration could not be grown because of very high equilibrium vapor pressure of nitrogen over InN, which is several orders of magnitude higher than that of AlN and GaN [3]. As a result, the non-equilibrium growth like metalorganic vapor phase epitaxy (MOVPE) was widely used for this alloy [4]. In fact, Matsuoka *et al.* found that the InGaN grown by MOVPE at high temperature of about 800 °C typically exhibited high crystalline quality, but the amount of InN in the solid was limited to low values because of the high volatility of N over InN [3]. To overcome this issue, growth conditions such as the reactor pressure and the source gas supplying ratio of ammonia as a nitrogen source to the sum of group-III source, have to be varied.

Currently, the investigation of N-polar GaN growth and its applications were actively studied because of their benefits of the reverse direction of the electric fields and/or the atomic arrangement compared with a usually obtained Ga-polar GaN [5]. In terms of indium-containing alloy materials such as InGaN, N-polarity has a benefit for capturing the indium atoms, because one nitrogen atom is bonded to three underlying gallium atoms. In our previous report, N-polar GaN films can be obtained by nitrided sapphire substrates [6]. In this paper, we report the growth of InGaN layer with and without the nitridation by MOVPE. The relationship between the nitidation of sapphire substrate and In-composition of InGaN were investigated by means of reciprocal space mappings (RSMs) measurements using high-resolution X-ray diffraction (XRD).

Experimental procedure

Epitaxial films were grown by MOVPE system with a horizontal type quartz reactor. Triethylgallium (TEG), trimethylindium (TMI) and ammonia (NH_3) were used as precursors for Ga, In and N, respectively. A *c*-plane (0001) sapphire substrates with 1^{o}-offcut toward the *a*-direction was used. In this work, four type of samples were fabricated, which were denoted as A1, A2, B1 and B2. After being loaded into the reactor, a sapphire substrate was cleaned at 1040^{o}C in hydrogen (H_2) atmosphere. Then the nitridation of the substrate was carried out at 1040^{o}C for 3 min in the atmosphere mixed with NH_3 and H_2. The InGaN film was grown for at 800^{o}C (A2). For the comparison, the growth of InGaN film without the nitridation process was performed (A1). Second set of InGaN films was grown on low-temperature (LT) GaN buffer layer with (B2) and without (B1) nitridation of sapphire substrate. This 20-nm-thick GaN buffer layer was annealed at 1010^{o}C at N_2 atmosphere prior to the InGaN growth. InGaN surface morphology was studied by differential interference optical microscope (OM, Olympus BX51). RSMs were measured by using the four-crystal X-ray diffractometer (XRD, Bruker-AXS D8 Discover). The RSMs of the asymmetric reflections around $(10\bar{1}5)$ were measured to investigate the In-composition and stain of the InGaN layers.

Results and discussion

The surface morphologies of InGaN films observed with OM are shown in Fig. 1. The figure 1 (a) and (b) shows surface morphology of the InGaN films with and without the nitridation of sapphire. The InGaN films without the nitridation (A1) have relatively small and many hexagonal hillocks on the surface as compared to the InGaN with nitridation (A2). The surface morphologies of InGaN (B1 and B2) on LT-GaN are shown in Fig. 1 (c) and (d). The smooth surface was observed in both samples. This is attributed to the effect of two-step growth process [7] that is normally used and well known to improve the crystalline quality. These results reveal that the introducing of nitridation process is realized to make a flat surface.

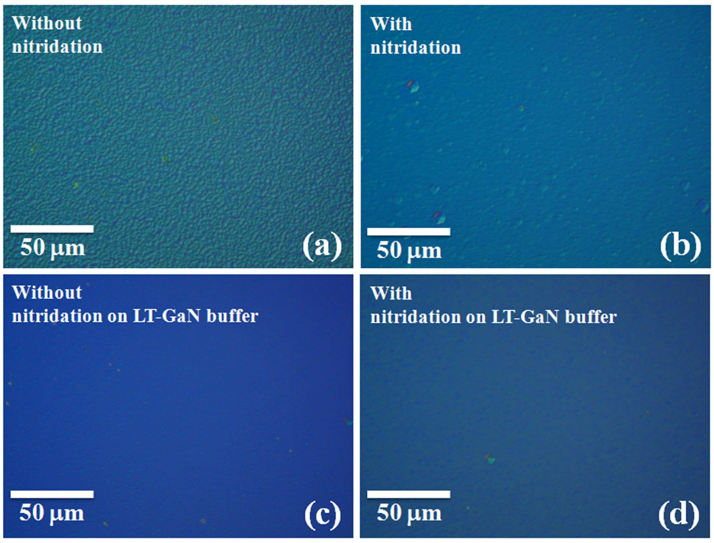

Fig. 1. Differential interference optical microscope image of samples A1(a), A2(b), B1(c), and B2(d).

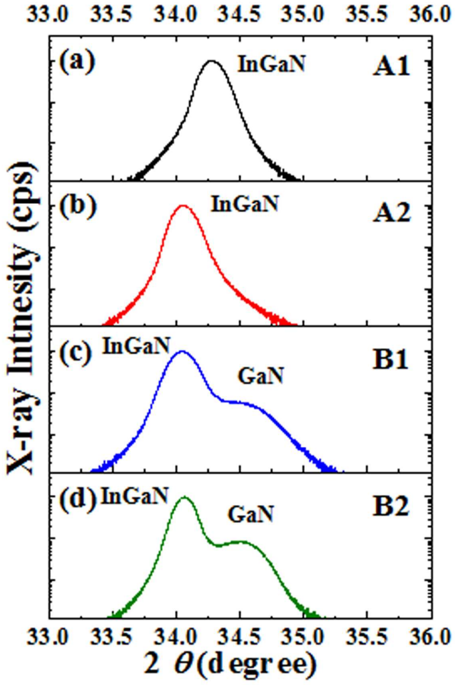

Fig. 2 Measured spectra in (0002) 2*θ*/*ω* of InGaN samples; InGaN without (a) and with (b) nitridation, InGaN on LT-GaN without (c) and with (d) nitridation. The set numbers are indicated at the right in each curve.

Figure 2 shows the 2*θ*/*ω* scan profiles of the (0002) symmetric X-ray diffraction from the InGaN samples. The X-ray spectra with full width at half maximum (FWHM) of InGaN is shown in Table 1. The sample A1 and A2 shows the clear InGaN peak without phase separation. The 2*θ* peak of sample A2 (34.04°) shifted toward much lower angle as compared to that of sample A1 (34.28°), which corresponds to the high In-incorporation of InGaN on nitrided sapphire. Also, the sample A1's FWHM of InGaN peak is almost same value as sample B even In-composition is high as shown in Table 1. On the other hands, the sample B1 and B2 (see Fig. (c-d)) shows the similar InGaN (0002) 2*θ* peak as 34.05° and 34.06°. This indicates that the nitridation of sapphire on LT-GaN is ineffective to increase In-incorporation of InGaN film. The GaN-buffer peak of the sample B1 and B2 was also seen as a subpeak at higher angle side in Fig. (c) and (d). It should be noted that these samples shows the difference in the shape. The InGaN and GaN peak of the sample B1 is relatively broader than those of the sample B2. Normally, the narrower peak is originated from uniformity of alloys without PS. The sample B2 shows much lower value of FWHM than the sample B1. In general, a use of LT-GaN buffer layer leads to a higher uniformity of crystal [7]. Our experimental set of nitridation also can be understood by the same effect. Evolution of AlN [8] layer due to nitridation is a kind of buffer layer for the LT-GaN layer growth.

We carried out RSMs around $(10\bar{1}5)$ asymmetric diffraction to investigate the in-plane strain and In-composition, and the result is shown in Fig.3. The method, i.e., determination of the In-composition of InGaN from strain measurement [9,10], was modified to estimate the in-plane strain (ε_a) and In-composition, as shown in the equations (1)-(6). If the InGaN is not strained, only one lattice parameter can be used to estimate the composition by using Vegard's law as shown in equation (1).

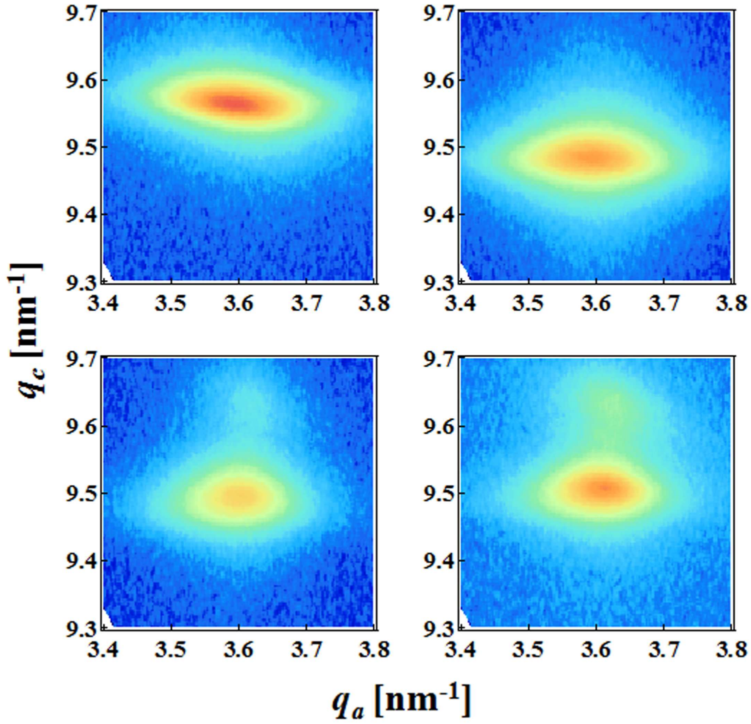

Fig. 3 Reciprocal space maps for InGaN$(10\bar{1}5)$ films; InGaN without (a) and with (b) nitridation, InGaN on LT-GaN without (c) and with (d) nitridation.

An initial estimation of the In-composition, x, can be given as follows

$$x = \frac{(c_o - c_{GaN})}{(c_{InN} - c_{GaN})}, \tag{1}$$

where c_0 is c-lattice constant measured by RMS, c_{GaN} and c_{InN} are c-axis lattice constant of GaN and InN, respectively [9]. The relationship between strains along each axis can be derived from Hooke's law as follows

$$\varepsilon_c = -2(\frac{C_{13}}{C_{33}})\varepsilon_a, \tag{2}$$

where ε_c, ε_a are the strain along c- and a-direction, C_{13} and C_{33} are elastic stiffness constants, respectively.

Since the a-axis lattice constant of the unstrained InGaN with In-composition x is $xa_{InN} + (1-x)a_{GaN}$, in-plane strain is represented as

$$\varepsilon_a = \frac{a_o}{\{xa_{InN} + (1-x)a_{GaN}\}} - 1, \tag{3}$$

where a_0 is a-lattice constant measured by RMS, a_{GaN} and a_{InN} are a-axis lattice constant of GaN and InN, respectively. The c-axis strain ε_c is estimated from ε_a with Poisson's ratio as

$$\varepsilon_c = -2\frac{\{xC_{13InN} + (1-x)C_{13GaN}\}}{\{xC_{33InN} + (1-x)C_{33GaN}\}}\varepsilon_a, \tag{4}$$

where C_{13InN},C_{13GaN}, C_{33InN} and C_{33GaN} are elastic stiffness constants of GaN and InN, respectively. The c-lattice constant c_x of the unstrained InGaN with In-composition x is obtained from c_o and ε_c as

$$c_x = \frac{c_o}{[1+\varepsilon_c]}. \tag{5}$$

Furthermore, since c_x must be consistent with the Vegard's law, improved value of x is obtained as

$$x_{improved} = \frac{(c_x - c_{GaN})}{(c_{InN} - c_{GaN})}. \tag{6}$$

The reference a and c lattice constants and the elastic constants of GaN and InN were obtained by ref [9]. Then, calculations using (3) to (6) are sequentially repeated, until $x_{improved}$ converges. The results of ε_a and x are shown in the Table 1. The indium-content and in-plane strain in InGaN grown without nitridation was estimated as 7.36% and -0.28% (compressive-negative strain in basal plane). On the contrary, InGaN on nitrided sapphire had 13.80% indium-content and -0.58% strain. If AlN layer is formed on sapphire by the nitridation, In-content can increase owing to the small lattice misfit on the nitrided surface. The lattice mismatch between InGaN and AlN is much smaller than that between InGaN and sapphire. If lattice mismatch is small, critical thickness of strain relaxation increases and strain relaxation rate at a certain thickness decreases. Consequently, despite the same growth condition between two samples, the higher compressive strain was appeared at sample A2.

Table 1. The in-plane strain, In-composition and FWHM of InGaN films.

Sample number	in-plane strain [%]	In-composition [%]	FWHM [arcsec]
A1	- 0.28	7.36	690
A2	- 0.58	13.80	705
B1	- 0.84	11.18	765
B2	- 0.93	9.67	645

Interestingly, larger in-plane strain of the second set (B1 and B2) is larger than that of the first set (A1 and A2). Also, there is no effect of nitridation for In-incorporation in the second set. Two samples show similar In-composition and strain values. Although the crystal quality of the InGaN film grown on LT-GaN is certainly improved by the nitridation of sapphire as shown in FWHM of X-ray $2\theta/\omega$ scan and InGaN $(10\bar{1}5)$ peak in RSM, the effect of AlN on the strain relaxation and the In composition might be not so large in this growth condition.

Conclusion

We investigated the nitridation effect for InGaN films using X-ray $2\theta/\omega$ scan and RSMs. Nitridation of a substrate enhanced the incorporation of indium in the InGaN film. Hexagonal hillocks were reduced and flat surface was obtained by introducing the nitridation. High in-plane strain was originated from formation of AlN films due to nitridation. In the case of InGaN grown on LT-GaN, nitridation had no effect on the In-composition and surface improvement. For the both experiments sets, crystal uniformity increased by applying the nitridation.

References

[1] T. Paskova, D. A. Hanser, and K. R. Evans, Proceedings of the IEEE, **98** (2010) 1324-1338.
[2] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64** (1994) 1687-1689.
[3] T. Matsuoka, N. Yoshimoto, T. Sasaki, and A. Katsui, J. Electron. Mater. **21**(1992) 157-163.
[4] I-hsiu Ho and G. B. Stringfellow, Appl. Phys. Lett. **69** (1996) 2701-2703.

[5] H. Masui, S. Keller, N. Fellows, N. A. Fichtenbaum, M. Furukawa, S. Nakamura, U. K. Mishra, and S. P. DenBaars, Jpn. J. Appl. Phys. **48** (2009) 071003.

[6] T. Matsuoka, Y. Kobayashi, H. Takahata, T. Mitate, S. Mizuno, A. Sasaki, M. Yoshimoto, T. Ohnishi, and M. Sumiya, Phys. Stat. Sol. (b) **243** (2006) 1446-1450.

[7] S. Nakamura, Jpn. J. Appl. Phys. **30** (1991) L1705-L1707.

[8] K. Uchida, A. Watanabe, F. Yano, M. Kouguchi, T. Tanaka, and S. Minagawa J. Appl. Phys. **79** (1996) 3487-3491.

[9] F.M. Morales, D. González, J.G. Lozano, R. García, S. Hauguth-Frank, V. Lebedev, V. Cimalla, and O. Ambacher, Acta Materialia **57** (2009) 5681-5692.

[10] M A Moram and M E Vickers, Rep. Prog. Phys. **72** (2009) 036502.