Effect of thickness on the microstructure of GaN films on Al_2O_3 (0001) by laser molecular beam epitaxy*

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Heteroepitaxial GaN films are grown on sapphire (0001) substrates using laser molecular beam epitaxy. The growth processes are *in-situ* monitored by reflection high energy electron diffraction. It is revealed that the growth mode of GaN transformed from three-dimensional (3D) island mode to two-dimensional (2D) layer-by-layer mode with the increase of thickness. This paper investigates the interfacial strain relaxation of GaN films by analysing their diffraction patterns. Calculation shows that the strain is completely relaxed when the thickness reaches 15 nm. The surface morphology evolution indicates that island merging and reduction of the island-edge barrier provide an effective way to make GaN films follow a 2D layer-by-layer growth mode. The 110-nm GaN films with a 2D growth mode have smooth regular hexagonal shapes. The X-ray diffraction indicates that thickness has a significant effect on the crystallized quality of GaN thin films.

Keywords: reflection high energy electron diffraction, thin films, laser molecular beam epitaxy, GaN, sapphires

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1. Introduction

As one of the most promising wide band gap III–V semiconductor materials, wurtzite GaN has attracted much attention due to its enormous applications in optoelectronic devices,[1−4] electronic devices,[5−10] etc. Due to a lack of inversion symmetry, the *c* axis of wurtzite GaN exhibits strong polarization. This spontaneous polarization enhances the functionality of GaN for electronic applications such as AlGaN/GaN heterostructures and relative devices. It is well known that smooth surfaces are essential for GaN-based devices. A smooth surface can greatly decrease the scattering of electrons. Thus, it is important to prepare *c*-axis-oriented GaN epitaxial thin films with smooth surfaces. In recent years, GaN (0001) has been grown directly on various substrates including SiC (0001), Si (111), and sapphire (0001).[11−13] Although SiC has the smallest lattice mismatch with GaN among these substrates, its high cost impedes the application of SiC semiconductors in commercial cheap devices. Si (111) and sapphires (0001) have a large lattice mismatch with GaN. This leads to the rough surface of prepared GaN thin films.[11,13,14] Buffer-insertion techniques can efficiently provide nucleation sites for the heteroepitaxial growth of GaN. By inserting AlN or GaN low-temperature buffer layers, both surface morphology and crystallization can be greatly improved. This has been applied widely to obtain high-quality GaN semiconductors[15−20] in recent years. As buffer layer techniques inevitably increase the complexity of experimental operation and the amount of resource waste, alternative effective methods to directly grow GaN films without buffer layers have been explored for many years.[21,22] Most studies have been devoted to understanding the growth kinetics and the properties of GaN films. However, research results about the direct growth behaviour of epitaxial GaN films without buffer layers are limited.

In order to prepare high quality epitaxial GaN thin films, it is essential to study and control the growth process of GaN. Reflection high-energy electron diffraction (RHEED) is one of the most useful techniques to *in-situ* monitor the growth process of thin films. The process of interfacial strain relaxation can be systematically analysed by measuring the position, the shape and the intensity distribu-

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tion of RHEED diffraction patterns.[23−25] Using an atomic force microscope (AFM), we can demonstrate the roughness of surfaces and the surface evolution, which indicate the movements and transitions of the surface atoms.

In this paper, GaN thin films with different thicknesses are epitaxially grown directly on sapphire (0001) substrates by laser molecular beam epitaxy (LMBE). The growth mode of GaN is *in-situ* monitored by RHEED. The effect of thickness on the microstructure of the GaN films is investigated by using RHEED, AFM and X-ray diffraction (XRD).

2. Experimental procedure

Before the growth of the GaN thin films, the sapphire substrates were cleaned by a standard degrease (acetone, ethanol and de-ionized water). Then, the sapphire substrates were transferred into an LMBE growth chamber. The background vacuum was 1×10^{-6} Pa. A KrF (248-nm wavelength and 30-ns pulse duration, complex 201 Lambata) excimer laser was focused onto the GaN (99.99%) target surface. The pulse rate and energy density were 2 Hz and 2 J/cm^2, respectively. The target was rotated during the ablation process to reduce possible non-uniform erosion. The distance between target and substrate was 55 cm. The substrate temperature was held at an optimal 700 °C. The deposition rate of the GaN was about 1.2 nm/min, as confirmed by a surface profiler (VEECO-DEKTAK 150, TMC). The growth process of the GaN thin films was *in-situ* monitored by RHEED using a camera-based video-recording system with a high-sensitivity charge-coupled device. The digital images of the RHEED pattern were recorded in an anti-Bragg condition using a 20-keV electron beam at a grazing incidence angle of 1°–3° to the substrate surface. The surface morphology of the GaN films grown in different growth modes was characterized by AFM (SPA-300 *hv*, Seiko). The XRD (Cu Kα radiation $\lambda = 0.154$ nm, D1 SYSTEM, BEDE) was used to characterize the crystallization of the GaN thin films. The chemical compositions were investigated by XPS (X-ray photoelectron spectroscopy) (XSAM800, Kratos).

3. Results and discussion

Figure 1 shows the RHEED pattern evolution in the growth process of GaN thin films. The RHEED pattern along the $[1\bar{1}00]$ axis of sapphire substrates is shown in Fig. 1(a). The clear bright streak indicates that the sapphire (0001) surface was smooth and well crystallized. As the growth of GaN started, the sapphire patterns disappeared and GaN patterns appeared. Along the sapphire $[1\bar{1}00]$ direction, images of a GaN $[11\bar{2}0]$ direction can be observed. Figure 1(b) shows the diffraction pattern after the growth of 5-nm GaN thin films. The RHEED pattern shows the spot-like diffraction characteristics. This reveals that the growth of the GaN film at this stage followed a three-dimensional (3D) island growth mode. It can be seen that the space between two in-plane diffraction spots became narrower than in the $[1\bar{1}00]$ sapphire substrates. This demonstrates that the in-plane lattice constant of GaN thin films increased and that the strain induced by the GaN/sapphire interface began to be relaxed. The growth of 15-nm-thick GaN is shown in Fig. 1(c). Clear spotted patterns can be observed. This indicates that the GaN thin films kept on growing in 3D island growth mode. The space between two in-plane diffraction spots became distinctly narrower. This reveals that the in-plane lattice constant of GaN thin films became larger and the strain induced by the GaN/sapphire interface was further relaxed. With the GaN growth proceeding, the distance between the two in-plane streaks almost had not changed, while the clear spots gradually changed to a clear and bright streaky shape. This indicates that the strain of the GaN thin films had been completely relaxed in the prior process and that the growth mode began to transform from 3D to Stransky–Krastonov (SK) when the GaN thin films were thicker than 15 nm. This demonstrates that the strain relaxation and the transformation of growth mode happened in different stages. Figure 1(d) shows the diffraction patterns after the growth of 30-nm GaN thin films. The streaks and spots patterns demonstrates that the GaN thin films were grown in SK growth mode. Figure 1(e) is the RHEED pattern after the growth of 60-nm GaN thin films. After further GaN growth, the RHEED patterns maintained a long duration of clear and bright streaks until the end of the growth of 110-nm GaN thin films, as shown by Fig. 1(f). This demonstrates that the GaN films kept on growing in two-dimensional (2D) layer-by-layer growth mode and had a smooth surface. According to the RHEED pattern results from Figs. 1(a)–1(f), the epitaxial relationship was confirmed to be $[11\bar{2}0](0001)$ GaN//$[1\bar{1}00](0001)$ sapphires.

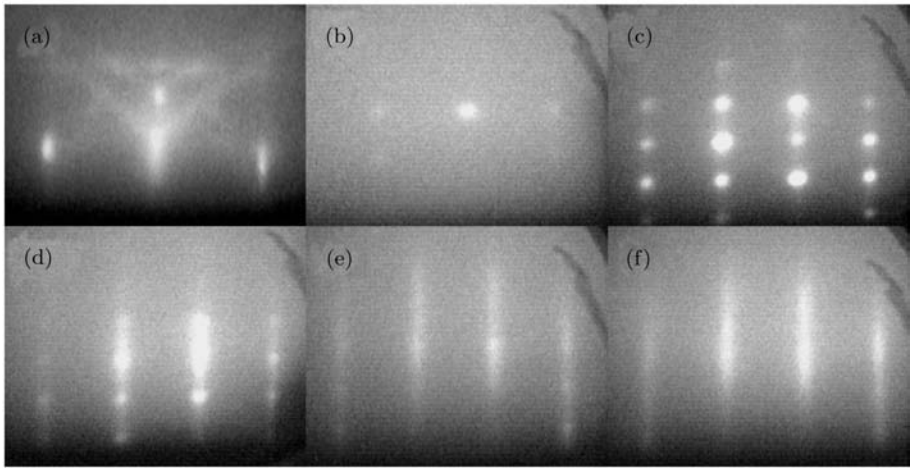


Fig. 1. The RHEED patterns of GaN thin films on sapphires (0001): (a) sapphires [1$\bar{1}$00] (0001), (b) GaN deposited 5 nm, (c) GaN deposited 10 nm, (d) GaN deposited 30 nm, (e) GaN deposited 60 nm, (f) GaN deposited 110 nm.

For a further understanding of the effect of thickness on the microstructure of GaN films, we analysed the strain relaxation process by calculating the lattice parameter relaxation state of the growth process. We calculated the relaxation of lattice parameter a by measuring the changes of r in the growth process, where r is the distance of the specular spot from the shadow edge of the RHEED screen. A schematic diagram of the epitaxial relationship between GaN and sapphires is shown by Fig. 2. By using the [11$\bar{2}$0](0001) GaN//[1$\bar{1}$00](0001) sapphire alignment, the lattice parameter state of GaN layers was estimated.

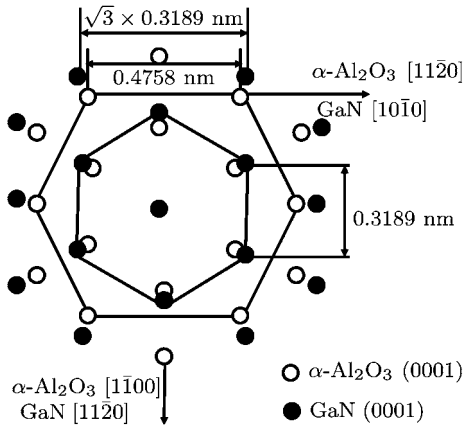


Fig. 2. Schematic diagram of the epitaxial relationship between GaN and sapphires.

The lattice relaxation state is plotted as a function of GaN thin film thickness in Fig. 3. When the thickness of the GaN films varied from 0 nm to 15 nm, the lattice parameter increased from 0.264 nm to 0.3186 nm. The lattice parameter for bulk GaN crystal is about 0.3189 nm, revealing that the strain almost relaxed completely during this stage. In this process, the transformation from the interface strain energy into the surface free energy occurred in the initial growth stage of GaN films, due to the large lattice mismatch (the lattice mismatch in the hexagonal [11$\bar{2}$0](0001) GaN($a_{\rm GaN}$ = 0.3189 nm)//[1$\bar{1}$00](0001), the sapphire alignment is estimated simply to be 14.6%), the films' surface cannot be kept smooth enough at an atomic level.

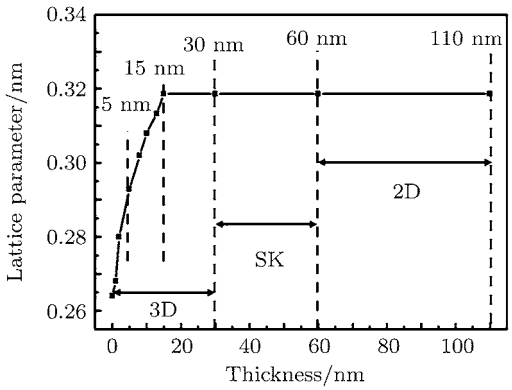


Fig. 3. The lattice relaxation state is plotted as a function of the thickness of the GaN thin films.

The GaN films began to grow in 3D mode. When the thickness of GaN varied from 0 nm to 5 nm, the strain began to be released and the strain relaxation was then fast. With GaN film growing from 5 nm to 15 nm, the strain was further released until the strain almost relaxed completely. In the whole process from 0 nm to 15 nm, the strain was released by enlarging the GaN surface area, which results in the observation of maintaining the 3D island growth mode. The 3D island mode can be attributed to the transformation from interface strain energy into surface free energy.[25] When the thickness of the GaN

films exceeded 15 nm, the lattice parameter is almost maintained as a constant value of 0.3186 nm, demonstrating that the strain has been almost completely relaxed in the prior process. Figure 3 shows that the strain is released when the thickness varies from 0 nm to 15 nm, but the growth mode is transformed when the thickness of GaN exceeds 30 nm. The transitions of the growth mode were not caused by strain relaxation. The strain relaxation result is consistent with the RHEED observation.

In order to investigate the effects of different thicknesses on the microstructure, an AFM was used to analyse the surface morphology evolution. We prepared three kinds of samples with 15-nm, 30-nm, and 110-nm GaN films on sapphires representing 2D, SK, and 3D growth mode, respectively. As shown in Fig. 4(a), the 15-nm-thick GaN film has the highest roughness with the root-mean-square (RMS) roughness value of 11.78 nm. As shown in the figure, different island sizes from 104 nm to 526 nm are observed and the shape of the islands are irregular. The 30-nm-thick GaN film on sapphire is shown in Fig. 4(b). The GaN films have a smooth surface with an RMS value 6.54 nm. Compared with the morphology of the 15-nm-thick GaN films, the size and diversity of the islands were reduced. A hexagon-like shape can be observed, demonstrating that the islands were merging, the density of islands was increasing and a direct reduction in the island-edge barrier occurred. As shown by Fig. 4(c), the 2D growth mode is readable for the 110-nm-thick GaN layer with an RMS value of 4.92 nm on sapphire. Compared with the above thinner films, 110-nm GaN layer has the smoothest surface. More interestingly, a hexagonal island of around 350 nm in size can be clearly seen from the AFM image. The RMS value is 0.93 nm in size for one hexagonal island, demonstrating that the GaN films are grown in 2D mode. According to the above-discussed strain relaxation process, the growth process was similar to the homoepitaxy (GaN on GaN) when GaN films exceeded 15 nm. Therefore, the growth process can be explained by thin-film growth theories.[26,27] According to this basic growth mechanism, sufficient surface diffusion is important in order to form smooth films. The island mergence can lead to a direct reduction in the island-edge barrier, which can increase surface diffusion to form a 2D layer-by-layer growth mode. The driving force for the evolution of the island shape toward being compact is the minimization of the total free energy of each island.

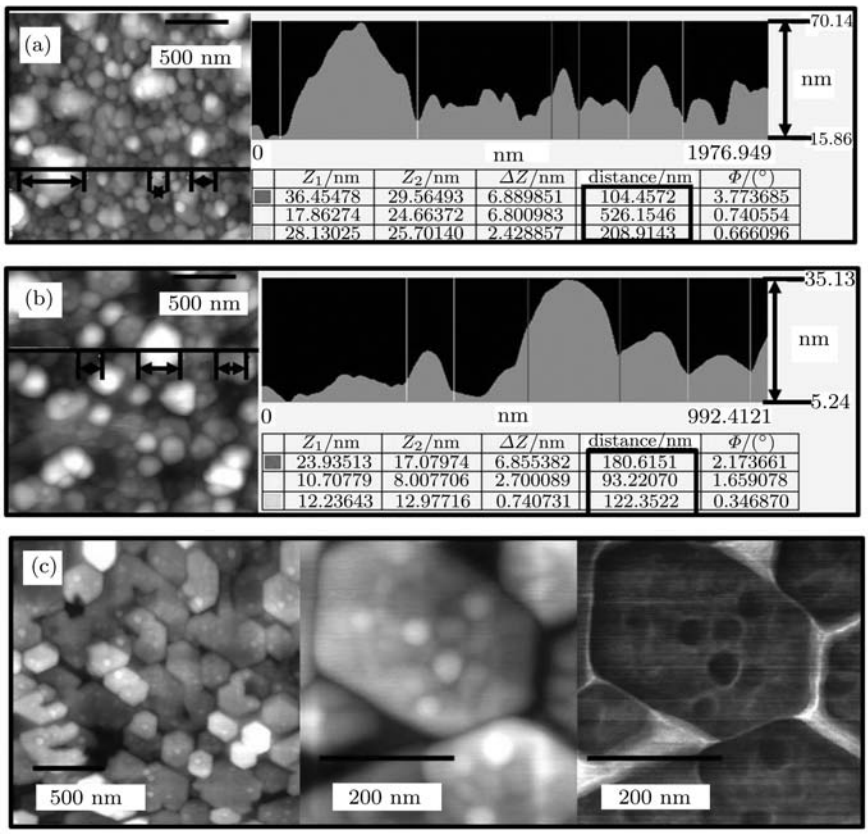


Fig. 4. Surface morphology of GaN films of different thicknesses: (a) 15 nm, (b) 30 nm, and (c) 110 nm.

We introduce a determinant factor[27]

$$F \propto \frac{1}{L} V \exp\left(-\frac{E}{KT}\right), \tag{1}$$

where L is the dimension of the island, V is the rate of migration and incorporation into a growing island, E is the island-edge barrier and KT is the thermal energy. Three factors can drive the growth mode to transform from 3D to 2D: (i) migration and incorporation of islands, (ii) the high density of islands, (iii) direct reduction in the island-edge barrier. From our result from the AFM, one expects to an observe improved 2D growth mode whenever the value of F is quantitatively enlarged. Our results of the direct deposition of GaN films on sapphires are different from the growth process of GaN films on a nucleation buffer layer.[28,29]

XRD was used to examine the epitaxial orientation, crystallization and lattice parameter of GaN films of different thicknesses. Figure 5(a) shows the θ–2θ scans of XRD of different kinds of GaN films with thicknesses of 15 nm, 30 nm and 110 nm, respectively. From the figure, we can see that GaN films grown in different modes on sapphires are all highly (0002)-oriented, while the GaN film with 2D growth mode has the highest (0002)-oriented diffraction peak. As a comparison, the full width at half maximum (FHWM) of the (0002) peak is shown in Fig. 5(b). It can be seen that the FHWM of the 2D growth mode is smaller than others, indicating that 110-nm GaN film has a higher crystalline quality. The early growth stage of the GaN layer in 3D and SK modes was essential in order to obtain subsequently deposited GaN films with a higher crystalline quality. In Fig. 5(c), the Φ-scan of the XRD investigation of the 110-nm GaN films revealed the nearly equal intensities of the six peaks and 30° in-plane rotation of the epitaxial GaN thin films on sapphires. It reveals that the epitaxial orientation relationship between GaN and sapphire is $[11\bar{2}0](0001)$ GaN//$[1\bar{1}00](0001)$ sapphires. According to the in-plane 2θ scan results (not shown here), the in-plane lattice parameter is 0.3176 nm. The XRD results are consistent with the analysis of the RHEED patterns and the AFM images.

The XPS was used to analyse the chemical compositions of the prepared 110-nm thin films. The full scan spectrum of the sample is shown by Fig. 6(a).

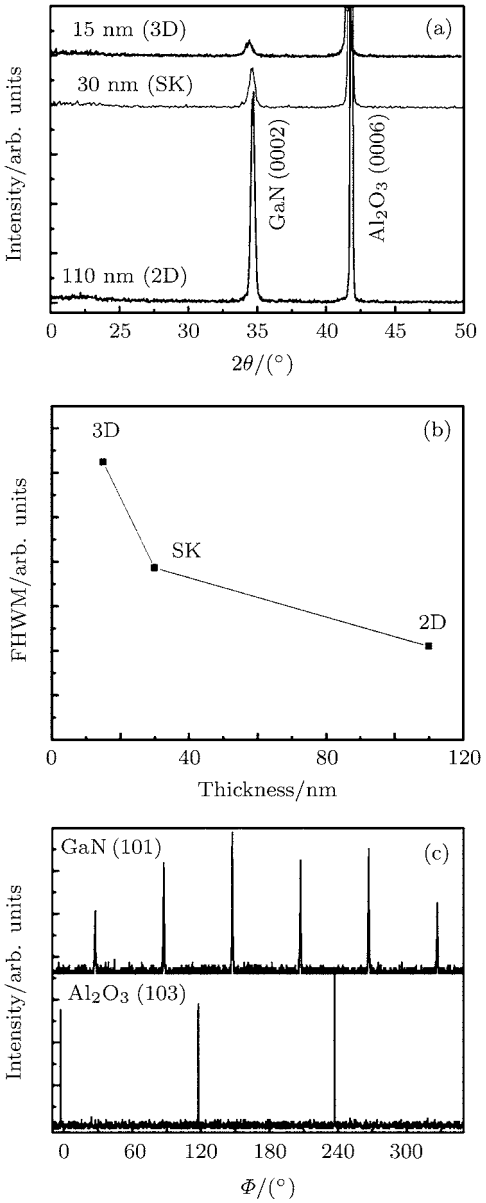


Fig. 5. The XRD patterns of GaN/sapphires: (a) θ–2θ scan of GaN thin films of different growth modes, (b) the comparison of the FHWM of the GaN (0002) peak of different growth modes, (c) the Φ-scan of GaN/sapphires.

The scan area is from 0 eV to 1100 eV. The Ga 3d, Ga 3p, G 3s, C 1s, N 1s, O 1s, Ga (LMM) and O (KLL) spectra can be observed. The C peaks derived from surface contamination. The O peak's position is 530.837 eV, as shown by Fig. 6(a). According to a previous report,[30] the O binding energy in the spectrum of 530 eV–530.9 eV was derived from chemical adsorption. The non-existent satellite peak of O (20.5 eV) in Ga_2O_3 indicates that there are no Ga–O bonds. The Ga3d (19.446 eV) spectrum is shown in Fig. 6(b), the N1s peak position is 396.983 eV, as shown in Fig. 6(c), indicating that the prepared sample is a pure GaN phase.

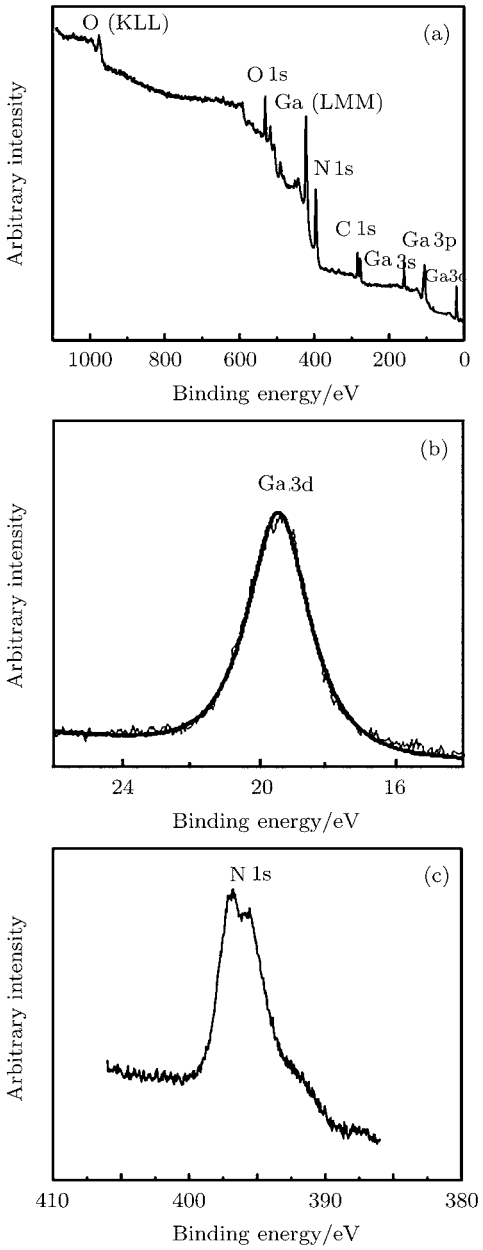


Fig. 6. The XPS measurement of the samples: (a) full spectrum, (b) Ga 3d spectrum, (c) N 1s spectra.

4. Conclusion

GaN thin films were epitaxially grown on sapphire (0001) substrates by LMBE. The transitions of growth mode from 3D island to SK, then to 2D layer-by-layer were observed by RHEED as the thickness was increased. When the thickness varied from 0 nm to 15 nm, the GaN films kept on growing in 3D mode. A transformation from interface strain energy into surface free energy occurred. For 15-nm GaN films, the strain was completely relaxed. When the thickness exceeded 15 nm, a transition of the growth mode from 3D to 2D can be observed. Island merging and the direct reduction of the island-edge barrier can make GaN films follow a 2D layer-by-layer growth mode. In this process, the surface free energy was decreased to minimize the total free energy. XRD and XPS demonstrated that the 2D growth mode for 110-nm hexagonal GaN films had a high crystalline quality without Ga_2O_3 formation. These results provide an effective method for the growth control of high crystallized quality epitaxial GaN films and thus have potential applications for GaN devices.

References

[1] Yang Z Q and Xu Z Z 1997 *Acta Phys. Sin.* **46** 606 (in Chinese)
[2] Nakamura S and Fasol G 2001 *Meas. Sci. Technol.* **12** 755
[3] Mukai T, Nagahama S, Sano M, Yanamoto T, Morita D, Mitani T, Narukawa Y, Yamamoto S, Niki I, Yamada M, Sonobe S, Shioji S, Deguchi K, Naitou T, Tamaki H, Murazaki Y and Kameshima M 2003 *Phys. Stat. Sol.* **200** 52
[4] Luo Y, Guo W P, Shao J P, Hu H, Han Y J, Xue S, Wang L, Sun C Z and Hao Z B 2004 *Acta Phys. Sin.* **53** 2720 (in Chinese)
[5] Feng Q, Gu W P, Hao Y, Ma X H, Wang C and Zhang J C 2009 *Acta Phys. Sin.* **58** 511 (in Chinese)
[6] Albrecht J D, Wang R P, Ruden P P, Farahmand M and Brennan K F 1998 *J. Appl. Phys.* **83** 4777
[7] Shur M S 1998 *Sol. Stat. Electron.* **42** 2131
[8] Mivazaki T, Fujimaki T and Adachi S 2001 *J. Appl. Phys.* **89** 8316
[9] Wakejima A, Ota K, Nakayama T, Ando Y, Okamoto Y, Miyamoto H, Kamiya S and Suzuki A 2007 *Appl. Phys. Lett.* **90** 3504
[10] Lei T, Ludwig K F and Moustakas T D 1993 *J. Appl. Phys.* **74** 4430
[11] Muto H, Asano T, Wang R P and Kusumori T 2005 *Appl. Phys. Lett.* **87** 2106
[12] Zhang C G, Bian L F, Chen W D and Hsu C C 2007 *J. Cryst. Growth* **299** 268
[13] Vispute1 R D, Talyansky V, Trajanovic Z, Choopun S, Downes M, Sharma R P, Venkatesan T, Wood M C, Lareau R T, Jones K A and Iliadis A A 1997 *Appl. Phys. Lett.* **71** 102
[14] Huang T F, Marshall A, Spruytte S and Harris Jr J S 1999 *J. Cryst. Growth* **200** 362
[15] Vispute R D, Choopun S, Enck R, Patel A, Talyansky V, Sharma R P, Venkatesan T, Sarney W L, Salamanca-Riba L, Andronescu S N, Iliadis A A and Jones K A 1999 *J. Electron. Mater.* **28** 275
[16] Rupp T, Henn G and Schröder H 2002 *Appl. Surf. Sci.* **186** 429
[17] Ohtaa J, Fujiokaa H, Takahashia H, Sumiyab M and Oshima M 2001 *J. Cryst. Growth* **233** 779
[18] Kuo C H, Fu Y K, Kuo C W, Pan C J and Chi G C 2007 *Appl. Phys. Lett.* **90** 2109
[19] Huang G S, Lu T C, Yao H H, Kuo H C, Wang S C, Lin C W and Chang L 2006 *Appl. Phys. Lett.* **88** 1904
[20] Chandrasekaran R, Moustakas T D, Ozcan A S, Ludwig K F, Zhou L and Smith D J 2010 *J. Appl. Phys.* **108** 3501

[21] Cazzanelli M, Cole D, Versluijs J, Donegan J F and Lunney J G 1999 *Mater. Sci. Eng.* B **59** 98

[22] Cazzanelli M, Vinegoni C, Cole D, Lunney J G, Middleton P G, Trager-Cowan C, O'Donnell K P and Pavesi L 1999 *Mater. Sci. Eng.* B **59** 137

[23] Wei X H, Zhang Y, Li J L, Deng X W, Liu X Z, Jiang S W, Zhu J and Li Y R 2005 *Acta Phys. Sin.* **54** 217 (in Chinese)

[24] Zhang C, Ye H, Zhang L, Huang P Y R and Liu X 2009 *Acta Phys. Sin.* **58** 7765 (in Chinese)

[25] Zhu J, Zhou L X, Huang W, Li Y Q and Li Y R 2009 *J. Cryst. Growth* **311** 3300

[26] Zhang Z Y and Lagally M G 1997 *Science* **276** 377

[27] Zhang Z Y and Lagally M G 1994 *Phys. Rev. Lett.* **72** 693

[28] Böttcher T, Einfeldt S, Figge S, Chierchia R, Heinke H, Hommel D and Speck J S 2001 *Appl. Phys. Lett.* **78** 1976

[29] Wu X H, Fini P, Keller S, Tarsa E J, Heying B, Mishra U K, DenBaars S P and Speck J S 1996 *Appl. Phys. Lett.* **35** 1648

[30] Amanullah F M, Pratap K J and Hari H V 1998 *Mater. Sci. Eng.* B **52** 93