

CONTROL OF THE POLARITY AND SURFACE MORPHOLOGY OF GAN FILMS DEPOSITED ON C-PLANE SAPPHIRE

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Abstract

Control of the polarity of GaN films deposited by metalorganic chemical vapor deposition was achieved by substrate nitridation and subsequent annealing of a buffer layer. The surface morphology and optical properties of 1.2 μm GaN films were influenced by the different growth mode due to the polar direction. Coaxial impact collision ion scattering spectroscopy revealed that the polarity composition of a buffer layer on nitrided sapphire varied by annealing in a H_2 atmosphere. It was considered that the systematic variation of the surface morphology was caused by the polarity composition of the buffer layer.

Introduction

GaN, InGaN and AlGaN which have been successfully used in blue light emitting devices [1] have a wurtzite crystal structure. Epitaxial films of these materials grow along the polar c-axis direction and consequently have a polarity as illustrated in Fig.1. The importance of the polarity for understanding the fundamental mechanism of spontaneous and stimulated light emission from the GaN/InGaN/GaN quantum well structure has been recognized. Although the polarity of GaN has been intensively studied, not all of the results are consistent [2]. In order to obtain a common view about the polarity of GaN film, not only the identification of polarity but also the mechanism determining the polar growth direction must be studied.

Irrespective of such growth techniques as metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), GaN epitaxial films are typically deposited on c-plane sapphire with a buffer layer deposited at low temperature [3]. There are many switching steps during GaN growth. For example, sapphire substrates are cleaned in a H_2 atmosphere at high temperature, the substrate temperature is ramped up after depositing the buffer layer, and the gas flow ratio (N_2 , H_2 , NH_3) in each step is changed to obtain high quality GaN films. Furthermore, the substrate is occasionally nitrided [4][5]. Each step involves the chemical reactions, which make the polarity issue complicated.

The polarity structure should be determined at the initial stage of the growth, i.e., at the interface since the rest of the film growth can be considered as a kind of homoepitaxy. The insert of a buffer layer forms another interface and substrate nitridation moderates the surface state [6]. We have investigated the influence of a buffer layer and substrate nitridation on GaN film growth from the point of view of these interfaces [7]. As a result of this study, it was possible to control the polarity of GaN films on c-plane sapphire [8].

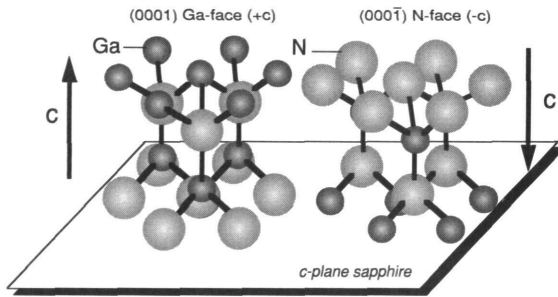


Fig.1 Schematic illustration of wurtzite GaN structure oriented along c-axis. Left side is (0001) Ga-face which is defined +c. Right side is (000 $\bar{1}$) N-face which is defined which is defined -c.

In this paper, GaN films with the different polarity were deposited under the same conditions except for the annealing time of the buffer layer. The systematic variation in the surface morphology will be presented. The influence of thickness and annealing time on the polarity of buffer layer was investigated in order to discuss the variation of surface morphology.

Experiment

GaN films with $1.2\mu\text{m}$ thickness were deposited on c-plane sapphire by a two-step atmospheric MOCVD method. Prior to deposition, the substrate was thermally cleaned in a H_2 gas flow at 1080°C for 10min. Substrate nitridation was carried out by heating at 1080°C in NH_3 for 5min. After deposition of a 160nm GaN buffer layer at 600°C , the buffer layer was annealed at 1040°C for up to 100min under a gaseous mixture of N_2 , H_2 and NH_3 . GaN films were deposited on the annealed buffer layer at 1040°C under the same conditions. The buffer layer as thick as 160nm was intentionally prepared for the purpose in this study. For comparison, high quality GaN films with 20nm buffer layer were also deposited on sapphire with and without nitridation. Identification of the polarity was carried out by coaxial impact collision ion scattering spectroscopy (CAICISS). The polarity of the GaN films was determined by comparison with CAICISS results for ZnO which not only has a wurtzite crystal structure but also lattice constants ($a=0.3250\text{nm}$, $c=0.5207\text{nm}$) close to those of GaN ($a=0.3189\text{nm}$, $c=0.5185\text{nm}$) [9].

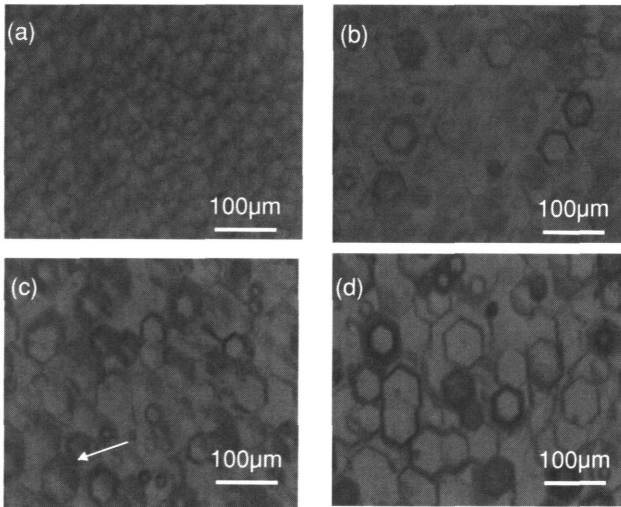


Fig.2 Surface morphology of GaN films deposited on the buffer layer whose polarity was controlled by the annealing time of (a) 30min, (b) 40min, (c) 60min and (d) 100min. GaN epilayers were deposited under the same conditions.

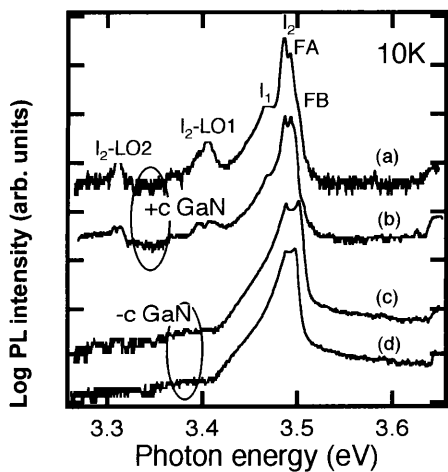


Fig. 3 PL spectra near band edge at 10K for +c and -c GaN films on (a) 20nm buffer layer, (b) 160nm buffer layer annealed for 10min. (c) GaN on 20nm buffer and (d) 160nm buffer layer annealed for 60min. The substrate was nitrided in (b)-(d).

Results and discussion

The surface morphology of GaN films on 160nm buffer layers annealed for 10min was featureless, i.e., smooth while those on buffer layers annealed for more than 30min were hexagonal facet as shown in Fig.2. The polarity of GaN films with smooth and hexagonal facet surface were determined Ga- (0001) (+c polarity) and N-face (0001) (-c polarity), respectively, which was consistent with our previous results [10]. The “house-shaped” hexagonal structures are observed to form hexagonal “columns” as indicated by the arrow in Fig. 2(c). The ratio of “house-shaped” structure with {1101} and (0001) planes to the hexagonal column with {1100} and (0001) will be discussed later. The size of the hexagonal facet could be systematically controlled up to 60 μ m by variation of the annealing time of the buffer layer. It is important that the polarity and surface morphology of GaN films deposited even under the same conditions varied systematically with the annealing conditions of buffer layer.

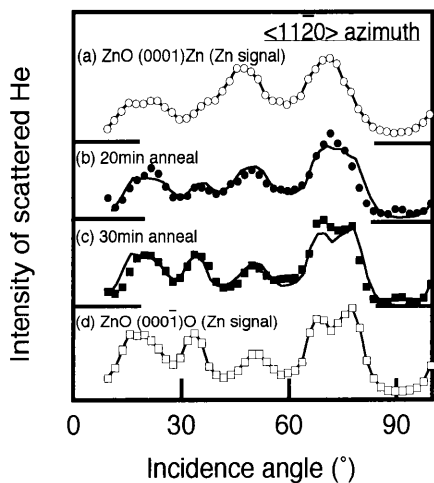


Fig. 4 CAICISS spectra of 160nm buffer layers on a nitrided sapphire for (b) 20min and (c) 30min. The lines in (b) and (c) are calculated line from the weight mean of the spectra of (a) +c and (d) -c ZnO (See the text).

The photoluminescence (PL) spectra for +c and -c GaN films are shown in Fig. 3. As can be clearly seen, the PL spectra varies significantly with the polarity. Although the peaks of +c GaN films can be identified, those of -c GaN films can not. PL properties should originate from the bulk GaN, or in other words, are never influenced by the polarity. Since the crystal structures of -c GaN are comparable to those of +c GaN films (See Fig.6), the difference in PL must be due to the different growth mode of the polar direction. It is possible that the amount of impurities depends on the polarity. Theoretical and experimental research about the incorporation of impurities is presently under way.

In order to consider the variations in surface morphology, the interfaces at the substrate or buffer layers were investigated. The nitrided substrate was investigated by reflection of high electron energy diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS). A spotty RHEED pattern, which could be assigned as wurtzite AlN (1120), was observed in the azimuth [1100] of sapphire. The binding energy of nitrogen from the nitrided sapphire was observed at 403eV between nitrogen of AlN (397eV) [11] and nitrogen (408eV). The nitrogen was incorporated into the substrate about one unit (1.2nm) from the surface. CAICISS analysis by Shimizu et.al. revealed that AlN formed by the nitridation had -c polarity (N-face) terminated with Al atoms [12]. Figure 4 (b) and 4(c) shows the CAICISS spectra for the buffer layer annealed for 20 and 30min, respectively. The lines in Fig.4 (b) and 4(c) are calculated from the weight mean of +c and -c ZnO spectra of Fig.4 (a) and 4(d). The ratio of +c to -c domains on the surface (+c:-c) was evaluated as 50:50 and 20:80 for Fig.4 (b) and 4(c), respectively. It was verified that the polarity ratio at the buffer-layer surface varied with annealing time.

The above results leads us to hypothesize that the buffer layer on a nitrided sapphire should have both +c and -c domains due to imperfect nitridation. Since H₂ cleaning removes oxygen, the non-nitrided surface should be covered with Al atoms. At the very initial stage of GaN buffer growth, nitrogen atoms are bound to Al atoms regardless of a nitridation. Nitrogen atoms are bonded to three Al atoms and have one bond pointing upwards normal to the surface on the nitrided sapphire, reflecting -c polarity of AlN formed by a substrate nitridation. In contrast, nitrogen atoms are bonded to one Al atom, and Ga atoms are bounded to three nitrogen

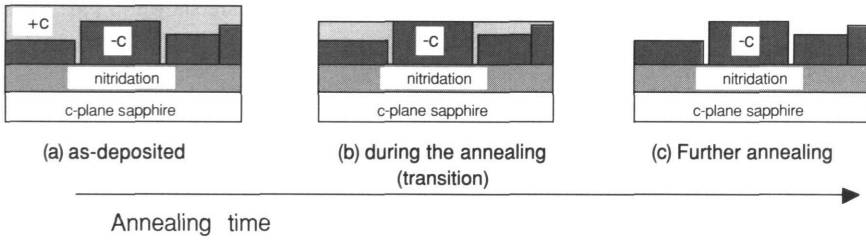


Fig. 5 Schematic illustration of the variation of buffer layer on a nitrided sapphire by the annealing. The annealing should enhanced the etching. (a) as-deposited buffer layer covered with +c changed to the buffer layer with (c) -c polarity through the transition (b).

atoms in the direction away from the surface on a non-nitrided sapphire. Both +c and -c nucleation due to imperfect nitridation should take place during the initial growth on nitrided sapphire. Taking the higher growth rate [13] and re-evaporation of the +c domain into account [7], we hypothesized that +c domains could cover -c domains at 600°C and that the selective evaporation of +c domains by subsequent temperature ramping (a type of an annealing) would leave -c domains in the buffer layer on the nitrided sapphire as illustrated in Fig.5.

In fact, the observed polarity of as-deposited 20nm buffer layer on nitrided sapphire was predominantly +c polarity and it turned to -c polarity after the annealing. The buffer layer was too thin to detect the transition from +c to -c polarity. It is expected that the polarity variation for the 160nm buffer layer should be an characteristic of the buffer layers on nitrided sapphire. Since the absorbance at 3.6eV from the 160nm buffer layer decreased with increasing annealing time, the reduction in the average thickness of the buffer layer was due to evaporation of +c domains as illustrated in Fig.5. Consequently, the ratio of +c to -c domains at the surface varied with the annealing time as shown in Fig.4. If it is accepted that the house-shaped and column hexagonal structure represent +c and -c polarity, respectively [13], the surface morphology of MOCVD-GaN films could represent the polarity composition at the buffer-layer surface acting as an indicator. Figure 6 shows that the column hexagonal facet of GaN films becomes dominant with

increased annealing time. The difference in the ratio between the buffer layer annealed for 30min and the GaN film on it will be pointed out. The transition in this case probably takes place critically during 20-30min annealing giving rise to large experimental errors, e.g., the variation with different batches, is considered to be one of the factors causing the difference. The polarity of a buffer layer should determine the polarity and surface morphology of the GaN films.

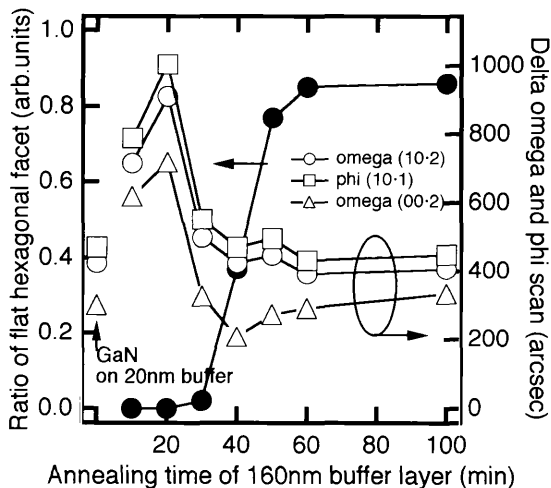


Fig. 6 Ratio of flat hexagonal facet of GaN films deposited on 160nm buffer layer annealed for up to 100min. The sapphire was nitrided. The values of crystal structure for those films and GaN film on 20nm buffer layer as a reference are also plotted.

domains in the buffer layer. It is reasonable to conclude that the polar direction of GaN film growth on c-plane sapphire is determined by the mechanism as reported in this study.

Conclusion

Control of the polarity of MOCVD-GaN was achieved by annealing of thicker buffer layers on nitrided sapphire. The properties of 1.2 μ m GaN was influenced by the different growth mode of the polarity. The mechanism determining the polar direction of GaN films was investigated from the view point of the substrate nitridation and the buffer layer. The nitrogen atom to Al atom bonding configurations at the interface of substrate were found to be modified

Based on the results in this study, the -c polarity in MBE-GaN films [14] should be ascribed to substrate nitridation which is typical for this deposition process, since radical nitrogen used in MBE method should be more reactive with the surface of sapphire. However, not all of the nitridation results in -c polarity of MOCVD-GaN films. The fact that MOCVD-GaN films with smooth surface (+c polarity) were obtained in spite of substrate nitridation [5,7] was explained by insufficient evaporation of +c

by substrate nitridation. Substrate nitridation, thickness of the buffer layer and annealing (gas ratio, temperature ramp time etc.) after deposition of the buffer layer play a dominant role in determining the polarity and surface morphology of MOCVD-GaN films. The systematic variation of the surface morphology was caused by the polarity composition of the buffer layer.

References

- [1] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto; Appl. Phys. Lett. **68**, 2105 (1996)
- [2] E.S. Hellman; MRS Internet J. Nitride Semicond. Res. **3**, 11 (1998)
- [3] I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu and N. Sawaki, J. Cryst. Growth **98**, 209 (1989)
- [4] S. Keller, B. P. Keller, Y.-F. Wu, B. Heying, D. Kapolnek, J. S. Speck, U. K. Mishra and S. P. DenBaars; Appl. Phys. Lett. **68**, 1525 (1996)
- [5] K. Uchida, A. Watanabe, F. Yano, M. Kouguchi, T. Tanaka and Minagawa; J. Appl. Phys. **79**, 3487 (1996)
- [6] Y. Bolan, P. Fini, S. P. DenBaars and J. S. Speck; Jpn. J. Appl. Phys. **37**, 4695 (1998)
- [7] S. Fuke, H. Teshigawara, K. Kuwahara, Y. Takano, T. Ito M. Yanagihara and K. Ohtsuka; J. Appl. Phys. **83**, 764 (1998)
- [8] M. Sumiya, T. Ohnishi, M. Tanaka, K. Ohtsuka I. Ohkubo, M. Kawasaki, M. Yoshimoto H. Koinuma and S. Fuke; Submitted to Appl. Phys. Lett.
- [9] T. Ohnishi, A. Ohtomo, M. Kawasaki, K. Takahashi, M. Yoshimoto and H. Koinuma, Appl. Phys. Lett. **72**, 824 (1998)
- [10] M. Sumiya, T. Ohnishi, H. Hesigawara, M. Tanaka, I. Ohkubo, M. Kawasaki, M. Yoshimoto, K. Ohtsuka, H. Koinuma and S. Fuke; Proc. of 2nd Intern. Symp. on Blue laser and Light Emitting Diodes, Chiba Japan, **339** (1998)
- [11] A. Yamamoto, M. Tsujino, M. Ohkubo and A. Hashimoto; J. Cryst. Growth **137**, 415 (1994)
- [12] S. Shimizu and S. Sonoda; Private communication, 2nd Intern. Symp. on Blue laser and Light Emitting Diodes, Chiba Japan (1998)
- [13] H. Yamane, M. Shimada, T. Endo and F. J. DiSalvo; Jpn. J. Appl. Phys. **37**, 3436 (1998)
- [14] S. Shimizu, Y. Suzuki, T. Nishihara, S. Hayashi and M. Shinohara; Jpn. J. Appl. Phys. **37**, L703 (1998)