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Etching and optical deterioration of nitrogen-face of wurtzite InN in NH₃ ambient

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This paper reports the deterioration of nitrogen (N)-face of wurtzite InN in the NH₃ ambient near the growth temperature. Using an atmospheric-pressure MOVPE system, both In-polar and N-polar InN are grown by controlling the nitridation temperature of a sapphire substrate. The N-face has a much larger etching rate (40 nm/h) compared with that of the In-face (14 nm/h). From the PL measurement from the front surface and the rear surface through the sapphire substrate, it is shown that the N-face of both In- and N-polar films shows a marked intensity reduction and a large blue shift of PL spectrum. These facts show that the N-face of InN is very unstable and deteriorates in the NH₃ ambient. The deterioration becomes severer at a temperature higher than 550°C. Since such a PL shift is due to the Burstein-Moss effect, the result indicates that the high density of donor-type defects are preferentially introduced on the N-face of InN. Further investigations will be needed to clarify whether such instability of N-face in the NH₃ ambient is related to the poorer quality of MOVPE InN.

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1 Introduction Indium nitride (InN) is an important III-nitride semiconductor with many potential applications [1]. Compared with MBE-grown InN, those grown by MOVPE have been less studied. A carrier concentration in the order of 10^{17} cm^{-3} has been realized for MBE InN [2,3], while that for MOVPE InN has been still in the middle of 10^{18} cm^{-3} [4]. Therefore, it is highly desirable to clarify the causes for the higher carrier concentration in MOVPE InN. It has been reported that the nitrogen-face of InN can be easily deteriorated by atomic hydrogen [5]. In this context, we have to pay attention to the behavior of InN in ammonia (NH₃) ambient, because NH₃ is the most commonly-used source material of nitrogen in MOVPE growth of InN and hydrogen atoms can be produced through the decomposition of NH₃. In many cases for the MOVPE on a sapphire (0001) substrate, InN is grown with In-polarity, independently of the buffer layers used. The fact may be related to the presence of hydrogen in the growth ambient. This is because the nucleation and growth of N-polar InN grains would be suppressed if N-polar grain is unstable in the NH₃ ambient. In this paper, we have prepared In- and N-polar InN on a sapphire (0001) substrate and compared their behavior in NH₃ at a temperature near the growth temperature (600°C). It is found that N-face of InN has a much larger etching rate and shows severer opti-

cal degradation in the NH₃ ambient compared with the In-face of InN. The hydrogen supplied by the NH₃ decomposition may be responsible for these results. Although such instability of the N-face of InN seems to be related to the higher carrier concentration and the preferential In-polar film growth for MOVPE InN, further investigations will be needed.

2 Experimental Using an atmospheric-pressure MOVPE system with a horizontal reactor, both In- and N-polar InN films with a thickness about 0.5 μm are grown on a sapphire (0001) substrates. The polarity of the film is controlled by the nitridation conditions of the sapphire substrate and the use of GaN buffer layer [6]. After the growth, InN samples are annealed at 500-650°C for 2-6 h in the NH₃ flow (6 slm). Annealing effects of InN are examined with PL measurement from the front or back surface of a film [7] using a He-Cd laser (442 nm wavelength) as an excitation source. A shift of PL peak to a higher energy side is used as a measure of the electrical/optical deterioration. This is based on the following reasons. The fact that the PL peak energy as well as the absorption edge for InN are markedly shifted to a higher energy side with increasing carrier (electron) concentration in the film has been experimentally confirmed [8]. It has been also re-

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ported that structural defects in InN tend to become donors [9,10] due to the low conduction band minimum (CBM) of InN [9]. Therefore, defects introduced by the annealing in NH_3 are also expected to be donor-type defects and increase carrier concentration in the annealed films. Thus, PL peak shift will give us the information about the degree of the electrical/optical deterioration. The thickness of InN before and after the annealing is measured to evaluate etching rate of InN.

3 Results and discussion Figure 1 shows the surface morphologies (SEM photographs) of In- and N-polar InN films grown on a sapphire substrate. They show the totally different surface features each other. In-polar InN is obtained on the sapphire substrate nitrided at a relatively low temperature ($\sim 900^\circ\text{C}$), while InN film with N-polarity is obtained when the sapphire substrate is nitrided at a relatively high temperature (1000°C). No buffer is used in these cases. The growth of N-polar InN seems to be due to the formation of N-polar AlN on the sapphire substrate surface as a result of the high temperature nitridation. Using N- and In-polar InN films shown Fig. 1, the annealing in the NH_3 flow is made. Figure 2 shows the changes in InN film thickness after the annealing at 600°C . One can see that the N-face has a much higher etching rate (40 nm/h) compared with that of the In-face (14 nm/h). This result shows the chemical instability of the N-face. The reaction of H with N atom on the surface may be responsible for the etching. Figure 3 shows the PL spectra for In- and N-polar InN films after the annealing in the NH_3 flow at 600°C . The spectra are measured by exciting the films from the surface and detecting the emission from the surface. For both films, the reduction of intensity and the blue shift of PL spectrum are observed. One can see that they are enhanced with increasing annealing time. Compared with the In-polar film, the N-polar InN is found to have a marked intensity reduction and a larger peak shift. In order to check the behaviour of the film surface faced to the sapphire substrate, PL measurement is carried out from the back surface of a film through the sapphire substrate, as well as from the surface side. Figure 4 shows the schematic drawing of the PL measurement situation and the measured results. The PL peak energy measured from the front surface and the substrate interface side is plotted as a function of annealing time in the figure. In the case of In-polar films, the PL peak measured from the back surface through the sapphire substrate (case **B** in Fig. 4) is markedly shifted to a higher energy side with increasing annealing time, while the PL peak energy obtained from the front surface shows a small change (case **A**). For an N-polar InN, on the other hand, the PL peak measured from the front surface (case **C**) is largely shifted and that measured from the back surface (case **D**) is small. Thus, the N-face shows a marked blue shift in the both cases. Since such a PL shift is due to the Burstein-Moss effect, it can be concluded that the high density of donor-type defects are preferentially introduced on the N-face of InN.

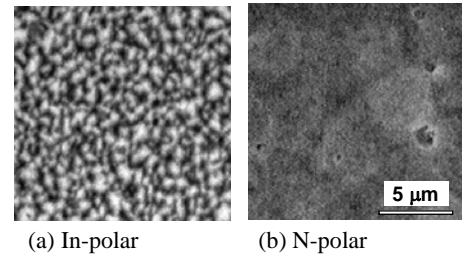


Fig. 1. Surface morphologies (SEM photographs) of In-polar and N-polar InN films

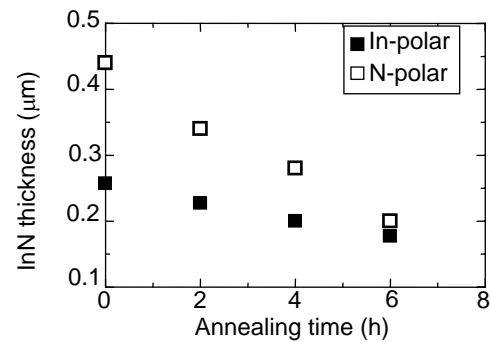


Fig. 2. Reduction of InN film thickness by the annealing at 600°C in the NH_3 flow.

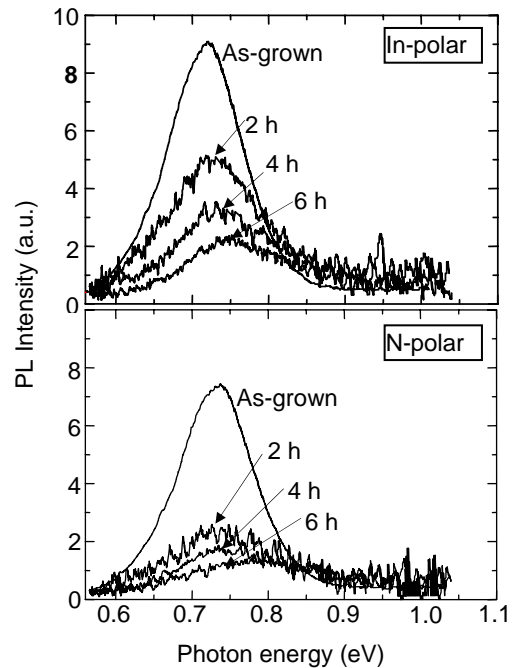


Fig. 3. PL spectra for In- and N-polar InN films after the annealing for different time.

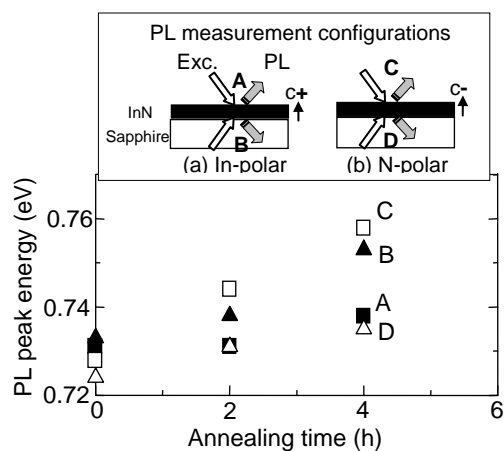


Fig. 4. PL peak energy as a function of annealing time for In-polar and N-polar InN measured from the front surface side or the sapphire substrate interface side.

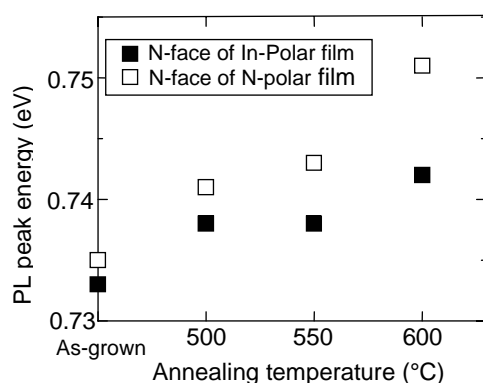


Fig. 5. PL peak energy for N-face InN as a function of annealing temperature.

Figure 5 shows the PL peak energy for N-face InN as a function of annealing temperature. One can see that the deterioration becomes severer at a temperature around 600°C. This is related to the enhanced thermal decomposition of NH_3 at a temperature higher than 550°C, as reported by Mesrine et al. [11]. It is noted that the N-face can be deteriorated even if it is faced to the sapphire substrate. This may be related to the relatively high residual carrier concentration for MOVPE InN. However, the situation is not so simple because the deterioration during the growth is not so severe compared with that during the annealing [7] and, furthermore, the residual carrier concentration is reduced with increasing NH_3/TMI molar ratio during the growth [4]. Further investigation will be needed to clarify these inconsistencies.

4 Conclusion Using an atmospheric-pressure

MOVPE system, both In-polar and N-polar InN are grown by controlling the nitridation temperature of the sapphire substrate. It is found that the N-face has a much higher etching rate (40 nm/h) compared with that of the In-face (14 nm/h). From the PL measurement from the front surface and the rear surface through the sapphire substrate, it is concluded that the N-face for both In- and N-polar films shows a marked intensity reduction and a large blue shift of PL spectrum compared with In-face. These facts show that the N-face of wurtzite InN is very unstable and deteriorates in the NH_3 ambient. The deterioration becomes severer at a temperature around 600°C. Since such a PL shift is due to the Burstein-Moss effect, it is concluded that the high density of donor-type defects are preferentially introduced on the N-face of InN. Although such instability of the N-face of InN seems to be related to the higher residual carrier concentration and the preferential In-polar film growth for MOVPE InN, further investigations will be needed to make them clear.

References

- [1] A. G. Bhuiyan, A. Hashimoto, and A. Yamamoto, *J. Appl. Phys.*, **94**, 2779 (2003).
- [2] H. Lu, W. J. Schaff, L. F. Eastman, J. Wu, W. Walukiewicz, D. C. Look, and R. J. Molnar, *Mater. Res. Soc. Symp. Proc.* **743**, L4.10 (2003).
- [3] C. S. Galliant, G. Koblmuller, J. S. Brown, S. Bernardis, J. S. Speck, G. D. Chern, E. D. Readinger, H. Shen, and M. Wraback, *WeG1-1, International Workshop on Nitride Semiconductors 2006*, Kyoto, Japan (2006).
- [4] A. Yamamoto, H. Miwa, Y. Shibata, and A. Hashimoto, *phys. stat. sol. (c)*, **3**, 1527 (2006).
- [5] Y. Hayakawa, D. Muto, H. Naoi, T. Araki, A. Suzuki, and Y. Nanishi, *Th-P140, 6th International Conference on Nitride Semiconductors*, Bremen, Germany (2005).
- [6] W.J. Wang, K. Sugita, Y. Nagai, Y. Houchin A. Hashimoto, and A. Yamamoto, *phys. stat. sol. (c)*, **4**, 2415 (2007).
- [7] H. Miwa, A. Hashimoto, and A. Yamamoto, *phys. stat. sol. (c)*, **3**, 1536 (2006).
- [8] A. Yamamoto, K. Sugita, H. Takatsuka, A. Hashimoto, V. Yu. Davydov, *J. Cryst. Growth*, **261**, 275 (2004).
- [9] J. Wu, W. Walukiewicz, S. X. Li, R. Armitage, J. C. Ho, E. R. Weber, E. E. Haller, Hai Lu, William J. Schaff, A. Barcz and R. Jakiela, *Appl. Phys. Lett.*, **84**, 2805 (2004).
- [10] X. Wang, S.B. Che, Y. Ishitani, and A. Yoshikawa, *Appl. Phys. Lett.*, **90**, 151901 (2007).
- [11] M. Mesrine, N. Grandjean, and J. Massies, *Appl. Phys. Lett.*, **72**, 350 (1998).