Transactions of the Materials Research Society of Japan 28 [3] 813-816 (2003)

Growth Process of GaN on Sapphire at High Growth Temperature by Gas Source Molecular Beam Epitaxy

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Annealing processes of GaN buffer layer and epitaxial growth processes at a high growth temperature using NH_3 gas source molecular beam epitaxy have been observed by in-situ reflection high energy electron diffraction and atomic force microscopy. It is observed that the surface morphology of annealed GaN buffer layer is changed to columnar structure with flat surfaces. It has been found that the growth kinetics of GaN epitaxial layer at 950 ℃ is different from the one of GaN epitaxial layer at below 900 ℃.

Key words: GaN, NH_3, Growth, GS-MBE, RHEED

1. INTRODUCTION

The GaN and related compounds of AlGaN are promising materials for opto-electronic devices in the ultra violet-wavelength region [1-4]. It is, however, difficult to obtain the high-quality GaN on a sapphire substrate with an atomically flat growing surface and low density of threading dislocation because of the large misfit of the lattice constants between GaN and sapphire substrate [5-14]. In order to realize the ideal GaN epitaxial layer on the sapphire substrate, it is essential to clarify the annealing process of GaN buffer layer and initial growth stage of GaN at high growth temperatures of above 900 ℃. However, there has been little work on the in-situ investigation of annealing and growth processes of GaN at high temperatures using NH_3 gas source molecular beam epitaxy [15,16].

In the present work, we have investigated the annealing process of GaN buffer layer and growth behavior of GaN epitaxial layer on sapphire(1000) substrate with NH_3 gas source molecular beam epitaxy (GS-MBE) by in-situ reflection high-energy electron diffraction (RHEED) and ex-situ atomic force microscopy (AFM) observations.

2. EXPERIMENT

GaN have been grown by using of a gas source molecular beam epitaxy equipment with an in-situ RHEED system. Since details of apparatus equipment were reported previously [9], we describe the outline in short. A growth chamber was evacuated by twin turbo molecular vacuum pumps mounted in two lines individually, and the base pressure was of 1 x 10^{-10} Torr. Al_2O_3(1000) wafer was used as substrates after thermal cleaning at a substrate temperature of 900 ℃. There were chemically cleaned with etching by dipping in a solution of before HF : H_2O = 1 : 50 before being set in the preparation chamber. The substrate was set on sample holder with Si substrate using as a thermal heater by directly passing a dc electric current through molybdenum electrodes. Prior to keeping growth temperatures from 600 to 950 ℃ , the substrates were thermally cleaned at 950 ℃ .

The substrate temperature was measured by an optical pyrometer. NH_3 gas was introduced onto the substrate surface through a delivery stainless tube. The pressure of NH_3 gas during GaN growth was preciously controlled by a mass-flow controller in the range of 2 x 10^{-6} to 2 x 10^{-4} Torr. The substrate surface and film growth processes in the initial stage were observed by in-situ the RHEED system operated at an acceleration voltage 10 kV and ex-situ atomic force microscope (AFM). The diffraction patterns for GaN growth sequences were detected by digital still camera with a mega-pixel CCD.

3. RESULTS AND DISCUSSIONS

3.1 GaN buffer layer

In previous study [9], we have reported that the growth process in the initial stage of GaN epitaxial film on γ-Al_2O_3/Si hybrid substrate at a growth temperature of 800 ℃ by using of GS-MBE and it is essential for high quality GaN layer to proceed the growth at a high temperature above 800 ℃. Therefore, NH_3 GS-MBE experiments have been performed at high growth temperatures from 800 to 950 ℃.

Figures 1 show AFM images and a RHEED pattern taken from a GaN buffer layer deposited on Al_2O_3(1000) surface at a temperature of 600 ℃ for 60 min. As seen in the AFM images shown in fig. 1(a) and (c), we can observe that the GaN buffer layer is deposited on substrate in an islanding growth mode. The RHHED pattern in fig. 1(e) is a spotty pattern consisting of extra streaks indicated formation of facet structure of GaN islands [17]. It is considered that the GaN buffer layer is grown in a single crystal mode.

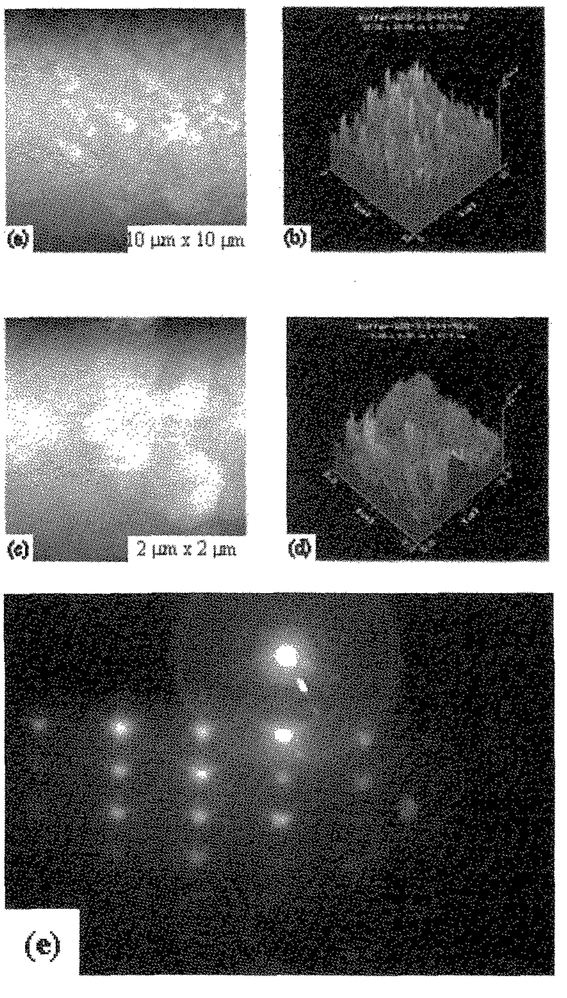

Fig. 1 AFM images and RHEED pattern for GaN buffer layer deposited on Sapphire substrate at 600 ℃ for 60 min. (a) scanning size is 10 μm x 10 μm, (b) the bird's-eye view of (a), (c) scanning size is 2 μm x 2 μm and (d) the bird's-eye view of (d). (e) is a RHEED pattern taking from the same sample.

3.2 Anneal processes of GaN buffer layer

Figures 2 show AFM and in-situ RHEED observations of GaN buffer layers annealed at fig. 2(a) 800 ℃, (b) 900 ℃ and (c) 950 ℃ for 10 min, respectively.

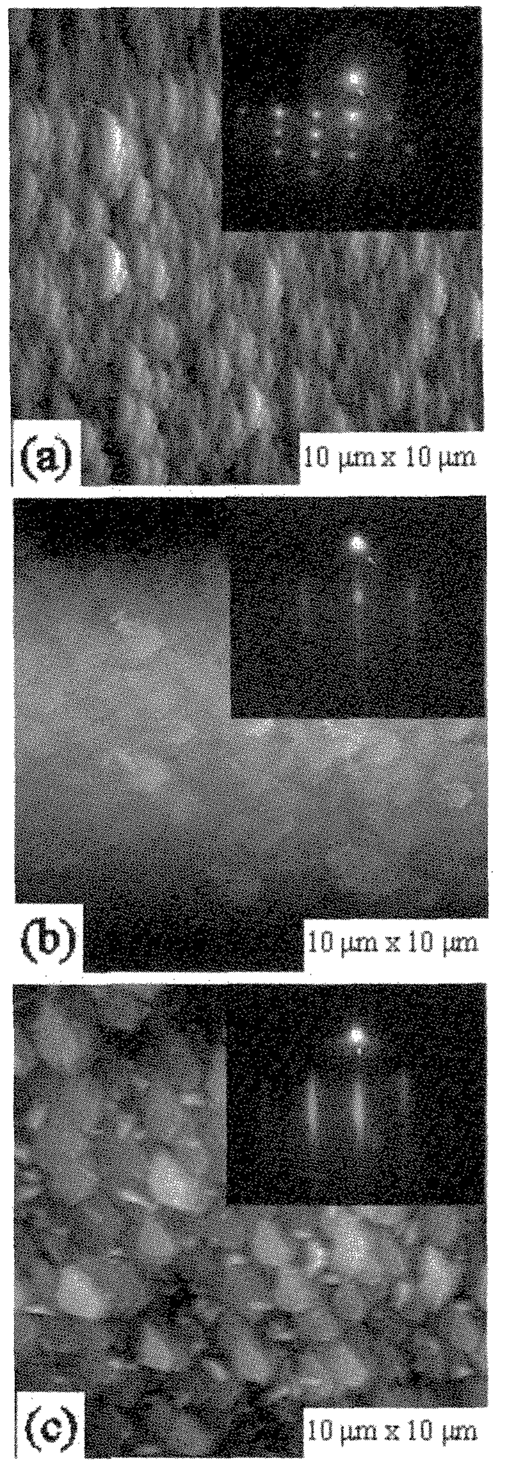

Fig. 2 AFM images and RHEED patterns taken from annealed GaN buffer layer at a temperature of (a) 800 ℃, (b) 900 ℃ and (c) 950 ℃.

In the case of annealing at a growth of 800 ℃, there exits a marked difference in island shape between the buffer layers as deposited (fig. 1(a)) and annealed (fig. 2(a)). It is found that the shape of GaN islands change to anisotropic one. However, it is found no change in

RHEED patterns between the annealed buffer layer (fig. 1(e)) and epitaxial layer of GaN (fig. 2(a)). It suggests that it is partially proceeding of solid phase growth of GaN buffer layer in islanding growth mode by thermal annealing at 800 ℃.

RHEED pattern changes from spotty pattern to streaky one by annealing at above 900 ℃ as shown in fig. 2(b). We can observe the streaks extend from each spot diffraction perpendicular to the shadow edge. This means that the flat surface is formed on the top of GaN islands by thermal annealing.

It is noted that sharp streak pattern is observed in fig. 2(c). It is found that the surface morphology of annealed GaN buffer layer is changed to columnar structure with flat surfaces as shown in fig. 2(c). These phenomena mean that the columnar structure of GaN is formed in solid phase epitaxy mode by the thermal annealing at 950 ℃.

3.3 Growth processes of GaN at high growth temperature

GaN epi-layer have been grown on annealed GaN buffer layer. Growth temperature is same as the annealing temperature. AFM image and RHEED pattern of figs. 3(a) is for the sample at a growth temperature of 800 ℃, (b) at 900 ℃ and (c) at 950 ℃, respectively.

It is found no change between the annealed buffer layer and epitaxial layer of GaN at a growth temperature of 800 ℃. It is suggested that there is no improvement of GaN epitaxial layer by growth at 800 ℃. It is found that coreless of GaN islands is occurred by growth at 900 ℃, but RHEED pattern changed to a ring pattern. Therefore, it is considered that a polycrystalline GaN islands is grown on the annealed buffer layer. In the case of a growth temperature of 950 ℃, it found that columnar structure of GaN islands changed to a hexagonal pyramid structure with a flat top surface and faceting shape shown in fig. 3(c).

These results suggest that there are two kinds of growth mechanisms corresponding to with two kinds of GaN island shape depending on the growth temperature. The kinetic process of GaN epitaxial layer growth can be considered to consist of the various processes of NH_3 adsorption, decomposition of adsorbed species and surface migration of Ga atoms. It is considered that the factor governing the marked difference of film growth has the relation to kinetic processes of NH_3 and Ga species. Further analysis of the kinetics of the growth process is in progress to make clear the mechanism of the present GaN epitaxial growth.

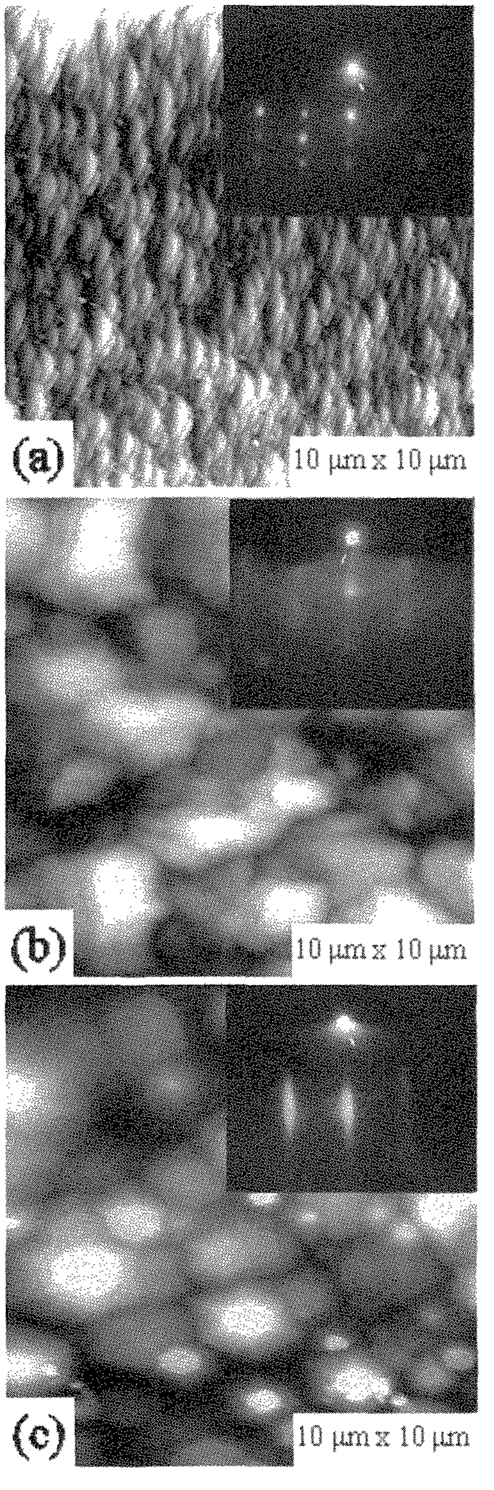

Fig. 3 AFM images and RHEED patterns GaN epitaxial layer at a growth temperature of (a) 800 ℃, (b) 900 ℃ and (c) 950 ℃. Growth times are 60 min, respectively.

4. CONCLUSIONS

Annealing processes of GaN buffer layer and epitaxial growth processes at a high growth temperature using NH_3 GS-MBE have been investigated by in-situ RHEED and ex-situ AFM observations. It has been clarified that the solid phase regrowth of GaN buffer is occurred by thermal annealing at above 800 ℃. It is observed that the surface morphology of annealed GaN buffer layer is changed to columnar structure with flat surfaces. It has been found that the growth kinetics of GaN epitaxial layer at 950 ℃ is difference from the one of GaN epitaxial layer at below 900 ℃.

Acknowledgment

This works has been party supported Grant-in-Aid for Scientific Research Ministry of Education, Science, Sports Culture of Japan, No. 1 3650014.

REFERENCES

[1] S. Nakamura, M. Senoh. S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, H. Umemoto, M. Sano and K. Chocho, J. Cryst. Growth, **189-190**, 820(1 998).
[2] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita. H. Kiyoku, H. Umemoto, M. Sano and K. Chocho, Jpn. J. Appl. Phys., **37**, L627(1998).
[3] T. Kobayashi. F. Nakamura, T. Tojyo, H. Nakajima, T. Asatsuma, H. Kawai and M. Ikade, Electron. Lett. , **34**, 1494(1998).
[4] S. Nakamura, M. Senoh. S. Nagahama, N. Iwasa, T. Yamada. T. Matsushita, Y. Sugimoto and H. Kiyoku, Appl. Phys. Lett., **70**, 2753(1997).
[5] F. Semond, Y. Cordier, N. Grandjean, F. Natali,, B. Damilano, S. Vezian and J. Massies, Phys. Status Solid **A.288**, pp.501-510(2001).
[6] M. J. Jurkovic, L. K. Li, B. Turk and W. I. Wang, Mater. Res. Soc. Symposium Proceedings, **595**, W8.1.1-7(2000).
[7] N. Ohshima, A. Wakahara, M. Ishida. H. Yonezu and A. Yoshida, Y. C. Jung and H. Kimura, J. Korean Phys. Soc., **34**, 359(1999).
[8] N.Ohshima, H. Yonezu, S. Uesugi, K. Gotoh and S. Yamahira, Mat. Res. Soc. Sympo. Proc., **512**, 405(1 998) .
[9] N. Ohshima, S. Okamoto, K. Shibata, Y. Orihashi, S. Kageyama, M. Ishida, T. Yazawa and G. Camargo, Trans. of Mat. Res. Soc. J., **27**, pp.475-478(2002).
[10] H. Tang, J.A. Bardwell, J.B. Webb, S. Moisa, J. Fraser and S. Rolfe, Appl. Phys. Lett., **79**, pp.2764-2766(2001).
[11] M.Y. Kong, J.P. Zhang, X.L. Wang and D.Z. Sun, J. Cryst. Growth, **227-228**, pp.371-375(2001).
[12] F. S. Juang and T. K. Chu, J. Cryst. Growth **225**, pp.145-149(2001).
[13] A. Stafford, S. J. C. Irvine, Z. Bougrioua, K. Jacobs, I. Moerman, E. J. Thrush and L. Considine, J. Cryst. Growth, **221**, pp.142-148(2000).
[14] A. J. McGinnis, D. Thomson, R. F. Davis, E. Chen, A. Michel and H. H. Lamb, J. Cryst. Growth, **222**, pp.452-458(2001).
[15] Y. Lan, X. Chen, Y. Cao, Y. Xu, T. Xu and J. Li, Z. Tao, J. Liang, J. Mater. Sci. Lett., **19**, pp.2215-2217(2000).
[16] S. Yu. Karpov, O. V. Bord, R. A. Talalaev and Yu. N. Makarov, Mater. Sci. Eng., B.82, Solid-State Mater. Adv. Technol., pp.22-24(2001).
[17] Y. Koide, S. Zaima, N. Ohshima and Y. Yasuda, Jpn. J. Apple. Phys., **28**, pp.L690-L693(1989).

(Received December 21, 2002; Accepted March 17, 2003)