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Simulation and Growth Study of V/III Ratio Effects on HVPE Grown GaN

Hongyun Li[1,2], *Lei zhang*[1], *Yongliang Shao*[1], *Yongzhong Wu*[1,*], *Xiaopeng Hao*[1,*], *Haodong Zhang*[1], *Yuanbin Dai*[1], *Yuan Tian*[1]

[1] State Key Lab of Crystal Materials, Shandong University, Jinan, 250100, P.R. China
[2] The First Accessorial Junior High School of Shandong University, Jinan 250100, P.R. China
[*]E-mail: wuyz@sdu.edu.cn, xphao@sdu.edu.cn

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The influence of V/III ratio (pressure ratio of group V (N) to group III (Ga) species) on GaN growth using HVPE was investigated by simulation and experiment. The GaCl and NH_3 concentration on the substrate becomes uniform for the higher V/III ratio. The FWHM of the (002) and (102) peak both decrease as the V/III ratio increase. SEM and AFM results indicate that the increment of V/III ratio is in favor of forming a smooth GaN film surface. The intensity ratio of I_{YL}/I_{BE} decreases with the increase of V/III ratio. The FWHM of band-edge emission peaks decreases as V/III ratio increases. Higher V/III ratio improved crystalline and optical quality of GaN.

Keywords: V/III; Simulation; Hydride vapor phase epitaxy; GaN

1. INTRODUCTION

GaN is an important semiconductor material which has been widely used in electronic and optoelectronic devices due to its wide band gap and stability at high temperatures [1, 2]. However, GaN crystal is very difficult to obtain and it has been mainly grown on foreign substrates. GaN epitaxial layers have high dislocation densities (10^8-10^{10} cm^{-2}) due to the lattice mismatch and the difference in thermal expansion coefficient between GaN and the foreign substrate [3, 4]. The high dislocation density is harmful to the performance of optical and electrical devices. Therefore, high quality GaN crystal with low dislocation density is in great demand. It is known that growth conditions affect the quality of GaN epitaxial layers and V/III ratio is a very important parameter for GaN growth [5, 6]. Zhao et al. studied the effects of V/III ratio in the initial growth stage on the properties of GaN epilayers grown on low-temperature AlN buffer layers by metal-organic chemical vapor deposition (MOCVD) [7]. Liao et al. reported that the best quality GaN films grown by MOCVD were achieved at a higher V/III ratio with a quenched yellow luminescence and an enhanced near band edge photoluminescence emission [8]. However, there are few reports on the influence of the V/III ratio on the quality of GaN epilayers grown by hydride vapor-phase epitaxy (HVPE). In this paper, we investigate the influence of V/III ratio on NH_3 and GaCl flow distribution, surface morphological, structural and optical properties of HVPE grown GaN by simulation and experiment.

2. EXPERIMENTAL

The GaN films were grown in a home-made vertical HVPE reactor. Template with 5 μm GaN layer grown by MOCVD on Al_2O_3 substrates were employed as starting substrate. Ga and NH_3 were used as gallium and nitrogen source, respectively. HCl gas reacted with liquid Ga at 820℃ to form GaCl, which was transported to the growth zone of the reactor and reacted with NH_3 at 1030℃ to form GaN deposition on the substrate. N_2 was used as a carrier gas. The reactor pressure was kept around atmospheric pressure. In order to ensure a change of the V/III ratio, NH_3 flow rate is kept constant (1000 sccm) and HCl flow rate is 20, 50 and 100 sccm, respectively. The V/III ratio for different HCl flow rate is 50, 20 and 10, respectively.

The effect of V/III ratio on air flow distribution was investigated using a three-dimensional computational fluid dynamics (CFD).

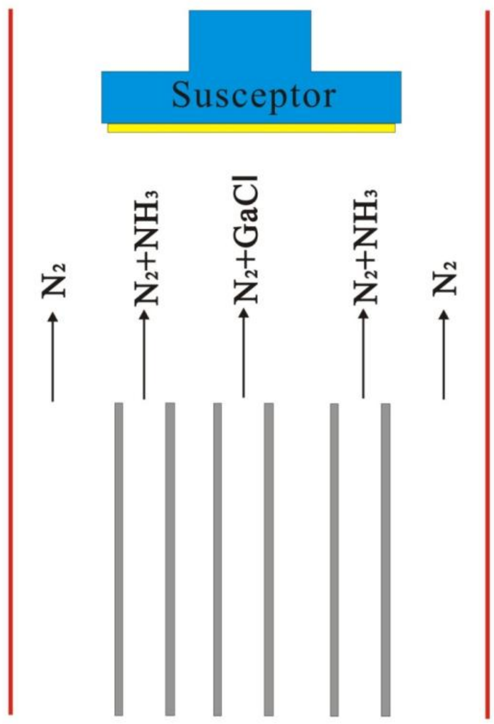

Figure 1. Schematic diagram of HVPE reactor profile

Fig.1 shows the schematic diagram of HVPE reactor profile. GaCl outlet is in the middle of reactor. NH_3 outlets are on the both sides of reactor. N_2 is used as carrier gas. The major assumptions for the simulation included constant susceptor temperature, convection-determined wall temperature, neglecting chemical reactions and thermal radiation, ideal gas and steady state.

The crystal quality of GaN films was characterized by high-resolution X-ray diffraction (HRXRD) using symmetrical (002) and asymmetrical (102) reflections. Scanning electron microscopy (SEM) images were taken with a Hitachi FESEM-4800 field emission microscope. AFM (Digital Instrument Dimension 3100) were used to investigate the surface morphology. Photoluminescence (PL) measurement was carried out at room temperature using 325 nm He–Cd lasers as excitation power.

3. RESULTS AND DISCUSSION

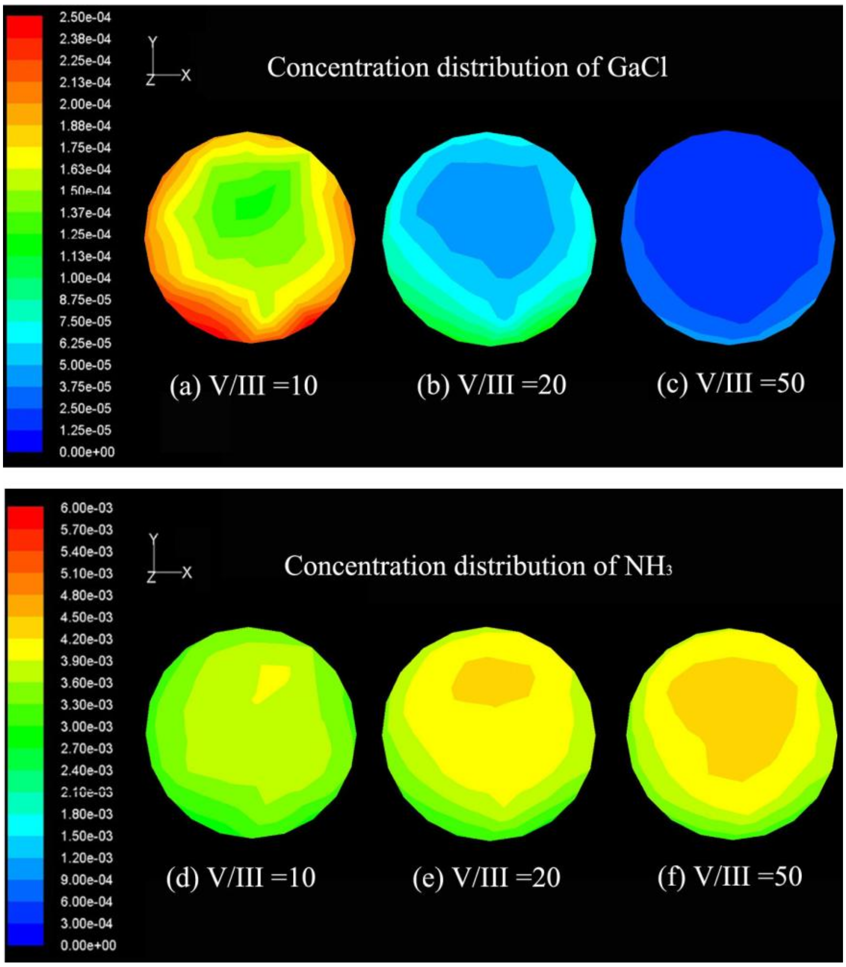

Figure 2. Simulation results of GaCl [(a) V/III =10 (b) V/III =20 (c) V/III =50] and NH_3 [(d) V/III =10 (e) V/III =20 (f) V/III =50] concentration distribution above the substrate with different V/III ratio (a) V/III =10 (b) V/III =20 (c) V/III =50

Fig. 2 shows the concentration distribution of GaCl and NH_3 on the substrate with different V/III ratio. The molar concentration of GaCl in the centre is lower than that near the edge on the substrate. The concentration distribution of NH_3 on the substrate is the reverse of GaCl. With increasing the V/III ratio, the molar concentration of GaCl on the substrate decreases while that of NH_3 increases. The GaCl concentration on the substrate becomes very uniform for high V/III ratio.

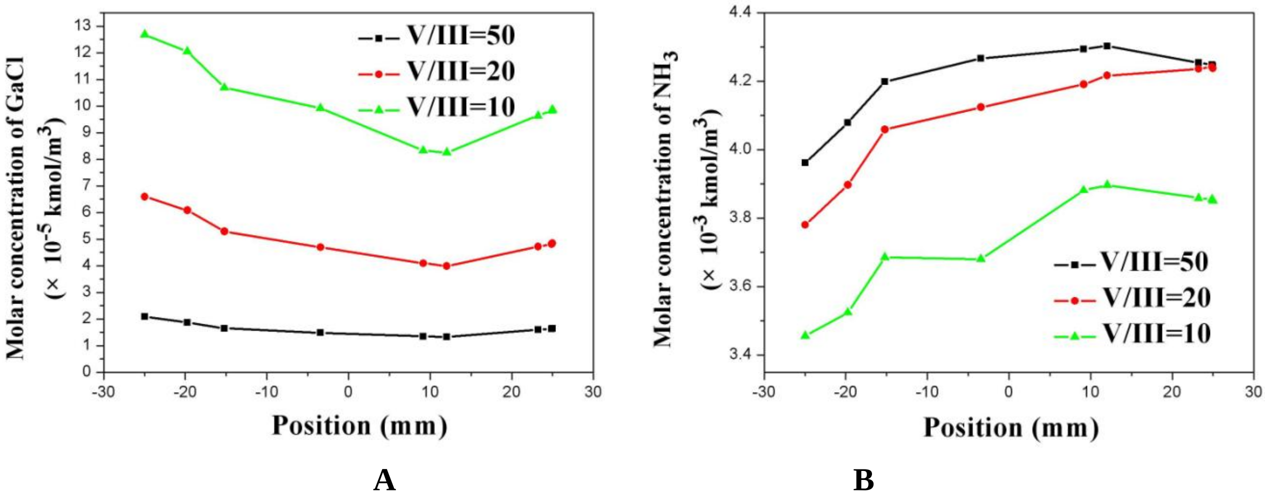

Figure 3. The molar concentration XY Plot picture of GaCl (a) and NH_3 (b) along the Y centerline of substrate

Fig. 3 illustrates the molar concentration XY Plot pictures of GaCl and NH_3 along the Y centerline of substrate. In Fig. 3a, the molar concentration of GaCl varies greatly and the range from 8.5×10^{-5} kmol/m^3 to 12.7×10^{-5} kmol/m^3 along Y centerline of substrate for a V/III ratio of 10. With increasing the V/III ratio, the variation of GaCl molar concentration along Y centerline of substrate becomes smaller. The molar concentration of GaCl becomes uniform and the range from 1.7×10^{-5} kmol/m^3 to 2.2×10^{-5} kmol/m^3 alone Y centerline of substrate when the V/III ratio is 50. As shown in Fig. 3b, the molar concentration of NH_3 increases as a result of increasing V/III ratio. All the molar concentration of NH_3 at different V/III ratio increases along the Y centerline of substrate. The change tendency is almost the same for NH_3. The uniform distribution of GaCl and NH_3 molar concentration on the substrate results in a uniform growth rate and better film properties [9-11]. Therefore, we predicted that increasing the V/III ratio will improve the properties of GaN films.

The crystal quality of GaN film was characterized by a HRXRD rocking curve. Fig. 4 depicts the ω-scans spectra of (002) symmetry planes and (102) asymmetry planes of GaN film grown under different V/III ratios. The full width at half maximum (FWHM) of (002) peak and (102) peak both decrease as the V/III ratio increases. For GaN film grown with V/III ratio of 50, the FWHM of (002) peak and (102) peak is 392 and 485 arcsec, respectively. The (002) plane rocking curves can be broadened by the screw or mixed dislocations, while (102) rocking curve can be broadened by all types dislocation including pure edge dislocations [12]. Previous studies has proven that the screw dislocation density and edge dislocation density are indirectly represented by the FWHM of HRXRD at (002) and (102) planes, respectively [13,14]. The narrow FWHM of (002) and (102) peak suggest that the dislocation densities are reduced as the V/III ratio increase. Therefore, we conclude that increasing the V/III ratio can effectively improve the crystal quality of the GaN.

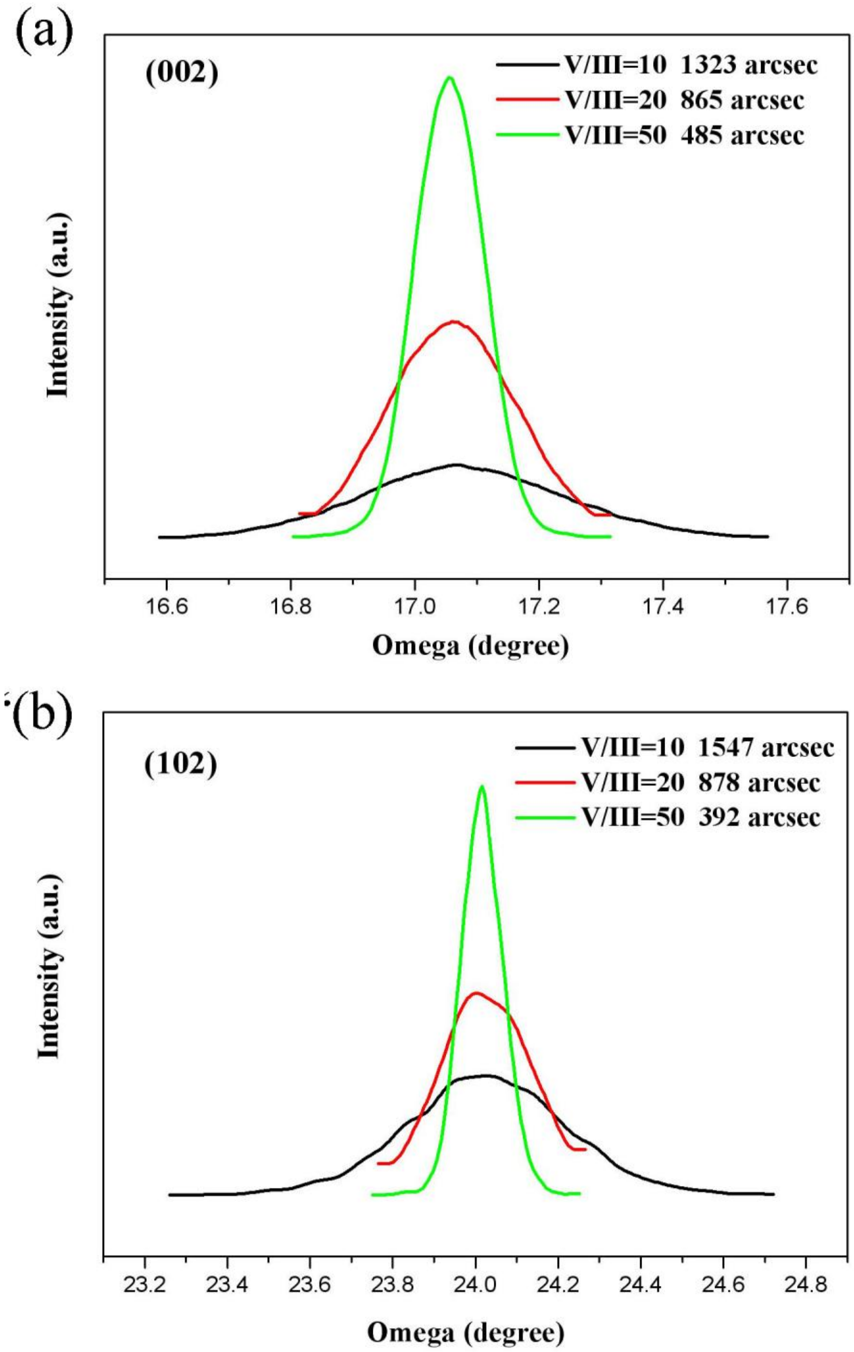

Figure 4. ω-scans spectra of (002) symmetry planes and (102) asymmetry planes of the GaN film grown under different V/III ratios.

SEM and AFM observations were performed to investigate the influence of the V/III ratio on the surface morphology of GaN layers. Fig. 5 shows the surface morphology of GaN films with different V/III ratio measured by SEM. When the V/III ratio is 10 (Fg. 5(a)) the surface is very rough and many dark dots are observed. With increasing the V/III ratio (V/III=20), the surface becomes smooth (Fg. 5(b)). The density of dark dots decreased.

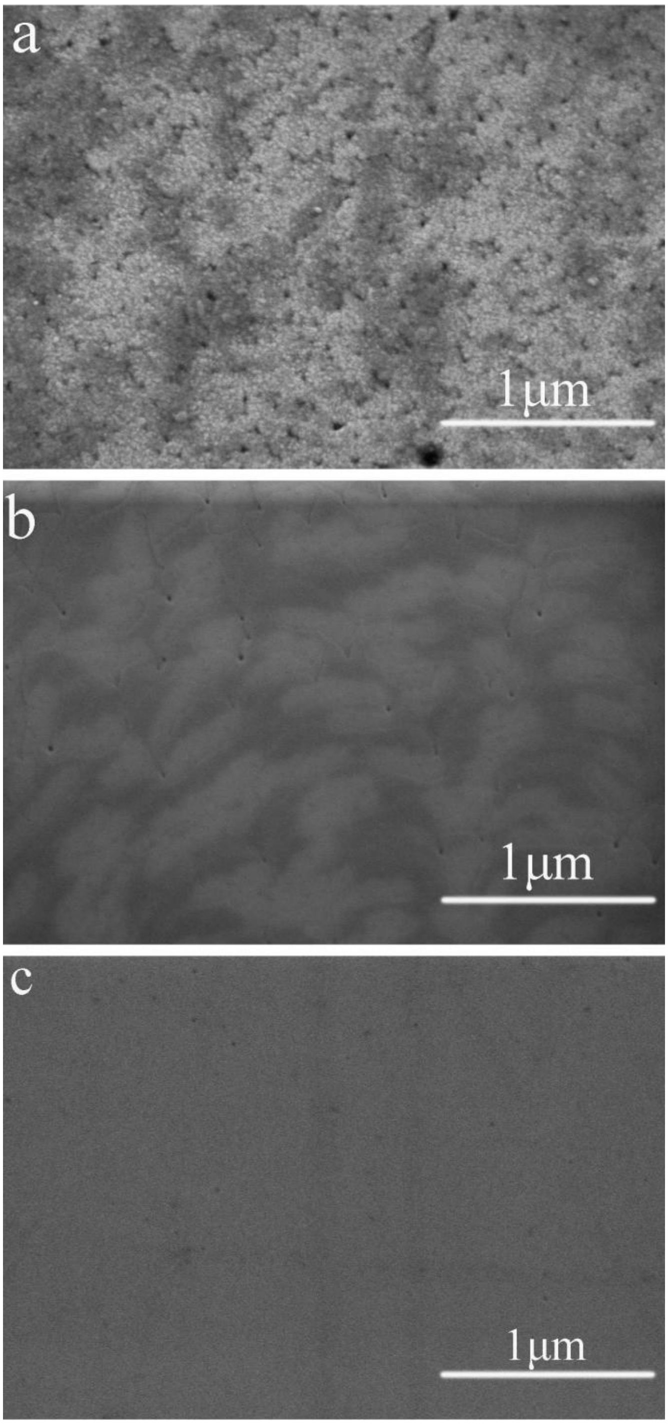

Figure 5. SEM images of GaN film with different V/III ratio (a) V/III =10 (b) V/III =20 (c) V/III =50

Further increasing the V/III ratio to 50, the surface is very smooth and only a few dark dots are observed (Fg. 5(c)). The surface morphology is improved by increasing the V/III ratio. Fig. 6a-c shows the 5μm×5μm area AFM images of GaN layers grown with V/III ratio of 10, 20 and 50, respectively. The lower V/III ratio reduces the nuclei density and promotes the three-dimensional (3D) growth mode [15]. Therefore, many island protuberances are observed when the V/III ratio is 10 (Fig. 6(a)).

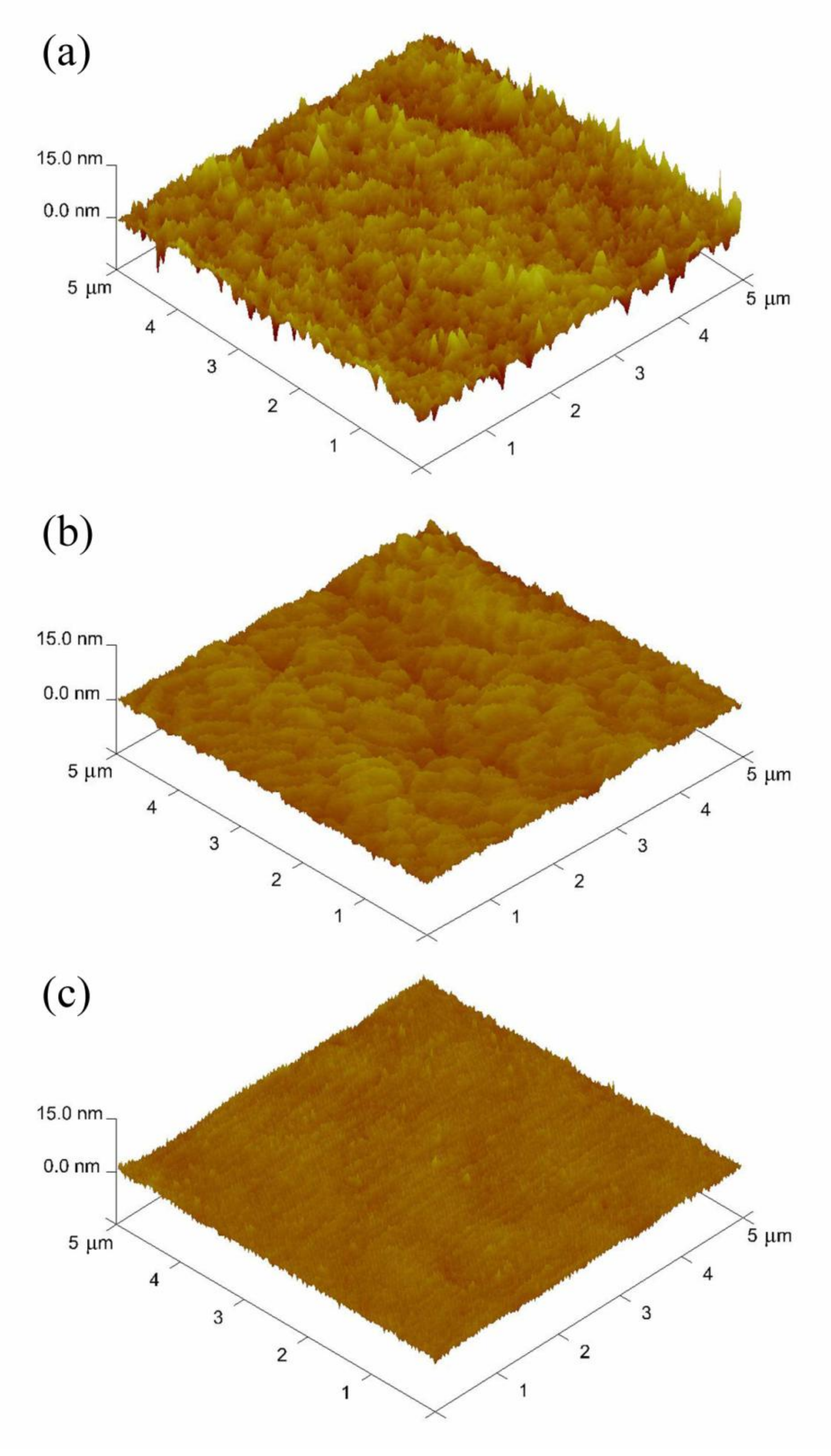

Figure 6. 5μm×5μm AFM images of GaN layers grown with V/III ratio of 10 (a), 20 (b) and 50 (c), respectively.

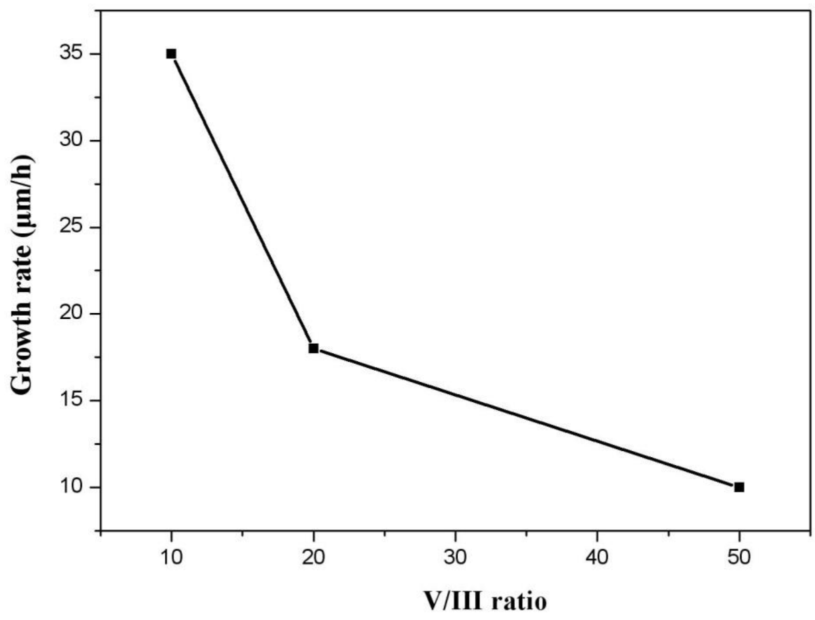

Figure 7. Growth rate of GaN films as a function of the V/III ratio.

When the V/III ratio is increased to 20 (Fig. 6(b)), the surface of GaN film consists of well-defined terraces. The surface morphology of GaN films with a V/III ratio of 50 (Fig. 6(c)) becomes very smooth and exhibits the best morphology among the three samples. The root-mean-square (RMS) roughness decreases from 1.850 nm to 0.818 nm with the increasing of V/III ratio, indicating an improvement of surface quality. The increment in V/III ratio is in favor of forming a smooth GaN film surface [8].

The dependence of growth rate of GaN on the V/III ratio is also investigated. Fig. 7 shows the growth rate of GaN films as a function of the V/III ratio. It can be seen that the growth rate decreases when the V/III ratio increases. In this paper, NH_3 flow rate is kept constant and HCl flow rate is changed. The growth rate is determined by the concentration of GaCl and it varied linearly with GaCl partial pressure [9]. Therefore, it is the lower growth rate in the GaN films grown with a higher V/III ratio.

Fig. 8a shows the PL spectra of GaN films grown with different V/III ratio measured at room temperature. The band-edge emission peaks at 3.42 eV and the yellow luminescence band at 2.1-2.5 eV are observed. The intensity ratio of the yellow luminescence band to band-edge emission (I_{YL}/I_{BE}) is strongly related to the dislocation densities [16]. The intensity ratio of I_{YL}/I_{BE} decreases with the increase of V/III ratio. The results indicate that the dislocation densities of GaN decreases with the increase of V/III ratio which is consistent with the HRXRD results. Fig. 8b shows the FWHM of band-edge emission peaks as a function of V/III ratio for GaN films. It is shown that the FWHM of band-edge emission peaks are in the range of 39.16-46.36 meV, and the value decreases as V/III ratio increases. Therefore, it can be concluded that the crystalline and optical quality of GaN film grown with higher V/III ratio is improved.

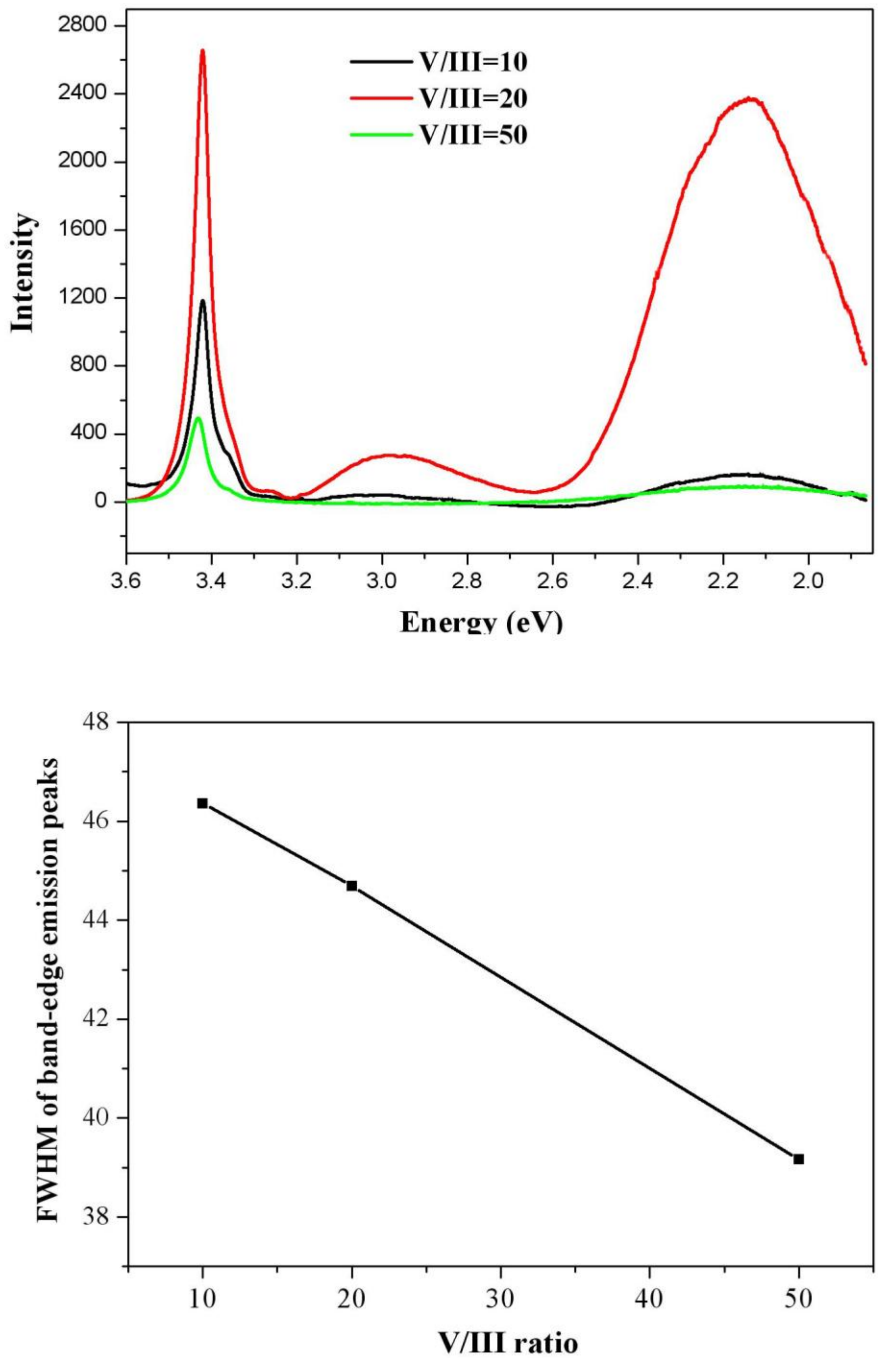

Figure 8. (a) The PL spectra of GaN films grown with different V/III ratio measured at room temperature. (b) The FWHM of band-edge emission peaks as a function of V/III ratio for GaN films.

4. CONCLUSIONS

The effect of V/III ratio on the growth of GaN with HVPE in a vertical reactor was studied. The simulation results show that the molar concentration of GaCl on the substrate decreases while that of NH_3 increases as increasing the V/III ratio. The molar concentration of GaCl on the substrate becomes very uniform when the V/III ratio is 50. SEM and AFM results indicate that GaN samples with higher V/III ratio have better surface morphology. The best quality GaN films were achieved under a V/III ratio of 50. The growth rate decreases as the V/III ratio increase. The PL spectra indicate that the optical quality of GaN film is improved with higher V/III ratio. These results confirm that increasing the V/III ratio could effectively improve the crystalline and optical quality of GaN films.

ACKNOWLEDGEMENTS
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