Effects of V/III ratio on the growth of *a*-plane GaN films*

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The non-polar *a*-plane GaN is grown on an *r*-plane sapphire substrate directly without a buffer layer by metal-organic chemical vapour deposition and the effects of V/III ratio growth conditions are investigated. Atomic force microscopy results show that triangular pits are formed at a relatively high V/III ratio, while a relatively low V/III ratio can enhance the lateral growth rate along the *c*-axis direction. The higher V/III ratio leads to a high density of pits in comparison with the lower V/III ratio. The surface morphology is improved greatly by using a low V/III ratio of 500 and the roughness mean square of the surface is only 3.9 nm. The high resolution X-ray diffraction characterized crystal structural results show that the rocking curve full width at half maximum along the *m* axis decreases from 0.757° to 0.720°, while along the *c* axis increases from 0.220° to 0.251° with the V/III increasing from 500 μmol/min to 2000 μmol/min, which indicates that a relatively low V/III ratio is conducible to the *c*-axis growth of *a*-plane GaN.

Keywords: V/III ratio, *a*-plane GaN, non-polar, metal-organic chemical vapour deposition

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1. Introduction

GaN-based semiconductors have been very important in material science over the last decade due to their potential device applications, such as lightemitting diodes (LEDs),[1] laser diodes (LDs),[2] and high-power transistors.[3] The majority of these GaN-based structures are grown along the [0001] *c* axis of a wurtzite crystal structure. Unfortunately, epitaxy toward the [0001] orientation leads to undesirable spontaneous and piezoelectric polarization effects, resulting in a quantum confined Stark effect (QCSE), which gives rise to internal electrical fields. These fields can spatially separate the electrons from the holes at the opposite interface of quantum wells and reduce the overlap of their wave functions, which causes a reduction of the recombination efficiency in light-emitting devices and a red shift of the emission wavelength.[4] To prevent these adverse effects, the interest in growing non-polar $(1\bar{1}00)$ *m*-plane[5] and $(1\bar{1}02)$ *a*-plane GaN[6] films has greatly increased. The $(11\bar{2}0)$ oriented *a*-plane GaN films have been grown on $(1\bar{1}02)$ non-polar *r*-plane sapphire by metal-organic chemical vapour deposition (MOCVD),[5] molecular beam epitaxy (MBE)[7] and hydride vapour-phase epitaxy (HVPE).[8] Usually a low-temperature (LT) GaN[9] or a high-temperature (HT) AlN[10] is used as the buffer layer for the growth of *a*-plane GaN on *r*-plane sapphire. Haskell *et al.*[11] presented an approach to the use of the epitaxial lateral overgrowth (ELOG) method to improve surface morphologies markedly but things become complicated. However, reports on the method of direct growth of *a*-plane GaN on *r*-plane sapphire substrate, especially on the effects of V/III ratio growth, are lacking.[12] In the present paper, attempts are made to understand the effects of V/III ratio growth on the surface morphology and structural properties of the resulting film by the method of direct *a*-plane GaN growth on *r*-plane sapphire substrates without any buffer layer.

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2. Experiment

Non-polar $(11\bar{2}0)$ a-plane GaN films were grown on $(1\bar{1}02)$ r-plane sapphire substrates by using the Thomos Swan (MOCVD) system. Trimethylgallium (TMG) and ammonia (NH_3) were used as precursors, with N_2 serving as the carrier gas. Following the *in situ* annealing of r-plane sapphire, nitridation was performed in a NH_3 ambient for 10 min at 600 °C and 9992.25 Pa. Four samples were grown at 1100 °C and 9992.25 Pa, the TMG flow rate was 30 μmol/min, the NH_3 flow rate was varied from 4000 μmol/min to 3000, 2000, and 1000 μmol/min (corresponding to V/III ratios of 2000, 1500, 1000, and 500, respectively), which were named as Samples A, B, C, and D.

Samples were characterized by atomic force microscopy (AFM) using a Digital Instruments NanoScope IIIa and high resolution X-ray diffraction (HRXRD) was performed on a Panalytical X'Pert PRO MRD.

3. Results and discussion

3.1. Surface morphology

Figure 1 shows the surface morphologies of the samples by AFM. From the figure we can see that the values of roughness mean square (RMS) of the surface over (10×10) μm^2 scanning areas of samples A to D are about 85.8 nm; 75.9 nm, 28.1 nm, and 3.9 nm, respectively. In Figs. 1(a)–1(c), although the films are all fully coalesced, which suggests that their growth modes are all two-dimensional (2D), differently sized pits are observed. These pits, which are surrounded with facets and named triangle pits, originate from the island growth and coalescing during the initial growth of the GaN bulk that results in the occurrence of triangle pits and wavy stripes.[13] At a relatively high V/III ratio (2000), the density of the pits is high and the size of the pits is large, which could be due to the fact that excess hydrogen atoms under the high V/III ratio facilitate the surface dissociation rate and damage the surface morphology.[14] With a lower V/III ratio achieved by reducing the NH_3 flow as shown in Figs. 1(b) and 1(c), the sizes of the pits become smaller and the pit density decreases due to the reduction of hydrogen atoms. At a relatively low V/III ratio (500), in Fig. 1(d), sample D shows the complete removal of all the large pits and becomes a smooth, pit free surface, although some additional stripe features along the [0001] direction can be observed. The pit disappearance results from not only the reduction of hydrogen but also the increase of

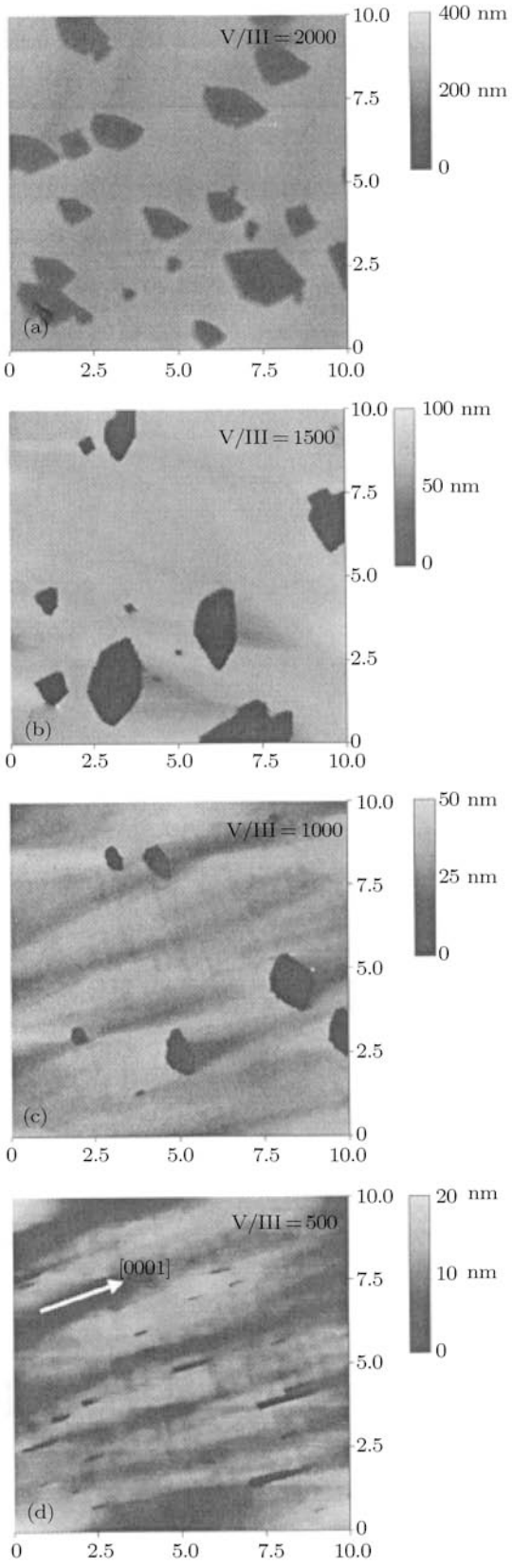


Fig. 1. AFM images of (10×10) μm^2 area scan to a-plane GaN surface with different V/III ratios.

lateral growth rate along the [0001] c direction, which can be observed from the image of sample D. The possible reason for the stripe forming is the faster growth rate along the c direction than along the m direction. Although the low V/III ratio condition benefits the 2D growth, some Ga atoms do not react due to insufficient N atoms, thereby causing a wavy surface. Sample D exhibits a very smooth surface with an RMS roughness of only 3.9 nm, which is much lower than that of the a-plane GaN film grown by MOCVD with only an HT-AlN buffer layer (15 nm),[15] but higher than those with an LT-GaN buffer layer (2.6 nm).[16]

The AFM results indicate that the surface morphology of the as-grown a-plane GaN film is affected greatly by the V/III ratio. The higher V/III value leads to high density of pits in comparison with the lower values of V/III ratio, the surface morphology is improved greatly by using the low V/III ratio. Therefore, it is possible to optimize 2D growth mode and create a flat surface a-plane GaN on low V/III ratio.

3.2. Crystal structure

Structural characteristics of the as-grown a-plane GaN films were evaluated by HRXRD. The geometry of the azimuth dependence XRD measurement is described in Fig. 2.

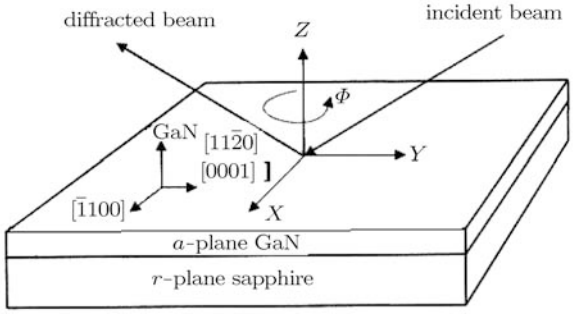


Fig. 2. Experimental geometry of the azimuthal angle dependent XRD measurement.

The double axis ω–2θ pattern diffraction of sample D (V/III ratio=500) is shown in Fig. 3, where the ω–2θ scans of the as-grown sample exhibit several peaks that are assigned to the diffractions from the (1$\bar{1}$02), (2$\bar{2}$04) crystal planes of the r-plane sapphire substrate and from the (11$\bar{2}$0) of a-plane GaN. No diffraction peak from the other GaN plane is observed. All these indicate that the GaN films are uniquely (11$\bar{2}$0) a-plane oriented. The other samples, A, B, and C, with different V/III ratios are all uniquely (11$\bar{2}$0)a-plane GaN, as evaluated by XRD.

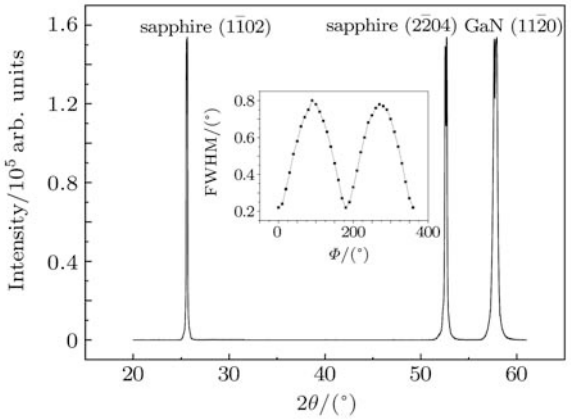


Fig. 3. Double-axis XRD ω–2θ pattern of a-plane GaN film on r-plane sapphire with a V/III ratio of 500 (sample D) and the inset shows the azimuthal angle Φ-dependent full width at half maximum (FWHM) of the (11$\bar{2}$0) ω rocking curves.

The inset shows the GaN(11$\bar{2}$0) ω scan FWHM as a function of the sample surface rotation Φ of sample D. Φ is the angle of rotation about the sample surface normal, defined as being zero when the projection of the incident beam is parallel to the [0001] GaN c direction. An M-shape azimuthal dependence over the 360° range is observed, with a period of 180°, which indicates the C_{2v} symmetry of a-plane GaN. This phenomenon is similar to the observation reported for MOCVD m-GaN on $LiAlO_2$.[17] Considering the fact that the lattice mismatch between a-plane GaN and r-plane sapphire is calculated to be 1.3% and ∼15% in [0001] and [$\bar{1}$100] directions of GaN, respectively, a large lattice mismatch between epitaxial films with their substrate exist invariably form a mosaic structure of slightly misorientation sub-grains. So the misorientation along the [$\bar{1}$100] direction among sub-grains of a-plane GaN is larger than that along the [0001] direction and so causes the anisotropy of a-plane GaN films.

Considering the structural anisotropy of a-plane GaN, XRD rocking curves of GaN (11$\bar{2}$0) reflection of all the samples were measured along the orthogonal GaN [0001] c axis and [$\bar{1}$100] m axis. The FWHM values of the XRD rocking curve (XRC) as a function of V/III ratio of the samples are shown in Fig. 4. Along the m axis, the FWHM values decrease from 0.757° to 0.720° with the V/III increasing from 500 to 2000. In contrast, along the c axis, the FWHM value increases from 0.220° to 0.251°. The opposite FWHM changes of two axes might result from the different migration lengths of the adatoms along the two directions. Because the nitrogen dangling bonds per unit along the

(0001) and ($\bar{1}100$) facets are 11.4 nm^{-2} and 6.1 nm^{-2}, respectively,[18] the difference in the number of nitrogen dangling bonds at the step edge for the two-crystal directions causes a difference in the migration length of gallium adatoms. The increase of FWHM values along the c axis might result from the lattice relaxation due to the formation of the voids in the GaN layer. In conclusion, the DCXRD results imply that a relatively high V/III ratio is effective to reduce the FHWM of XRC along the m axis but increases the XRC along the c axis.

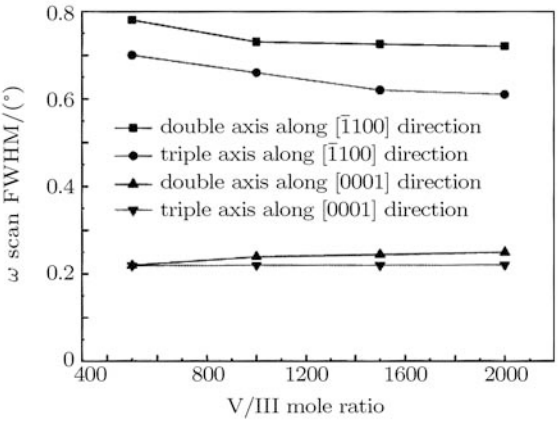


Fig. 4. FWHM values for XRD rocking curve, each as a function of V/III ratio.

Sample D has the most flat surface morphology and relatively good crystal quality. Double-axis and triple-axis XRD rocking curves are shown in Fig. 5(a). When the incident X-ray beam is parallel to the [0001] direction of the as-grown GaN film, the FWHM of the double axis rocking curve is 0.219° (791 arcsec), which indicates a reasonable quality of epitaxial film. The FWHM of the double axis rocking curve is only 89 arcsec broader than that of the triple axis rocking curve, which suggests that it has mosaicity rather than nonuniformity of strain of the as-grown films, which makes a dominant contribution to the broadening of the double axis rocking curve. In Fig. 5(b), when the incident X-ray beam is parallel to the [1$\bar{1}$00] direction, the FWHM of the double axis rocking curve is 0.757° (2725 arcsecs), which is much higher than that (1044 arcsecs) of the a-plane GaN film grown with only an HT-AlN buffer layer,[10] or that (1440 arcsecs) of the a-plane GaN film with only an LT-GaN buffer layer by MOCVD.[15] As for the triple-axis rocking curve in this direction, the FWHM of the triple-axis rocking curve is 0.702° (2527 arcsecs), which is 198 arcsecs lower than that of the double-axis of the as-grown sample. This result indicates that it is not only mosaicity but also nonuniformity of strain that makes a contribution to the widening of the double-axis rocking curve. In the same way, on a higher V/III ratio of the samples C, B, and A, the FWHM values of the double-axis rocking curve are higher than those of the triple-axis along both the c axis and the m axis, indicating that there is nonuniformity of strain along both of the two directions.

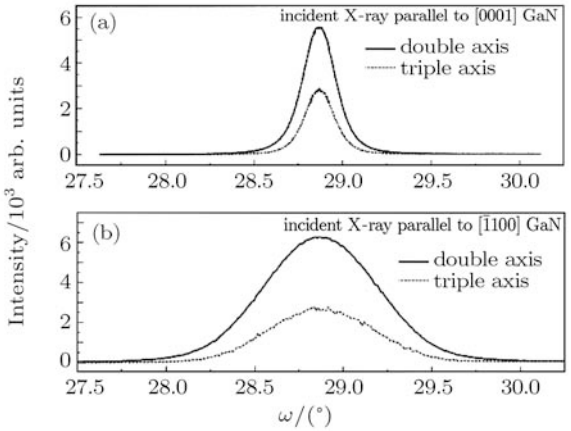


Fig. 5. Double-axis and triple-axis XRD rocking curves of sample D on-axis reflection with the incident beam parallel to (a) the GaN [0001] direction and (b) the GaN [$\bar{1}$100] direction.

4. Conclusions

The non-polar a-plane GaN on r-plane sapphire substrate is grown without a buffer layer by MOCVD and the effects of V/III ratio growth conditions are investigated. The AFM results show that the triangular pits are formed at a relatively high V/III ratio and a relatively low V/III ratio enhances the lateral growth rate along the c axis direction. The high V/III ratio leads to a high density of pits compared with the low V/III ratio and the surface morphology is improved greatly by using a low V/III ratio of 500. The RMS of the AFM of the sample is 3.9 nm. The HRXRD characterized crystal structural result implies that the FHWM of the XRC along the m axis decreases but the XRC along the c axis increases with the increase of the V/III ratio. Therefore, on a low V/III ratio of about 500, it is possible to make the a-plane GaN grow directly on r-plane sapphire substrates with flat surfaces and a relatively high crystal quality.

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