REVIEWS

Hydride vapor phase epitaxy for gallium nitride substrate

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Abstract: Due to the remarkable growth rate compared to another growth methods for gallium nitride (GaN) growth, hydride vapor phase epitaxy (HVPE) is now the only method for mass product GaN substrates. In this review, commercial HVPE systems and the GaN crystals grown by them are demonstrated. This article also illustrates some innovative attempts to develop homebuilt HVPE systems. Finally, the prospects for the further development of HVPE for GaN crystal growth in the future are also discussed.

Key words: hydride vapor phase epitaxy; gallium nitride; substrate

Citation: J Hu, H Y Wei, S Y Yang, C M Li, H J Li, X L Liu, L S Wang, and Z G Wang, Hydride vapor phase epitaxy for gallium nitride substrate[J]. J. Semicond., 2019, 40(10), 101801. http://doi.org/10.1088/1674-4926/40/10/101801

1. Introduction

Gallium nitride (GaN) has many noticeable characteristics, such as a wide band gap of 3.4 eV, a high electric breakdown field of 3.3×10^6 V/cm, and a high electron saturation velocity of 2.7×10^7 cm/s, which have led it to be widely applied in optoelectronic devices and power electronic devices. The great success of GaN LEDs is based on their heteroepitaxy structures, even though they have many defects and dislocations due to lattice mismatches. To improve the performance of optoelectronic and power electronic devices, the homoepitaxy GaN device is a promising way of using GaN substrates.

GaN bulk crystals are difficult to obtain by conventional melt solidification crystal growth processes^[1, 2], therefore HPNS (high-pressure nitrogen solution growth)^[3], Na-flux growth^[4, 5], ammonothermal growth^[6, 7], and hydride vapor phase epitaxy (HVPE)^[8–10] have been introduced to grow the GaN bulk crystal. Compared to other growth methods, HVPE has the advantages of relatively simple equipment and process, large size, high growth rate and acceptable low impurity, which makes HVPE the most promising method for GaN substrates.

Commercial 2 inch GaN substrates produced by HVPE with a thread dislocation density (TDD) in the order of 10^6 cm⁻³ are already available from many corporations, and 4 inch or larger scale GaN substrates are also available on the market. In addition, via homebulit HVPE, the lowest TDD 3 × 10^2 cm⁻², of 5 mm-thick 2 inch GaN has been obtained by pit-assisted growth^[11], and the largest diameter GaN substrate (175 mm) has been obtained by the tiling technique^[12].

HVPE equipment is a key factor to obtain a high-quality GaN substrate. Consequently, equipment vendors have laun-

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Received 16 JANUARY 2019; Revised 15 MAY 2019.

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ched commercial equipment to produce GaN substrates of various sizes. Meanwhile, prototype HVPE equipment for higher quality GaN substrates are also in development. In our paper, we review the commercial and prototype HVPE systems for GaN substrates. Finally, we will share our thoughts about the development about HVPE equipment in the future.

2. The principle of HVPE

HVPE is a chemical vapor deposition technology that uses hydride (AsH₃, PH₃, NH₃) and chloride (GaCl, GaCl₃, InCl) as source materials for the reaction. According to the function, the HVPE reactor chamber can be divided into two zones: a low-temperature feedstock zone and a high-temperature growth zone, where chemical reaction processes can be described as follows:

High-purity HCl gas reacts with liquid Ga in the low-temperature feedstock zone (~ 850 °C) to generate GaCl gas with a small amount of by-product, which is transported by N₂ or other carrier gas to the high-temperature growth region (~ 1050 °C) where GaCl and NH₃ are mixed and reacted. The reaction product, GaN, is then deposited on the substrate to form GaN film. The chemical reactions are:

Low-temperature feedstock zone:

$$Ga(I) + HCI(g) \Leftrightarrow GaCI(g) + \frac{1}{2}H_2(g).$$
(1)

High-temperature growth zone:

$$GaCI(g) + NH_{3}(g) \Leftrightarrow GaN(s) + HCI(g) + H_{2}(g). \quad (2)$$

The HVPE reactor system is mainly composed of a gas supply system, a reaction chamber, a heating system, and an exhaust gas system. According to the direction of gas flow in reaction chamber, the HVPE reactor can be divided into two types: vertical HVPE reactors and horizontal HVPE reactors. Fig. 1 shows schematic diagrams of two kinds of typical HVPE reactor.



Fig. 1. Schematic view of (a) horizontal HVPE reactor and (b) vertical HVPE reactor.



Fig. 2. Reactor geometry of Aixtron AIX-HVPE horizontal guartz reactors.



Fig. 3. (Color online) AIXTRON vertical HVPE system. (a) Concentric inlet geometry. (b) Schematic sketch of its reactor components.

3. Commercial HVPE

Since HVPE was first applied in the growth of III-nitride semiconductor in the last century^[13–15], several types of HVPE equipment have been made available on the market.

The earliest commercial HVPE equipment was the Aixtron AIX-HVPE horizontal quartz reactor^[16], which is shown in Fig. 2. This reactor can be divided into 5 zones depending on the temperature. The HCl gas with carrier gas (the mixture of N₂ and H₂) goes through zone 1 to zone 2, where HCl reacts with molten metallic Ga at high temperature in an inner quartz tube. The product of the reaction, GaCl and some byproducts are then transferred to zone 3. They are then injected to the surface of a rotating substrate holder via a shower header in zone 4. The 2-inch wafer can then be loaded onto the substrate susceptor, which is rotated. Meanwhile, the NH₃ is mixed with carrier gas (N₂) in the lower quartz inner tube and transferred separately to zone 4, where the two species, NH₃ and GaCl are mixed and reacted into the GaN, which is deposited on the surface of wafer. Through zone 5, exhaust gas is transported to the exhaust gas treatment system. Various works have been applied on this HVPE reactor^[16–20], and 120 μ m thick GaN layer are successfully epitaxy on 2-inch sapphire substrates without cracks^[21].

A vertical HVPE system that was developed by AIXTRON was commercialized in 2007s^[22, 23]. This system is able to grow thick 2-inch GaN substrates. The section of concentric reactor inlet geometry and the schematic sketch of its reactor components in this HVPE reactor are shown in Figs. 3(a) and 3(b), respectively.

Some specific designs have been developed to improve the total growth rate and growth uniformity. The inlet design



Fig. 4. (Color online) Photograph of a 6.3 mm thick GaN boule grown by Aixtron vertical HVPE.

is concentric and two sheath flows are designed to avoid prereaction between two reactive species GaCl and NH₃, and to reduce parasitic deposition on the wall and reactor volume. The GaN seed holder can be raised upwards by the boule retraction unit as the GaN film epitaxy grows thicker to keep the distance between the gas inlet and substrate surface constant and optimal. Meanwhile the RF power is completely dissipated in the graphite susceptors, keeping the whole growth zone temperature even and making it a true hot wall reactor. An advanced design is used to lead the exhaust gas out when its temperature is above 350 °C. Ammonium-chloride (NH₄Cl), a white powder, is formed in the reactor below 350 °C, which would bring growth defects and result into the blockage of the exhaust gas tube.

With this vertical HVPE, at the growth rate of 250 μ m/h, 2 mm thick crack-free GaN films are produced with the etch pit density (EPD), while the layer can reach as low as 5 \times 10⁵ cm^{-2[20, 24]}.

Using the same reactor, GaN boules with thicknesses of 2.6, 5.8 and 6.3 mm were successful grown by Ritcher *et al.*^[25–27], with a high growth rate above 400 μ m/h. A GaN film with thickness of 6.3 mm is shown in Fig. 4. Dislocation densities as low as 6 × 10⁵ cm⁻² are observed in 6.3 mm GaN boules.

Kyma Technologies, Inc. have launched HVPE equipment, named Kyma100TM HVPE System^[28], which is shown in Fig. 5(a). This is a vertical HVPE that can produce GaN substrate with a growth rate above 500 μ m/h. This equipment is qualified to produce three 2 inch or single 4 inch GaN substrates in one run. Moreover, their background impurity concentration is less than 1 × 10⁷ cm⁻³

In addition to the Kyma100TM HVPE System, Kyma has also developed another HVPE equipment, which is named K200TM HVPE Growth Tool^[29], as shown in Fig. 5(b). This is a fully automated HVPE that can realize pro-long growth of 200 or 150 mm GaN substrates.

There are other vendors can provide the HVPE systems, such as Oxford Instruments, TGO TECH CO.LTD, TRINITRI-Technology LLC and so on.

4. Developing prototype HVPE

4.1. Halogen-free VPE

For general HVPE system, due to the existence of NH_3 and GaCl, the long-duration growth of GaN crystal is limited by the accumulation of NH_4Cl .

Halogen-free vapor phase epitaxy (HF-VPE) is a similar technique to general HVPE, whose Ga precursor is Ga vapor



Fig. 5. (Color online) The appearance of (a) the Kyma100[™] HVPE System, (b) K200[™] HVPE Growth Tool.

and is directly vaporized from melted Ga instead of GaCl gas. The reaction in this process is:

$$Ga(g) + NH_3(g) \rightarrow GaN(s) + \frac{3}{2}H_2(g).$$
 (3)

The absence of chlorine makes HF-VPE a reasonable approach to avoid NH₄Cl ash in the exhaust gas tube in the downstream of the reactor chamber. This technique is able to meet the requirements for prolonging the time of stable growth of GaN crystal.

Although HF-VPE has some limitations, such as low grow rate and high Ga source temperature, in the 2000s several groups tried to use the HF-VPE process to grow GaN^[30, 31]. Nakamura *et al*.^[32–35] recently proposed a new HF-VPE design, as shown in Fig. 6(b). The crucible and seed holder are made of graphite encapsulated by TaC to suppress unintentional impurity incorporation and allow a Ga source temperature as high as 1500 °C^[36–39]. In addition, a N₂ sheath gas is added between the III gas and V gas to prevent the direct reaction of NH₃ with molten Ga, which would result in the boiling and/or creeping of the liquid Ga source, and spurt the Ga droplet onto the surface of GaN substrate and worsen the GaN crystal's quality. By using this HF-VPE, a 55 μ m thick GaN substrate has been successfully grown on the MOCVD-GaN template at a growth rate of more than 100 μ m/h.

Subsequently, Nakamura *et al.*^[33] added a fin-shaped porous TaC ceramic component to the Ga evaporator, as shown in Figs. 6(a) and 6(c). The porous TaC structure was used to infiltrate the Ga solution by capillarity, which increased the evaporation area and evaporation rate of Ga by



Fig. 6. (Color online) (a) Photograph of fin-shaped porous TaC ceramic component to the Ga evaporator. (b) Schematic drawing of the modified HF-VPE. (c) Photograph of evaporator wetted with molten Ga.



Fig. 7. (Color online) (a) Scheme of the evaporation cell. The arrows stand for three flows in the reactor: A: transport flow for Ga vapor, B: separation flow, C: NH₃ with a carrier gas. (b) Numerical simulation of HTVPE reactor temperature distribution.

fivefold. Consequently, the growth rate of GaN increased 3–5 times, reaching 500–800 μ m/h

Lukin *et al.*^[40, 41] conducted a GaN crystal growth simulation and experiment based on a modified HF-VPE, which they described as high-temperature vapor phase epitaxy (HTVPE)^[42], as shown in Fig. 7(a).

Compared with the HF-VPE mentioned above, the distance between Ga source and substrate is increased, which reduces the thermal coupling in the two temperature zones and alleviates the problem of thermal field interference. This further results in two temperature zones that can be independently controlled by an induction heating module, which increases the flexibility of temperature control. The simulated temperature distribution for typical growth process is shown in Fig. 7(b), where the gallium temperature is 1340 °C, substrate temperature is 1100 °C. The modeling and simulation are performed by COMSOL Multiphysics software, and the fused silica was simplified as a transparent component in radiation, which is the major heat transport mechanism in the target studied system.

Additionally, a Ga evaporator is covered with a molybdenum cap or pyrolytic boron nitride to reduce the introduction of C impurities. A 15 \times 15 mm² substrate was grown with a growth rate of 165 μ m/h, demonstrating the potential of growing thick-film GaN by this modified HF-VPE.

4.2. Tri-halide vapor phase epitaxy (THVPE)

THVPE is an interesting alternative to the conventional HVPE, it uses gallium tri-chloride (GaCl₃) as the III-precursor, instead of using gallium mono-chloride (GaCl) as the III-precursor in conventional HVPE, the precursor GaCl₃ can be supplied into the growth zone by two approaches, the first approach is directly evaporation or sublimation from the GaCl₃^[43-46], the second is the reaction of metallic Ga metal with Cl₂ in the source zone^[47–50], the first approach is less general due to the high hygroscopic nature of GaCl₃ powder materials, which could bring the purity problem^[49], bellowing we would focus on the second approach. The dominant che-



Fig. 8. (Color online) Schematic illustration of (a) nozzle structure in ID-HVPE and (b) ID-PMG method.

mical reaction on the THVPE reactor can be written as follows: The source zone:

$$Ga(I) + \frac{1}{2}CI_2(g) \rightarrow GaCI(g), \qquad (4)$$

$$GaCl(g) + Cl_2(g) \rightarrow GaCl_3(g).$$
 (5)

The growth zone:

$$GaCl_3(g) + NH_3(g) \Leftrightarrow GaN(s) + 3HCl(g).$$
 (6)

For conventional HVPE, its growth rate is currently up to 1870 µm/h^[51]. However, at the same growth temperature, the faster the growth rate, the lower the crystal guality, this is due to the insufficient migration of precursors on the crystal surface. Although the mobility can be enhanced with increasing temperature, it is not feasible to increase the crystal growth guality by increasing the temperature, because the maximum growth temperature is limited to 1000-1100 °C thermodynamically by the change of free energy^[47]. A higher temperature would decrease the equilibrium constant since the GaCI-NH₃ reaction of conventional HVPE is a near equilibrium exothermic reaction, while the equilibrium constant of THVPE would increase with a higher temperature^[48, 52]. This means that, the superior quality GaN growth is possible to be accomplished by THVPE at a higher temperature than HVPE, which has been proved by experiments mentioned below.

Besides thermodynamic analysis on THVPE, many experiment related with GaN epitaxy by THVPE has been completed in recent years^[47, 50, 53–55].

The experiments conducted by Hisashi Murakami *et al.*^[47] showed that, with an increasing growth temperature, a higher quality GaN obtained. Specifically, the corporation of O, C, and Cl impurities are less even on the N-polarity GaN, and the dark spot reduced, that is due to the high mobility of precursor at high temperature, which correspond to the conclusion mentioned above. Afterwards, the maximum growth rate reported is 190 µm/h when growth temperature was 1050 °C. Besides, their group have achieved 0.5–1.3 mm thick GaN layer homoepitaxial growth by THVPE at 1280 °C at a growth rate of 95–275 µm/h on ammonothermal GaN substrates^[55], the full widths at half maximum (FWHMs) and basal plane stacking fault (BSF) density reached 28 arcsec and

8.3 \times 10 cm⁻¹, respectively when grown at 275 μ m/h, the growth rate of THVPE is already sufficient for epitaxial GaN thick film.

From the progress shown above, THVPE has showed a potential for epitaxy low-cost, high-crystalline-quality GaN substrates, which is hopeful to replace conventional manufacturing method of GaCl-based HVPE in the future.

In the other hand, the growth temperature of GaN growth with GaCl₃ generally exceeds 1100 °C, up to 1350 °C. Therefore, more stringent requirements are imposed on the heating and thermal insulation system of the equipment. What's worse, differ from conventional HVPE, in which both HCl and N₂ exhaust gas are easily soluble in water, so the exhaust gas treatment is relatively easy, Cl₂ gas in THVPE is water-insoluble, so additional treatment method are required to treat Cl₂. Accordingly, Tri-halide VPE needs more improvements to meet the industrial growth of GaN substrates.

4.3. Large-scale or multi-wafer HVPE

Large-scale or multi-wafer HVPE is an effective way to mass production of GaN substrate. However, the large size of the reactor chamber requires complex design and narrow operating window to keep the uniform growth of GaN substrates.

Zhang *et al.*^[56, 57] have adopted new intake nozzle structures on their own homebuilt 4-inch (option to 3×2 inch) vertical HVPE and achieved the highly uniform growth of multiwafer 2 inch and single-wafer 4 inch GaN substrate, which can provide a new way to improve the quality of GaN crystal growth.

First, they added an inner dilution gas (ID) pipe (the section is shown in Fig. 8(a)) between V and III group concentric gas-flow channel to adjust the GaN film thickness distribution, with a specially designed modified gas intake setup, which they called ID gas periodically modulated growth (ID-PMG) method. In other words, the ID gas flow rate changed periodically to adjust the precursor concentration distribution at the substrate surface, the schematic illustration is shown in Fig. 8(b).

The modulation effect of ID-PMG method in ID-HVPE are analyzed by numerical simulation, the simulated precursor concentration distribution above wafers surface is shown in Fig. (9a). Eventually, they have successfully made a HVPE react-



Fig. 9. (Color online) Schematic of (a) simulated mole fraction of precursor in ID-HVPE and (b) thickness distribution of GaN substrate along the diameter.



Fig. 10. (Color online) Schematic of (a) new designed nozzle structure in PD-HVPE and (b) simulated mass fraction of precursor in ID-HVPE system and PD-HVPE system on various gas flow rate.

or that is able to grow three high-uniformity $(\pm 3\%-4\%)$ 2 inch substrates at a time, which is a huge improvement compared to that of \pm 30% grown by the conventional multiwafer HVPE. The thickness distribution of GaN layer is shown in Fig. 9(b). Besides, the crystal quality and surface morphology were also improved because the ID gas has suppressed the parasitic reaction.

When applying this modification into single 4 inch GaN wafer growth, the thickness inhomogeneity was worsened to 14% again. Consequently, further improvements have been developed based on their work. For example, an extra dilution and push gas (PD) pipe (the structure of the modified HVPE gas nozzle is shown in Fig. 10(a)) has been added in the center of gas channels in the HVPE system to redistribute the distribution of GaCl and NH₃ upon the wafer. The effect of new design on precursor concentration distribution on wafer surface has been simulated, as shown in Fig. 10(b). Consequently, by the optimal gas-flow rate, a single 4 inch GaN substrate with outstanding thickness uniformity has been obtained and the experimental results show that the thickness inhomogeneity of 4-inch GaN substrates can be reduced to $\pm 1.8\%$ compared to the $\pm 14\%$ grown with conventional nozzle. This excellent result shows that this technique offers an effective way to research and develop a HVPE reactor to grow large-size uniform GaN substrates.

According to the report on the website, recently a 2×12 inch HVPE equipment has been introduced by Sino Nitride

Semiconductor Co, which has successfully grown 15–25 μ m GaN/Al₂O₃ composite substrates using a multi-wafer HVPE. The thickness uniformity of each wafer was about 10%, and the average thickness variation among 21 wafers was less than 5% in the same run.

Yi *et al.*^[58–60] have designed and developed two types of multi-wafer HVPE systems, five-susceptor, 6×4 inch HVPE systems and 6×6 inch HVPE systems, their reactor models are shown in Figs. 11 and 12, respectively. The gas flows of both are transported from the center nozzle to the edge of the reactor chamber. The growth processes of these two growth systems were explored by experiments analysis and numerical simulation, specifically, the effect of basic growth condition, such as V/III ratio, gas flow rate and temperature has been investigated thoroughly, but further research is needed to achieve GaN substrate growth successfully since there are no full images of GaN substrates.

4.4. In situ removal of foreign substrate

At present, the most common process for making a freestanding GaN substrate is to use a laser to lift off the GaN thick film from foreign substrate after the HVPE growth GaN process. When the GaN thick film cools with a foreign substrate, the wafer is prone to bending and cracking due to the lattice mismatches and thermal mismatches. To solve this problem, various buffer layers or weak bonding layers have been introduced to achieve self-separation of the GaN substrates^[18, 61–63].



Fig. 11. (Color online) 3D simulation model of five-susceptor, 6×4 inch HVPE reactor.



Fig. 12. (Color online) Schematic diagram of the HVPE (a) from the vertical cross section view, (b) from the top view.

Recently, the in situ removal technology of GaN substrates has been realized by Moon Sang Lee *et al.*^[64–66]. The in situ removal of Si is accomplished by a backflow HCl gas, which flows through multiple holes in the susceptor to backetch the Si substrate, as shown in Fig. 13. Meanwhile, bottom-purge N₂ has been applied to prevent a reaction between GaN growth by-product and Si on the backside of the Si wafer, which would reduce the etch rate and non-uniform etching of the Si substrate.

Lee *et al.*^[64] have shown that in situ separating the GaN layer from the silicon substrate by HCl etching at high temperature can avoid the strain accumulation in the GaN layer during the cooling process. This new process has effectively suppressed the formation of cracks in the GaN layer during cooling. The 2-inch freestanding crack-free GaN substrate with a thickness of 400 μ m has been obtained, as shown in Fig. 14, The (0002) plane FWHM of the GaN wafer was 65 arcsec, and the EPD was less than 1 × 10⁶ cm⁻².

Additionally, according to the researcher, this modified HVPE is a very promising candidate for the production of freestanding 8-inch GaN substrates.

GT Advanced Technologies has also developed HVPE with an in situ laser to lift off the foreign substrate, as published in a presentation made by Raghavan at the LED Forum 2013 in Taipei, China.

5. Conclusion and perspectives

Recently, the increasing demand for high-quality and

low-cost GaN substrates has led to various attempts and modifications to be made to develop the HVPE system and corresponding epitaxial GaN processes. Nowadays, GaN substrates can be up to 6 inches in diameter, or even bigger^[12]. However, the mass production of GaN substrates is limited and is still mainly 2 inches in diameter. In the future, if no cheap high-quality native GaN substrates become available, it would be difficult for further realize high performance GaN power devices and GaN laser devices, it would also be difficult to expand the application of GaN-based devices.

This paper describes the principles of HVPE and their different structural designs. It then summarizes the commercial HVPE reactors, and their modifications and innovations. It finally discusses the GaN substrate grown by these reactors.

Even though the GaN substrate grown by HPVE has shown great potential. There are many obstacles needed to be cleared:

First, when the substrates diameter expands from 2 inch to 4 inch or larger, the separation of substrate from foreign substrates become increasing hard, most of them would crack, even if few of them successfully separated from foreign substrates, the wafer would fall into strongly bowed and highly stressed state, which is an issue hard to solve, resulting in the large size GaN substrate unacceptable expensive.

Second, Ammonia chloride (NH₄Cl) ash would form in the reactor downstream when the temperature down to 350 °C, the NH₄Cl powder bring the blockage problem, which cannot avoid since the existence of NH₃ and HCl in reactor



Fig. 13. (Color online) Schematic diagram of the HVPE reactor and magnified detail of growth/etch zone.



Fig. 14. (Color online) Photograph of a freestanding GaN substrate by in situ removal Si substrate.

chamber. The NH_4Cl problem is one of the main factors that hinder the long-duration growth of GaN boule.

The last obstacle is parasitic deposition. the parasitic deposition in the reactor chamber would cost part of precursor, reduce growth rate and yield, what's worse, the by-product GaN particles which fall down to the wafer surface, bring many defects, such as threading dislocation caused by a combination of parasitic deposition and anisotropy of the growth.

Although so many challenges to solve, the rapidly development on HVPE growth of GaN in recent years are inspiring. We have enough reason to believe that in the near future, high-quality, low-cost large-size freestanding GaN substrates will be realized by a modified HVPE reactor, which is able to grow GaN boule for a long duration or grow multi-GaN wafers in a batch. This would impressively increase the performance of homoepitaxy GaN-based devices and enable them to applied more widely and play a significant role in energy-saving.

Acknowledgments

This work was supported by the National Key Research

and Development Plan (No. 2017YFB0404201) and the National Science Foundation of China (Nos. 61774147, 61874108).

References

- Van Vechten J A. Quantum dielectric theory of electronegativity in covalent systems. III. pressure-temperature phase diagrams, heats of mixing, and distribution coefficients. Phys Rev B, 1973, 7, 1479
- [2] Karpiński J, Jun J, Porowski S. Equilibrium pressure of N₂ over GaN and high pressure solution growth of GaN. J Cryst Growth, 1984, 66, 1
- [3] Leszcynski M, Grzegory I, Bockowski M. X-ray examination of GaN single crystals grown at high hydrostatic pressure. J Cryst Growth, 1993, 126, 601
- [4] Yamane H, Shimada M, Clarke S J, et al. Preparation of GaN single crystals using a Na flux. Chem Mater, 1997, 9, 413
- [5] Murakami K, Matsuo D, Imabayashi H, et al. Effects of solution stirring on the growth of bulk GaN single crystals by Na flux method. Jpn J Appl Phys, 2013, 52, 08JA03
- [6] Dwiliński R, Doradziński R, Garczyński J, et al. Excellent crystallinity of truly bulk ammonothermal GaN. J Cryst Growth, 2008, 310, 3911
- [7] Ehrentraut D, Pakalapati R T, Kamber D S, et al. High quality, low cost ammonothermal bulk gan substrates. Jpn J Appl Phys, 2013, 52, 08JA01
- [8] Kelly M K, Vaudo R P, Phanse V M, et al. Large free-standing GaN substrates by hydride vapor phase epitaxy and laser-induced liftoff. Jpn J Appl Phys, 1999, 38, L217
- [9] Motoki K, Okahisa T, Matsumoto N, et al. Preparation of large freestanding GaN substrates by hydride vapor phase epitaxy using GaAs as a starting substrate. Jpn J Appl Phys, 2001, 40, L140
- [10] Oshima Y, Eri T, Shibata M, et al. Preparation of freestanding GaN wafers by hydride vapor phase epitaxy with void-assisted separation. Jpn J Appl Phys, 2003, 42, L1
- [11] Lee M, Mikulik D, Yang M, et al. Nearly perfect GaN crystal via pitassisted growth by HVPE. CrystEngComm, 2017, 19, 2036
- [12] Yoshida T, Imanishi M, Kitamura T, et al. Development of GaN substrate with a large diameter and small orientation deviation. Phys Status Solidi B, 2017, 254, 1600671
- [13] Maruska H P, Tietjen J J. The preparation and properties of vapordeposited single-crystal-line GaN. Appl Phys Lett, 1969, 15, 327
- [14] Wickenden D K, Faulkner K R, Brander R W, et al. Growth of epitaxial layers of gallium nitride on silicon carbide and corundum

substrates. J Cryst Growth, 1971, 9, 158

- [15] Seifert W, Fitzl G, Butter E. Study on the growth rate in VPE of GaN. J Cryst Growth, 1981, 52, 257
- [16] Parillaud O, Wagner V, Buehlmann H J, et al. Localized epitaxy of GaN by HVPE on patterned substrates. MRS Int J Nitride Semicond Res, 1998, 3, e40
- [17] Richter E, Gramlich S, Klein A, et al. Direct growth of GaN on (0001) sapphire by low pressure hydride vapour phase epitaxy. Phys Status Solidi A, 2001, 188, 439
- [18] Hennig C, Richter E, Weyers M, et al. Self-separation of thick two inch GaN layers grown by HVPE on sapphire using epitaxial lateral overgrowth with masks containing tungsten. Phys Status Solidi C, 2007, 4, 2638
- [19] Wang C, Anthony C H, Seyboth M, et al. Influence of growth parameters on crack density in thick epitaxially lateral overgrown GaN layers by hydride vapor phase epitaxy. J Cryst Growth, 2001, 230, 377
- [20] Hemmingsson C, Paskov P P, Pozina G, et al. Growth of bulk GaN in a vertical hydride vapour phase epitaxy reactor. Superlattices Microstruct, 2006, 40, 205
- [21] Richter E, Hennig C, Weyers M, et al. Reactor and growth process optimization for growth of thick GaN layers on sapphire substrates by HVPE. J Cryst Growth, 2005, 277, 6
- [22] Schineller B, Kaeppeler J, Heuken M. Vertical-HVPE as a production method for free-standing GaN-substrates. Konferenzprotokoll, AIXTRON AG, Austin, Texas, 2007
- [23] https://compoundsemiconductor.net/article/84531/Aixtron_take s_HVPE_vertical_for_cheap_GaN_substrates, Aixtron takes HVPE vertical for cheap GaN substrates - News
- [24] Hemmingsson C, Paskov P P, Pozina G, et al. Hydride vapour phase epitaxy growth and characterization of thick GaN using a vertical HVPE reactor. J Cryst Growth, 2007, 300, 32
- [25] Richter E, Zeimer U, Hagedorn S, et al. Hydride vapor phase epitaxy of GaN boules using high growth rates. J Cryst Growth, 2010, 312, 2537
- [26] Richter E, Gründer M, Schineller B, et al. GaN boules grown by high rate HVPE. Phys Status Solidi C, 2011, 8, 1450
- [27] Richter E, Gründer M, Netzel C, et al. Growth of GaN boules via vertical HVPE. J Cryst Growth, 2012, 350, 89
- [28] http://www.kymatech.com/news/224-kyma-adds-gallium-oxideepiwafers-to-its-product-portfolio-2, Kyma Enters Gallium Nitride Crystal Growth Equipment Market
- [29] http://www.kymatech.com/products/crystal-growth-tools/545hydride-vapor-phase-epitaxy-hvpe-growth-tool, K200[™] HVPE Growth Tools
- [30] Shin H, Thomson D B, Schlesser R, et al. High temperature nucleation and growth of GaN crystals from the vapor phase. J Cryst Growth, 2002, 241, 404
- [31] Bohnen T, Ashraf H, van Dreumel G W G, et al. Enhanced growth rates and reduced parasitic deposition by the substitution of Cl₂ for HCl in GaN HVPE. J Cryst Growth, 2010(312), 2542
- [32] Nakamura D, Kimura T, Horibuchi K. Halogen-free vapor phase epitaxy for high-rate growth of GaN bulk crystals. Appl Phys Express, 2017, 10, 045504
- [33] Nakamura D, Kimura T. Significant increase in GaN growth rate by halogen-free vapor phase epitaxy with porosity-controlled evaporator. Appl Phys Express, 2017, 10, 095503
- [34] Nakamura D, Kimura T. Ultrahigh-yield growth of GaN via halogen-free vapor-phase epitaxy. Appl Phys Express, 2018, 11, 065502
- [35] Kimura T, Horibuchi K, Kataoka K, et al. Macro-defect-free homoepitaxial GaN growth through halogen-free vapor-phase epitaxy on native GaN seeds. J Cryst Growth, 2018, 494, 17
- [36] Nakamura D, Suzumura A, Shigetoh K. Sintered tantalum carbide coatings on graphite substrates: Highly reliable protective coatings for bulk and epitaxial growth. Appl Phys Lett, 2015, 106,

082108

- [37] Nakamura D. Simple and quick enhancement of SiC bulk crystal growth using a newly developed crucible material. Appl Phys Express, 2016, 9, 055507
- [38] Nakamura D, Shigetoh K, Suzumura A. Tantalum carbide coating via wet powder process: From slurry design to practical process tests. J Eur Ceram Soc, 2017, 37, 1175
- [39] Nakamura D, Kimura T, Narita T, et al. TaC-coated graphite prepared via a wet ceramic process: Application to CVD susceptors for epitaxial growth of wide-bandgap semiconductors. J Cryst Growth, 2017, 478, 163
- [40] Lukin G, Schneider T, Barchuk M, et al. Modified high temperature vapor phase epitaxy for growth of GaN films: Modified HTVPE for growth of GaN films. Phys Status Solidi A, 2017, 214, 1600753
- [41] Schneider T, Lukin G, Zimmermann F, et al. Studies on high temperature vapor phase epitaxy of GaN. J Cryst Growth, 2017, 468, 212
- [42] Lukin G, Röder C, Barchuk M, et al. Investigation of GaN layers grown by high temperature vapor phase epitaxy: Investigation of GaN layers grown by high temperature vapor phase epitaxy. Phys Status Solidi C, 2014, 11, 491
- [43] Yuri M, Ueda T, Lee H, et al. Vapor phase epitaxy of GaN using gallium tri-chloride and ammonia. In: Compound Semiconductor Electronics and Photonics. Vol. 421. Pittsburgh: Materials Research Soc, 1996, 195
- [44] Takahashi N, Matsumoto R, Koukitu A, et al. Vapor phase epitaxy of In_xGa_{1-x}N using InCl₃, GaCl₃ and NH₃ sources. Jpn J Appl Phys Part 2-Lett, 1997, 36, L601
- [45] Topf M, Steude G, Fischer S, et al. 1998 Low-pressure chemical vapor deposition of GaN epitaxial films. J Cryst Growth, 1998, 189/190, 330
- [46] Varadarajan E, Puviarasu P, Kumar J, et al. On the chloride vaporphase epitaxy growth of GaN and its characterization. J Cryst Growth, 2004, 260, 43
- [47] Murakami H, Takekawa N, Shiono A, et al. Tri-halide vapor phase epitaxy of thick GaN using gaseous GaCl₃ precursor. J Cryst Growth, 2016, 456, 140
- [48] Kumagai Y, Takemoto K, Hasegawa T, et al. Thermodynamics on tri-halide vapor-phase epitaxy of GaN and In_xGa_{1-x}N using GaCl₃ and InCl₃. J Cryst Growth, 2001, 231, 57
- [49] Yamane T, Hanaoka K, Murakami H, et al. Tri-halide vapor phase epitaxy of GaN using GaCl₃ gas as a group III precursor Phys. Status Solidi C, 2011, 8, 1471
- [50] Iso K, Takekawa N, Matsuda K, et al. Tri-halide vapor-phase epitaxy of GaN using GaCl₃ on polar, semipolar, and nonpolar substrates. Appl Phys Express, 2016, 9, 105501
- [51] Yoshida T, Oshima Y, Watanabe K, et al. Ultrahigh-speed growth of GaN by hydride vapor phase epitaxy. Phys Status Solidi C, 2011, 8, 2110
- [52] Gil E, André Y, Cadoret R, et al. Hydride vapor phase epitaxy for current III–V and nitride semiconductor compound issues. In: Handbook of Crystal Growth. 2nd ed. Boston: North-Holland 2015, 51
- [53] Takekawa N, Hayashida N, Ohzeki D, et al. Growth temperatures and the excess chlorine effect of N-polar GaN growth via tri-halide vapor phase epitaxy. J Cryst Growth, 2018, 502, 7
- [54] Iso K, Matsuda K, Takekawa N, et al. Quasiequilibrium crystal shape and kinetic Wulff plot for GaN grown by trihalide vapor phase epitaxy using GaCl₃. Phys Status Solidi B, 2017, 254, 1600679
- [55] Iso K, Matsuda K, Takekawa N, et al. Thick nonpolar m-plane and semipolar (10(1)over-bar(1)over-bar) GaN on an ammonothermal seed by tri-halide vapor-phase epitaxy using GaCl₃. J Cryst Growth, 2017, 461, 25
- [56] Liu N, Wu J, Li W, et al. Highly uniform growth of 2-inch GaN wafers with a multi-wafer HVPE system. J Cryst Growth, 2014,

10 Journal of Semiconductors doi: 10.1088/1674-4926/40/10/101801

388, 132

- [57] Cheng Y, Liu P, Wu J, et al. High uniform growth of 4-inch GaN wafer via flow field optimization by HVPE. J Cryst Growth, 2016, 445, 24
- [58] Han X F, Hur M J, Lee J H, et al. Numerical simulation of the gallium nitride thin film layer grown on 6-inch wafer by commercial multi-wafer hydride vapor phase epitaxy. J Cryst Growth, 2014, 406, 53
- [59] Han X F, Lee J H, Lee Y J, et al. Numerical analysis on the origin of thickness unevenness and formation of pits at GaN thin film grown by HVPE. J Cryst Growth, 2016, 450, 66
- [60] Han X F, Lee J H, Lee Y J, et al. 3D numerical analysis of influence of the non-uniform deposition rate on the hillock density at HVPE-GaN surface. J Cryst Growth, 2017, 474, 81
- [61] Luo W, Wu J, Goldsmith J, et al. The growth of high-quality and self-separation GaN thick-films by hydride vapor phase epitaxy. J Cryst Growth, 2012, 340, 18

- [62] Amilusik M, Sochacki T, Łucznik B, et al. Analysis of self-lift-off process during HVPE growth of GaN on MOCVD-GaN/sapphire substrates with photolitographically patterned Ti mask. J Cryst Growth, 2013, 380, 99
- [63] Sui Y, Wang B, Zhao Z, et al. Facet growth of self-separated GaN layers through HVPE on large square-patterned template. J Cryst Growth, 2014, 394, 11
- [64] Lee M, Mikulik D, Yang M, et al. The investigation of stress in freestanding GaN crystals grown from Si substrates by HVPE. Sci Rep, 2017, 7, 8587
- [65] Lee M, Mikulik D, Kim J, et al. A novel growth method of freestanding GaN using in situ removal of Si substrate in hydride vapor phase epitaxy. Appl Phys Express, 2013, 6, 125502
- [66] Lee M, Mikulik D, Park S. The investigation of in situ removal of Si substrates for freestanding GaN crystals by HVPE. RSC Adv, 2018, 8, 12310