REVIEWS

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# The fabrication of AlN by hydride vapor phase epitaxy

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**Abstract:** Aluminum nitride (AlN) is the promising substrates material for the epitaxial growth of III-nitrides devices, such as high-power, high-frequency electronic, deep ultraviolet optoelectronics and acoustic devices. However, it is rather difficult to obtain the high quality and crack-free thick AlN wafers because of the low surface migration of Al adatoms and the large thermal and lattice mismatches between the foreign substrates and AlN. In this work, the fabrication of AlN material by hydride vapor phase epitaxy (HVPE) was summarized and discussed. At last, the outlook of the production of AlN by HVPE was prospected.

**Key words:** hydride vapor phase epitaxy; aluminum nitride; templates; free standing substrate

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## 1. Introduction

Aluminum nitride (AlN) is one wide band gap semiconductor (up to 6.2 eV) with high-electrical resistivity (approximately $10^{10}$ Ω·cm), high coefficient of heat conductivity (3.2 W/(cm·K)), excellent acoustic wave velocity and good tolerance to chemical environments[1, 2]. The thermal expansion coefficients and lattice constants of AlN is similar to those of GaN. Therefore, AlN can be used as substrates for the epitaxial growth of AlGaN alloys with large Al content with the unique advantage than other foreign substrates. Hence, it is the most suitable substrates material for AlGaN/GaN high-electron mobility transistor seems[3], ultraviolet laser diodes and AlGaN-based deep ultraviolet light-emitting diodes (DUV-LED)[4–9]. Currently, the deep ultraviolet LED with small size, high brightness, high luminous efficiency and environmental protection features[10–15], is the ideal substitute for mercury lamp.

Though many achievements have been obtained on the research of AlN, more and more efforts should be put into the development of AlN crystal quality. In addition, it is rather difficult to obtain the high quality thick AlN wafers with crack-free and large size because of the large thermal and lattice mismatches between the foreign substrates and AlN. It was well known that the dislocation was disadvantageous to the internal quantum efficiency of deep ultraviolet devices[16]. Many growth techniques have been applied to increase the crystal quality of AlN, such as flux/solution growth[17, 18] including ammonothermal method[19] and physical vapor transport (PVT) seeded sublimation method[20–24], metalorganic chemical vapor deposition (MOCVD) growth including migration-enhanced MOCVD (MEMOCVD) method, modified MEMOCVD method, flow-modulation MOCVD method, nano-patterned sapphire substrates method, nano concavo–convex sapphire substrate method[25–31] and so on.

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Actually, AlN free-standing substrates have been obtained by PVT seeded sublimation method and the dislocation density is the lowest compared with other methods. However, the transmittance of deep ultraviolet light of AlN substrate grown by PVT was very low currently. Compared with above growth methods, hydride vapor phase epitaxy (HVPE) has many advantages, such as the simple equipment, the rapid growth rate, uniformity in large-area and low density of impurity, which make HVPE become the most perspective practical method for AlN substrates. In this paper, the recent results on the preparation of AlN by HVPE were summarized and discussed.

## 2. AlN growth by HVPE: Theory

HVPE is a promising method for growth of III-nitrides. It had been used to manufacture commercial 2-inch and 4-inch GaN substrates[32]. Generally, the HVPE reactor have two heated zones: the feedstock zone and the growth zone, which are independently heated[33]. First of all, the gaseous sources will be obtained by chemical reaction when HCl gas flows over metal sources at low-temperature feedstock zone. The mixture gases ($H_2$ and $N_2$) are used as carrier gas. Ammonia gas is used as N source and group-III nitrides will be grown at high-temperature growth zone.

However, the chemical nature of intermediates in AlN growth is extremely complex compared to GaN growth. Fig. 1 shows the gas phase during the growth which contains a huge number of chemical species[34]. The Gibbs energy for different chemical reactions have been presented by computational analysis and experiments. According to the thermodynamics theoretical calculation and experimental, Timoshkin *et al.* proved that the $AlCl_3NH_3$ (g) formed AlN (s) and HCl (g) at the temperature above 900 K or so. On the opposite, the $AlCl_3NH_3$ (g) formed the AlCl (g), HCl (g), $N_2$ (g) and $H_2$ (g), which were more stable than solid AlN in the temperature range above 1400 K. Therefore, the AlN would be formed at the temperature 900 K and ceased above 1400 K.

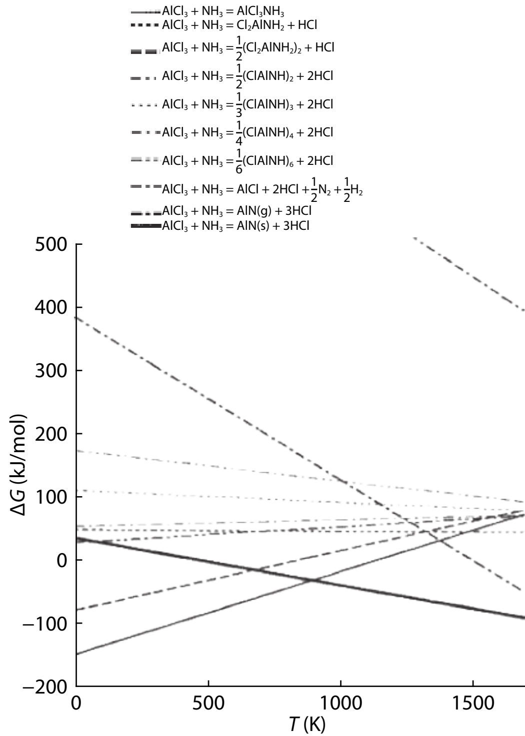


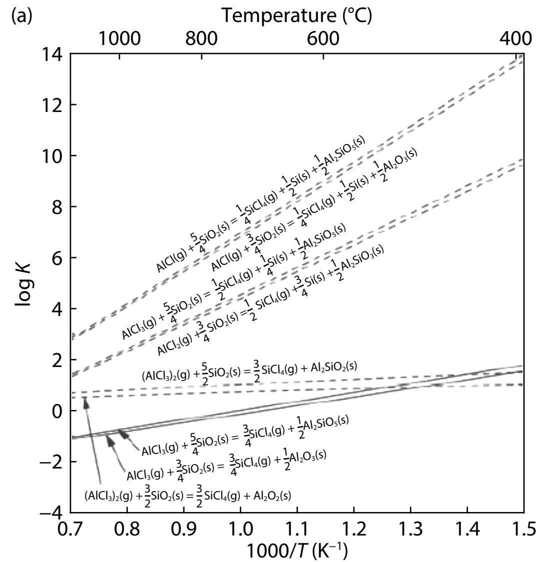

Fig. 1. Gibbs energy diagram for different chemical species during the growth AlN grown by CVD[34].

Generally, the HVPE system has a quartz reactor. However, as is widely known, the quartz ($SiO_2$) react with AlCl at high growth temperature, which will damage the quartz reactors and induce pollution for AlN growth. Fig. 2(a) shows the chemical reaction between the values of $K_i$ and the change of temperature[35]. The $K_i$ is defined as the thermodynamically feasible reactions equilibrium constants. The chemical reaction will be stop when it is negative. Kumagai *et al.* proved that the $K_i$ of chemical reaction between AlCl and quartz was very large. However, the $K_i$ of chemical reaction between $AlCl_3$ and quartz was the smallest. Besides, it would became negative at the temperatures higher than 700 °C. Fig. 2(b) shows the relationship between the temperature and the partial pressures. The partial pressure of $AlCl_3$ is as much as 100 times than AlCl at the temperature of 500 °C. Thus, the temperature of the source-zone could be fixed at approximately 500 °C.

## 3. AlN growth by the low-temperature HVPE: Exploration

HVPE has the advantage of high growth rate, compared with other CVD methods. In the incipient stage, most of researcher focused on the fabrication of thick AlN substrates. Fig. 3 shows the schematic diagram of low-temperature HVPE growth equipment[36]. It is horizontal hot-wall reactor. The heating system consisted of two parts: the left part was growth zone and the right part was source zone. The carrier gas was Ar. The temperature of growth zone for AlN was limited to a narrow range from 700 to 1200 °C.

There have been many reports about thick AlN substrates grown by HVPE with high growth rate. In 2000, Nikolaev *et al.* fabricated the AlN wafers up to 3 × 3 $cm^2$ with thickness of 0.05 to 1 mm using HVPE technique, as shown in Fig. 4(a)[37]. In 2001, Melnik *et al.* used HVPE technique to fabricate 0.1 to 0.5 mm thick AlN on SiC[38]. In 2003, Melnik *et al.* fabricated single crystal AlN and the diameter of AlN was up to 1.75-inch with 0.3 mm thick shown in Figs. 4(b) and 4(c)[39]. In 2005, Kovalenkov *et al.* obtained 2-inch AlN freestanding wafers with thickness of 75 $\mu$m [shown in Fig. 4(d)[40]].



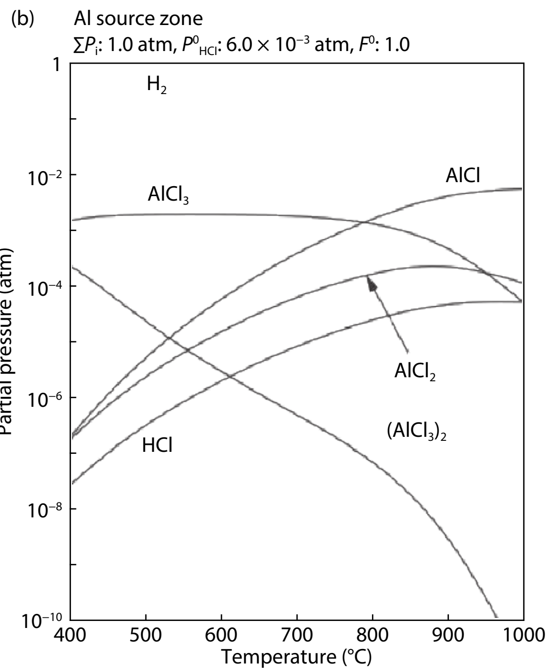




Fig. 2. (a) The chemical reaction between the values of $K_i$ and the change of temperature. (b) The relation between temperature and partial pressures[35].

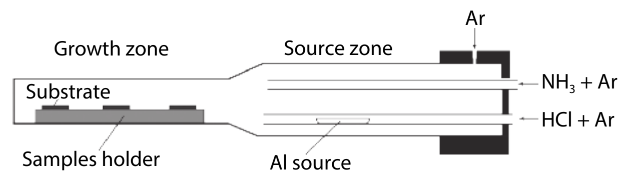



Fig. 3. The schematic diagram of low-temperature HVPE equipment[36].

However, few people clarified the influences of growth principles on the quality of AlN layers. In the references, the thick AlN films usually had a rough surface and poor quality.

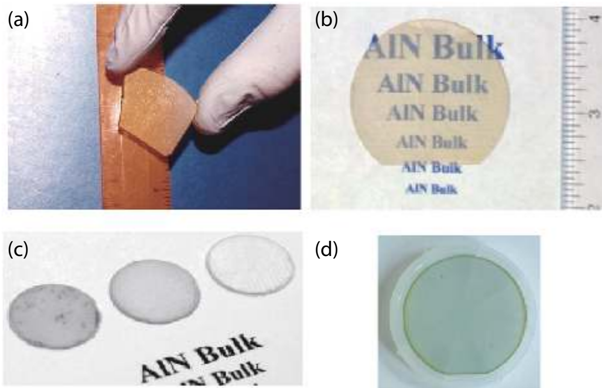



Fig. 4. (Color online) The photo of thick AlN substrates: (a) the free-standing AlN wafer[37], (b) and (c) the 1.75-inch and 1-inch diameter AlN wafers[39], and (d) 2-inch 75 μm AlN wafer[40].

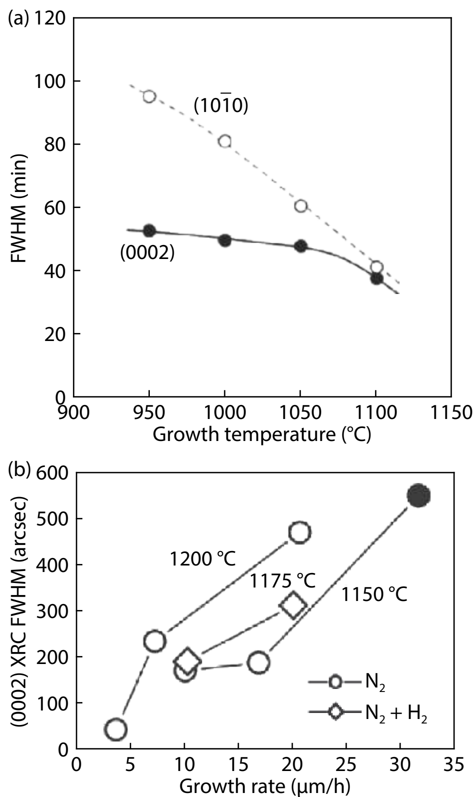



Fig. 5. (a) The double crystal XRC-FWHM values of (0002) and (10$\bar{1}$0) planes for AlN films grown from 950 to 1100 °C[41], (b) the relationship between XRC-FWHM values of AlN (0002) rocking curves and growth rates at temperatures of 1150, 1175 and 1200 °C[42].

Subsequently, most of researcher focused on the effect of substrates and growing conditions. In 2002, Ledyaev *et al.* investigated the effect of growth temperature on the surface morphology and the crystalline quality of the AlN layers on 6H-SiC (0001) by HVPE[36]. They proposed that the layers grown at 900 °C had the best morphological and structural characterisitics.

Subsequently, many researchers reported the results that the crystalline quality of AlN would be improved by raising the growth temperature[41–43]. Fig. 5(a) shows the double crystal X-ray rocking curves (XRC) with full-width at half-maximum (FWHM) values of (0002) and (10$\bar{1}$0) planes for AlN films grown from 950 to 1100 °C; Fig. 5(b) shows the relationship between XRC-FWHM values of AlN films (0002) and growth

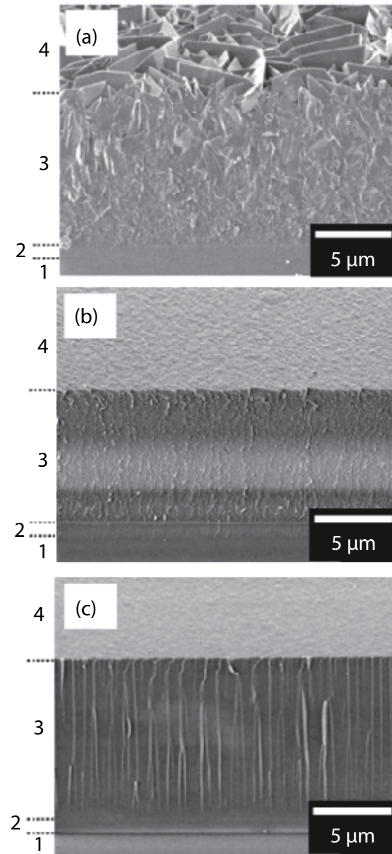



Fig. 6. The SEM cross-section images of AlN films at temperatures (a) 1100, (b) 1150, (c) 1200 °C[42].

rates at temperatures of 1150, 1175 and 1200 °C. It was found that the XRC-FWHMs values of (0002) and (10$\bar{1}$0) would be decreased by raising the growth temperature. Besides, From the Fig. 5(b), the XRC-FWHM value was lower when the growth rate was lower. In other words, the high quality AlN films could be obtained when the growth rate was lower because of the temperature limiting to 1200 °C. It seems that the low growth rate is beneficial for the improvement of AlN crystal quality.

The surface morphology also improved by raising the growth temperature. Figs. 6(a)–6(c) shows the scanning electron microscope (SEM) images of AlN films grown at temperatures of 1100, 1150 and 1200 °C, respectively. The characteristics of AlN were poly-structures (Fig. 6(a)), flat structures (Fig. 6(b)) and very flat structures (Fig. 6(c)). Obviously, the higher growth temperature resulted in higher crystal quality.

In 2016, Zhang *et al.*[44] reported the influence of the initial growth condition of AlN thin films grown on various substrates by the low-temperature HVPE. The substrates include 6H-SiC, GaN/sapphire templates and sapphire. The thickness of AlN thin films was around 200 nm. It was easy to achieve high-quality AlN films grown on GaN/sapphire and 6H-SiC substrates at 1000 °C. The different results on different substrates were explained by the lattice mismatch between the substrates and epilayers. However, at the initial growth stage, the morphology of AlN films was randomly distributed 3D islands. Fig. 7 shows the atomic force microscopy (AFM) images of the surface morphology of the initial growth stage of AlN grown by HVPE[45]. When the growth time was 10 min (the thickness around 50 nm), the surface was dominated by hexagonal-prism-shaped islands. As the growth time in-

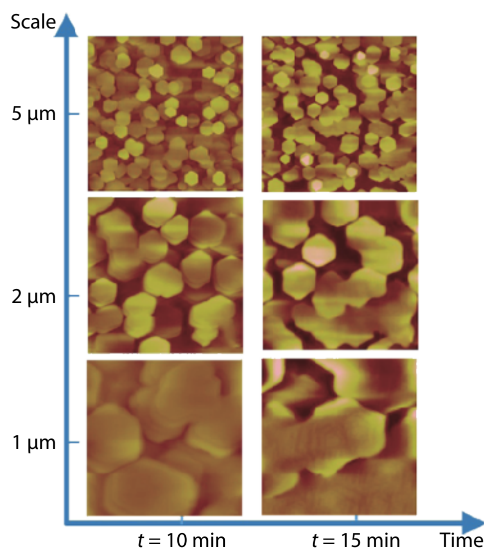



Fig. 7. (Color online) The surface morphology of AlN grown at initial stage[45].

creased to be 15 min, the islands tended to be coalescent.

The AFM images changed as the thickness increased. Figs. 8(a)–8(c) show the surface morphology of AlN with thickness of 390, 650 and 1200 nm, respectively. The RMS was measured to be 3.1, 3.5 and 4.2 nm for Figs. 8(a), 8(b) and 8(c), respectively. The result indicated that considerable improvement in the quality of AlN films could be produced by HVPE.

The migration of Al atoms will influence the quality and the growth rates. The lower atomic mobility, the worse quality. Moreover, the temperature of HVPE growth zone was limited to 1200 °C. In order to increase the crystalline quality and the growth rate, high temperature is required. The migration of chemical species adsorbed on growth surface can be promoted with increasing growth temperature. Then, the Al atoms are easily accommodated to the appropriate site for epitaxial growth. Therefore, the high growth temperature is essential to grow the high-quality AlN.

## 4. AlN growth by the high-temperature HVPE: Technology

When the temperature of hot-wall HVPE system is above 1200 °C, the quartz tube and reactors will be softened. However, the lower migration of Al adatoms n growth front induced by low growth temperature led to poor-quality of AlN films[26]. In order to promote the surface migration of Al adatoms, the high-temperature HVPE (HT-HVPE) has been designed for AlN growth. The HT-HVPE has a special advantage that the growth zone temperature is below 1000 °C, but the temperature of substrates can be above 1450 °C.

### 4.1. HT-HVPE

Generally, there were three methods to get the growth temperature above 1450 °C without softening the quartz tube. The first was using high-power lamp to heating the carbon susceptor, as shown in Fig. 9(a)[46]. In this schematic, only the temperature of substrate region can be heated above 1450 °C without softening the quartz tube. However, all the light should be focused on one plane to keep the uniformity of temperature, which make a greater requirement for the light reflector. The second was induce heating, as shown in

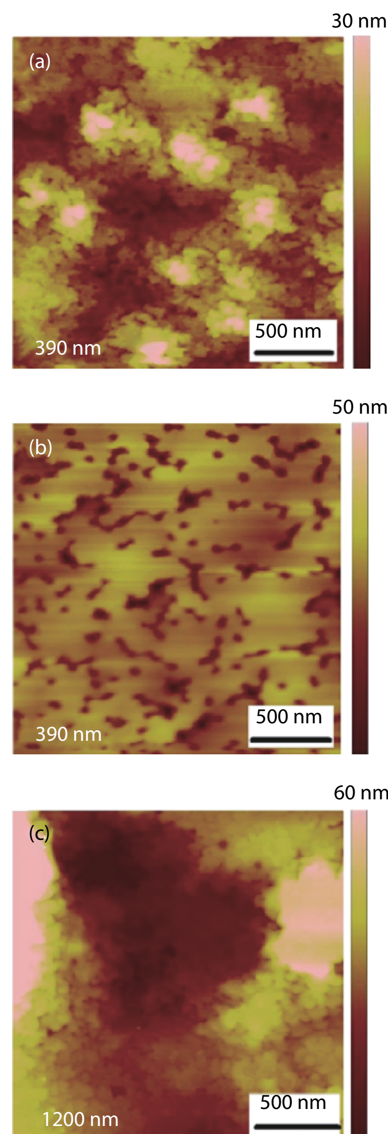



Fig. 8. (Color online) The AFM pictures of AlN with various thickness (a) 390, (b) 650, (c) 1200 nm grown on sapphire substrates[44].

Fig. 9(b)[47]. The vertical HT-HVPE system consists of a rotating graphite susceptor heated by induce current in a vertical water-cooled cold-wall reactor. The deposition temperature was measured on the susceptor surface using a dual wavelength pyrometer and the deposition temperature was enabled to 1800 °C[47, 48]. The mainly challenges for manufacturing HT-HVPE instruments is aslo the huge number of chemical issues and unintentional Si doping[35]. The vertical cold-wall HT-HVPE is easier contaminated due to vertical structural design, the complex easily falls to the surface of the substrate. The third method was to add an internal heating part to increase the local temperature of substrate in conventional horizontal hot-wall HVPE system, as schematically shown in Fig. 9(c). The growth zone temperature is kept at low temperature by heating the hot-wall electric furnace. Additionally, a resistance heating susceptor is set in the quartz reactor and directly heated the substrates[41, 49]. The combination of the two heating systems enable to heat the substrates up to high temperature. In this method, the complex fallen to the surface of substrate could be avoided.

Using of the HT-HVPE system, AlN films with high crystalline quality have been obtained. Besides, the growth rate is

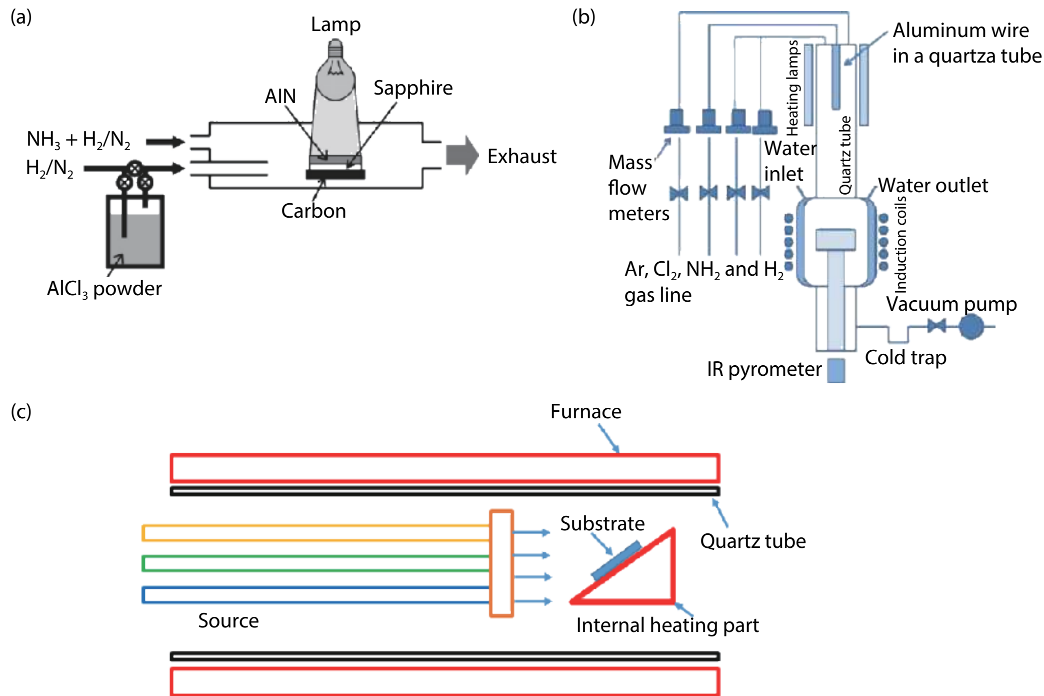



Fig. 9. (Color online) (a) Schematic diagram of the HT-HVPE system with high-power lamp[46]. (b) The vertical cold-wall HT-HVPE system with induce heating method[47]. (c) The conventional HVPE system with internal heating part.

Fig. 10. (Color online) Nomarski micrographs of AlN layers: (a) directly growth, (b) two-step (c) three-step[54].

significantly enhanced compare to low temperature HVPE system. Based on the GaN growth techniques, for example, step-growth using buffer layers[50], epitaxial lateral overgrowth (ELOG)[51] and templates with low temperature protective or nucleation layer[52, 53], are able to apply for obtaining the high quality AlN crystals, high quality AlN can be achieved.

### 4.2. Step-growth technique

In 2007, Nagashima *et al*. reported the results of AlN grown on sapphire substrate by HT-HVPE using step-growth technique. The temperatures for the growth were above 1200 °C and the rate of growth reached 57 $\mu$m/h[54]. Fig. 10 shows nomarski photograph of AlN layer with difference step-growth technique. The surface morphology showed huge hexagonal islands, hillock texture and mirror-like for direct, two-step and three-step growth, respectively. The smooth surface of AlN films can be obtained using three-step growth technique. All those facts verify that step-growth technique is help to improve the crystal quality and to improve surface morphology.

In 2017, Su *et al*.[55] used the transmission electron microscopy (TEM) technique to investigate the dislocation evolution in AlN films using step-growth technique. They provided plentiful details about dislocation evolution of AlN films. Because of lattice mismatch between two layers, high-density mixed dislocations formed at initial growth, shown in Figs. 11(a) and 11(b). Subsequently, the dislocation reduced by forming dislocation loops and bending using step-growth technique. The simplified model of step-growth technique was suggested, as shown in Figs. 11(c) and 11(d). The density of dislocations was significantly reduced by inter-reaction with bending and gathering to the centers through the step-growth technique.

### 4.3. AlN templates with low temperature protective or nucleation layer

The initial growth stage is critical for high-quality AlN growth. In 2007, Akiyama *et al*. proved that *c*-plane sapphire could be easily decomposed at temperature over 1200 °C in $H_2$ gas[56]. The interface between sapphire and epitaxial layer will form various pits and then reduced the crystal quality of AlN epitaxial layer. In order to avoid the chemical etching, AlN templates with low temperature protective or nucleation layer using high temperature HVPE have been proposed.

The nucleation layers act as a buffer layer not only protect the sapphire substrate but also reduce the lattice mis-

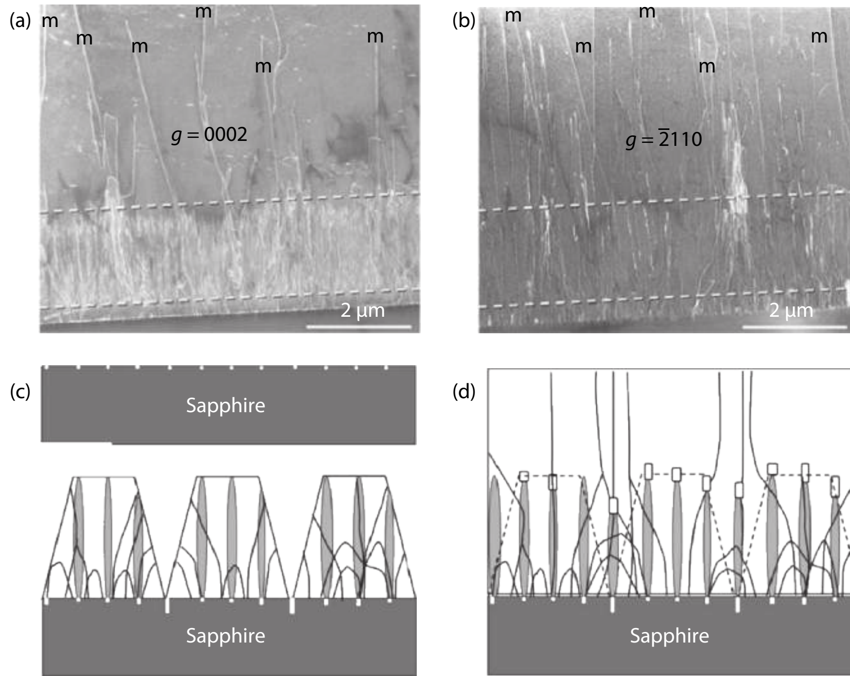



Fig. 11. The TEM images of the AlN films: weak beam dark field (a) $g = 0002$ and (b) $g = \bar{2}110$. (c) and (d) The schematic diagram of dislocation evolution by step-growth technique[55].

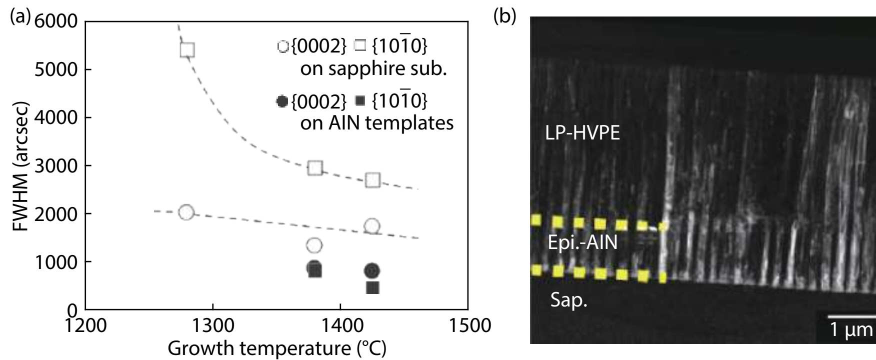



Fig. 12. (Color online) (a) The XRC-FWHMs values of AlN films grown on AlN templates and sapphire substrates without nucleation layers[55]. (b) Dark-field TEM image of dislocation evolution in AlN grown on AlN/sapphire templates with $g = (11\bar{2}0)$[58].

match between sapphire substrates. It is expected to have the parameters include the appropriate thickness, the largest nucleation islands size as well as the lowest islands density[57]. The crystalline quality of AlN films can be improved by the optimization of growth conditions. As shown in Fig. 12(a), the XRC-FWHMs values of AlN films grown on AlN/sapphire templates and sapphire without nucleation layers[54]. Obviously, the crystal quality became better with enhancing the growth temperatures. At the same high temperature, the crystal quality of AlN epilayer grown on AlN/sapphire templates was better than that grown on sapphire without nucleation layer. Fig. 12(b) shows the dark field TEM picture of dislocation evolution grown on AlN/sapphire template. The density of dislocations decreased through the nucleation layers.

The surface morphology at different growth temperature on sapphire with nucleation layers were also studied. In 2007, Tsujisawa *et al.* studied the influence of the temperature on the surface morphology of AlN epilayers grown by HVPE[58]. Fig. 13 shows the AFM images of AlN grown at various temperatures. The growth mode evolved to layer-by-layer as the growth temperature increased and clear atomic steps were observed when the growth temperature was more than 1400 °C, as shown in Figs. 13(c) and 13(d).

In 2008, Tajima *et al.* investigated the influence of thin nucleation layers for the grown AlN layers by HVPE[59, 60]. It was fund that the thin nucleation layers protected the sapphire substrate from the chemical corrosion at high temperature with $H_2$ gas. As a result, the crystal quality was improved. Subsequently, in 2012, Balaji *et al.* used low temperature nucleation layers for the growth of AlN films epilayer by HVPE[61]. It was fund that the crystal quality and surface morphology improved when enhancing the deposition temperature from 650 to 850 °C for nucleation layers. Besides, the preferred orientation of AlN epilayers was [0001] when the growth temperature of nucleation layers was 850 °C. On the contrary, the polycrystalline structure with a $[10\bar{1}1]$ preferred orientation would be obtained when the growth temperature of nucleation layers was 650 °C, as shown in Fig. 14. In 2016, Miyake *et al.* successfully obtained the highest crystal quality AlN

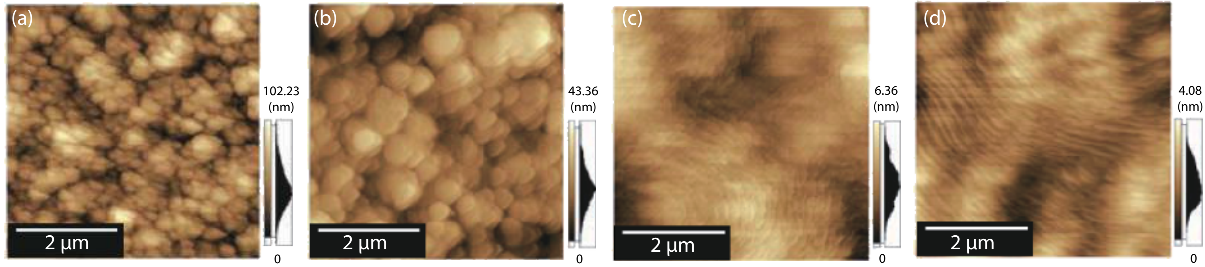



Fig. 13. (Color online) The AFM images of AlN grown at different temperatures: (a) 1150, (b) 1200, (c) 1400, and (d) 1450 °C[58].

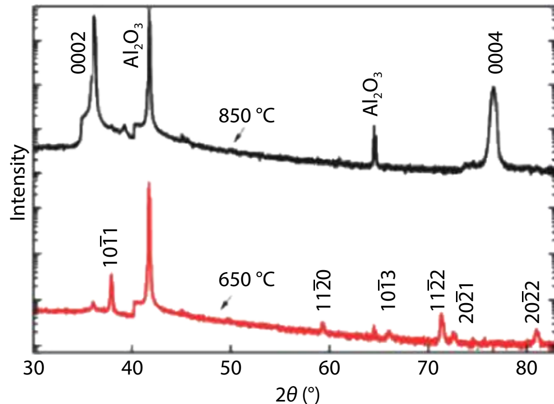



Fig. 14. (Color online) The XRD $\theta$–$2\theta$ scans of AlN nucleation layers grown at 850 and 650 °C[61].

films with (0002) and (10$\bar{1}$2) XRC-FWHMs values of 16 and 154 arcsec, respectively, by high temperature annealing techniques in $N_2$–CO gas[62].

In 2017, the dislocation evolution in AlN films using different kind of buffer layers was studied by TEM[63, 64]. Figs. 15(a)–15(c) show the dark field TEM pictures for three samples with different buffer layers. The cross section TEM images were composed of three regions named region I, II and III, which represented dislocation formation zones, growth mode changing zones and dislocation reaction zones, respectively. In the buffer layer belonged to region I with the highest density of dislocations. When the growth mode changed, the dislocation density rapidly decreased via dislocation inclination. In region III, the density further decreased where the inclination of dislocations promoted dislocation annihilation by forming dipoles half-loop. By controlling the growth buffer layers conditions, high quality AlN films could be obtained.

### 4.4. The epitaxial lateral overgrowth (ELOG) technique

The ELOG technique was successfully used in the growth of GaN with the low dislocation density in 1997[51]. Based on the previous studies of III-nitrides, the ELOG technique was also helpful to reduce the dislocation density of AlN templates[65]. Fig. 16 shows the schematic diagram of dislocation evolution by ELOG technique. The grooving technology provided partial dislocations and reduced the dislocation density of epitaxial layer. High quality AlN films have been reported using different ELOG techniques.

In 2009, Okumura *et al.* obtained crack-free AlN by HVPE on patterned AlN/sapphire templates[66], as shown in Fig. 17(a). The optical microscopy pictures of surface showed very smooth without cracks. For reference, the surface of AlN grown on flat sapphire was also shown in Fig. 17(b), in which high-density and large cracks were observed. 6H-SiC is also one suitable substrate for the growth of AlN and the thermal expansion coefficient of 6H-SiC is smal-

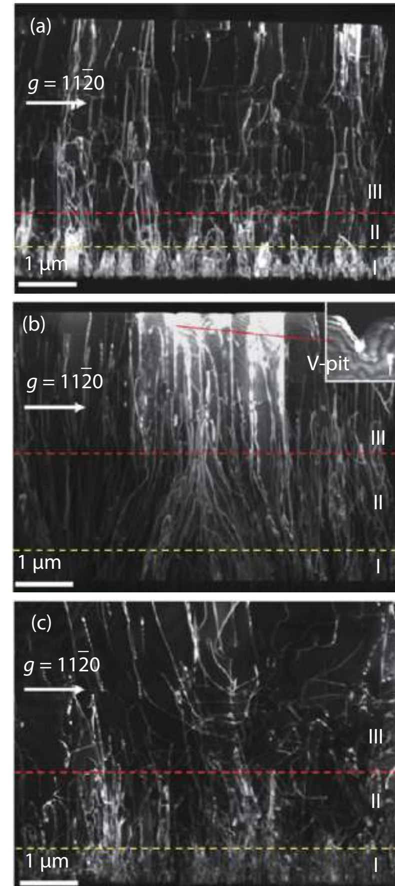



Fig. 15. The dark field TEM images for AlN epilayer grown with buffer layers, $g = 11\bar{2}0$[63].

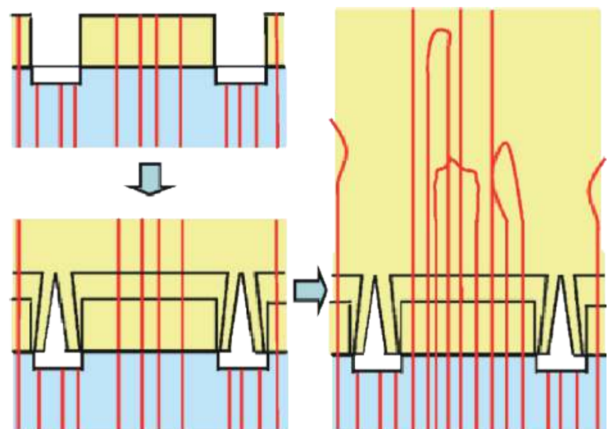


Fig. 16. (Color online) The schematic diagram of dislocation evolution by ELOG technique[65].

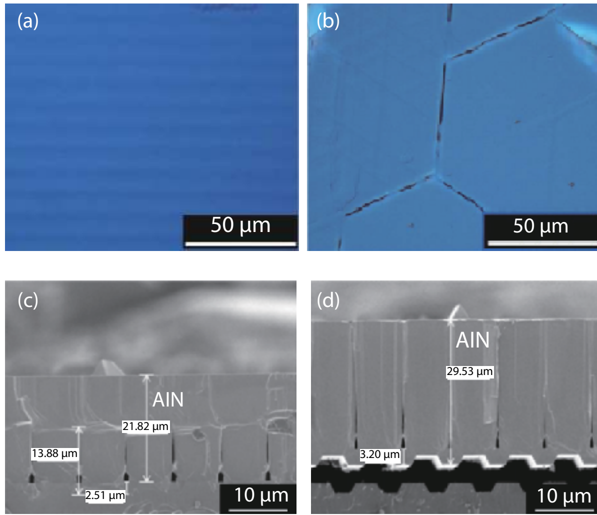



Fig. 17. (Color online) The optical microscopy pictures of AlN grown on: (a) patterned substrate and (b) flat substrate[66]. The cross-sectional SEM of AlN grown on patterned 6H-SiC with trench along (c) <1$\bar{1}$00> and (d) <11$\bar{2}$0> direction[67].

ler than that of AlN, which results in tensile stress[33]. The cracks generally will form during the cooling process. ELOG was also used in the AlN growth on SiC. Figs. 17(c) and 17(d) showed the cross-sectional SEM image of AlN grown on 6H-SiC with trench along <1$\bar{1}$00> and <11$\bar{2}$0> directions, respectively. It could be seen that the growth of AlN on SiC with <1$\bar{1}$00> trenches was easily coalesced than that along <11$\bar{2}$0>[66, 67].

### 4.5. The other technique

Recently, the patterned sapphire substrate (PSS) technique, the sputtered AlN technique, the nano-patterned sapphire substrate (NPSS) technique and other methods were reported and a series of meaningful results were obtained[68–70]. In 2019, the crack-free AlN layer with thickness of 9 ± 1 $\mu$m was obtained through nano-patterned sapphire substrate (NPSS) by high temperature HVPE[70]. The XRC-FWHM values of (0002) and (10$\bar{1}$2) rocking curves were 102 and 219 arcsec, respectively.

In situ formation of viods during high temperature growth were reported in 2016[71]. The formation of voids not only reduced the density of threading dislocations but also relaxed the strain of AlN films. Fig. 18(a) shows the section STEM of AlN epilayer with voids. Obviously the dislocations was blocked by the voids. Fig. 18(b) shows the Rman shift of $E_2$ (high) mode for samples with and without voids. respectively. The strain decreased obviously for the sample with voids.

## 5. Free-standing AlN growth by HVPE: Expectation

All the researches aim to obtain high crystal quality and crack-free free-standing AlN substrates with lager size. During the progress several methods were proposed.

### 5.1. Chemical etching technique

SiC, sapphire and Si wafers are usually used as substrates AlN growth by HVPE. Sapphire and SiC are difficult to chemically etch. However, Si is easily removed by chemical etching[73]. Using Si as the substrates, the first free-standing AlN wafers up to 3 × 3 cm$^2$ in size with thickness of 1 mm

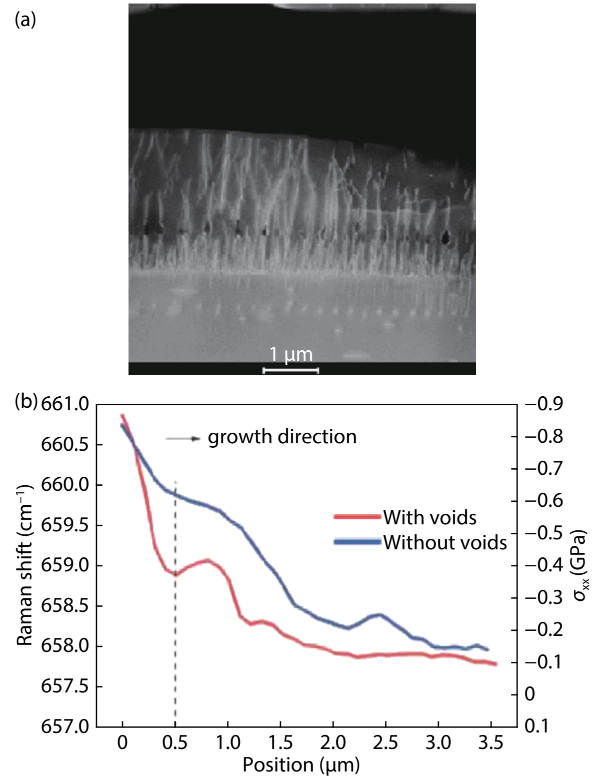



Fig. 18. (Color online) (a) The section STEM images of AlN films with voids. (b) The dependence of Raman shift of $E_2$ (high) mode on the position of samples with and without voids[71]. The horizontal line is the stress-free frequency 657.4 cm$^{-1}$[72].

was obtained in 2000[37]. After growth, Si substrates was removed by chemical etching (shown in Fig. 4(a)). However, the FWHM of (0002) $\omega$-scan was 40 arcmin, indicating the poor crystal quality.

### 5.2. Self-separation technique

The separation of the thick AlN layers from foreign substrates is critical for fabrication of freestanding substrates. The void assisted self-seperation technique was a promising method.

In order to develop the method, the chemical stability of AlN and sapphire substrate in various temperature and gas were investigated[56, 74, 75]. Akiyama *et al.* proved that sapphire and AlN would be decomposed in $H_2$ carrier gas when the temperature at 1200 °C. Besides, the decomposition rate increased markedly with increasing substrates temperature. When the gaseous of $NH_3$ through the reaction chamber, the decomposition of AlN would stop.

Following those results, 100 nm AlN/sapphire template was etched in mixed gas composed of $H_2$, $N_2$ and $NH_3$ at 1450 °C. The interface beneath the thin AlN film generated a large density of voids[76, 77]. Fig. 19(a) shows the cross-sectional SEM of voids in the interface below the 100-nm AlN buffer. Fig. 19(b) shows the photograph of self-separation AlN substrates with thickness of 79 $\mu$m. The self-separation occurred during cooling down from growth temperature to room temperature.

### 5.3. Homo-epitaxial growth technique

The homo-epitaxial growth technique was applied to fabricate free-standing AlN on PVT-AlN substrates[78–82]. Using PVT-AlN as the substrates, a 114 $\mu$m thick free-standing AlN

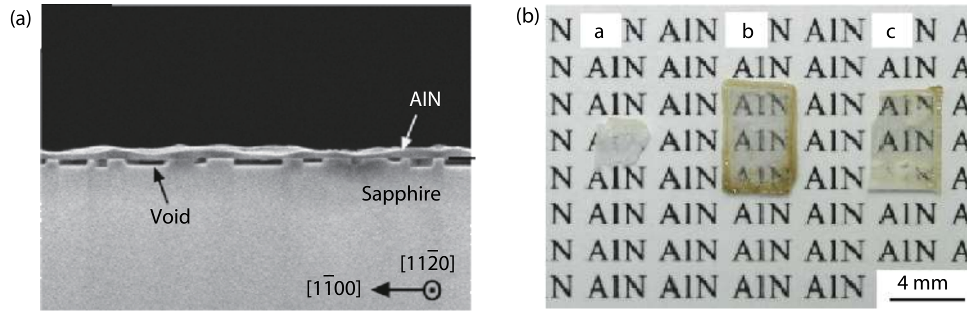



Fig. 19. (a) The corss-sectional SEM of voids in the interface below the 100-nm AlN buffer. (b) The photograph of self-separation AlN substrates with thickness of 79 $\mu$m[76].

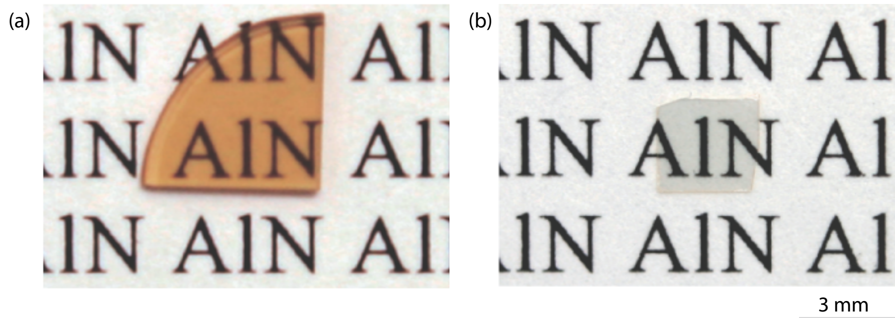



Fig. 20. (Color online) The photographs: (a) the PVT-AlN substrates, (b) the free-standing AlN substrates[79].

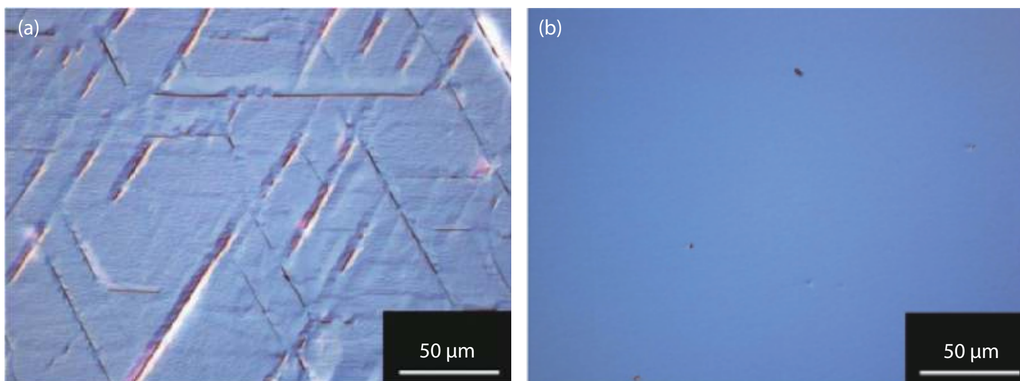



Fig. 21. (Color online) The optical microscopy figures of AlN thick films grown by HVPE on (a) on-axis and (b) miscut 5° PVT-AlN substrates[80].

substrates was obtained grown by HVPE[79]. In addition, the $E_2$ (high) peak position of both the substrates and the thick AlN films are 657.4 cm$^{-1}$, which indicates the strain state was free[72]. Fig. 20(a) shows the PVT-AlN substrates used for HVPE growth and Fig. 20(b) is the free-standing AlN substrates (3 × 3 × 0.114 mm$^3$) separated from PVT-AlN grown by HVPE. The XRC-FWHM values of (0002) and (10$\bar{1}$1) rocking curves of the free-standing AlN were 31 and 32 arcsec, respectively, indicating very high crystal quality.

Nomura *et al*. investigated the influence of miscut angles of AlN substrates prepared by sublimation method on the surface morphology b of AlN grown by HVPE. The miscut angle was inclined toward the <11$\bar{2}$0> direction[80]. Figs. 21(a) and 21(b) show the optical microscopy figures of AlN thick films grown on on-axis and miscut 5° PVT-AlN substrates, respectively. Despite the homo-epitaxial growth, the surface of AlN on the on-axis substrates also appeared a lot of cracks. In contrast, no cracks appeared on the sample grown on the miscut angle substrates.

At last, the difference growth techniques of free-standing AlN have been summarized. The advantages and the best results are shown in Table 1. The self-separation technique may be the most promising growth technology in the near future.

## 6. Prospect

In recent years, with the rapid increase of the market for high-quality AlN substrate with low-cost and large size, various techniques and modification have been made in HVPE growth system and processes. At present, the HVPE system still plays an important role in the fabrication of thick AlN layers with high ultraviolet transmittance, which is very important for AlN-based deep ultraviolet optoelectronics. However, the threading dislocations and the residual stress primarily limited its application.

The difference of lattice constants and thermal expansion coefficients will result in the crack and strain in the AlN wafers, which is an issue need to be solved. Another issue is

Table 1. The freestanding AlN fabricated with different techniques.

| Parameter | Chemical etching technique[83] | Self-separation technique[76, 77, 84] | Homo-epitaxial growth technique[79, 81, 85] |
|---|---|---|---|
| Size ($cm^2$) | 5 × 5 | 4 × 6 | 3 × 3 |
| Thickness ($\mu$m) | 112 | 79 | 114 |
| FWHM of symmetric (arcsec) | 2907 | 2034 | 31 |
| FWHM of skew-symmetric (arcsec) | 1322 | 1104 | 32 |
| Advantage | Simple | Low cost | High quality |

the threading dislocations. Nowadays, the high quality AlN with large size grown by HVPE are still under research. We believe that with the efforts of researchers, 2-inch AlN freestanding substrate with high crystal-quality and high ultraviolet transmittance will be realized in 3 years. Due to the lack of native substrate, the dislocation density of AlN grown by HVPE will be around $10^6$ $cm^{-2}$ and it is difficult to decrease furthermore. In addition, the cost for freestanding AlN substrate produced by HVPE will be higher than that grown by PVT due to the limitation of growth rate of HVPE. However, we noticed that AlN grown by PVT will absorb the deep ultraviolet light seriously. Until now, HVPE is still one promising method to produce the ultraviolet transparent AlN freestanding substrate.

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