Research on the status of GaN single crystal growth

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Abstract. GaN is a third-generation semiconductor. As an ideal material of the new generation semiconductor today, it has many features such as high saturated electron mobility and wide band. The methods of GaN growth developed rapidly recently. We reviewed recent artiles and then we collect the various of methods about the GaN single crystal growth, after that we compare the difference among these method. This paper mainly talks about three methods of growing GaN single crystal: The Ammonothermal method, the Sodium-flux growth method, and the Halide vapor phase epitaxy (HVPE), and we collect both of the advantages and disadvantages. By putting all characteristics of each methods together we found that combining the HVPE method and Ammonothermal method together can connect the advantages together and avoid some of these disadvantages. We can use the HVPE method to grow the GaN seed and expand the crystal using the Ammonothermal method may be a good choice to grow the GaN single crystal at a low cost. Because if we start with Ammonothermal method, it is easy to form the polycrystalline and if we use the HVPE method to grow large crytal, it is too expensive to do so. Therefore, combining two methods can avoid the disadantages in each other and save the cost when growing.

Keywords: gallium nitride crystal growth, ammoniathermal method, hydride vapor phase epitaxy, HVPE, sodium-flux method.

1. Introduction

GaN is a kind of semiconductor with direct band gaps. Its width of the forbidden band is 3.4 eV, and the band of the alloys formed with AlN and InN can continuously adjust from 0. 65 to 6.2 eV. It covers the spectrum between deep ultraviolet, near-ultraviolet, and visible lights [1].

GaN is unstable at a high temperature and decomposes into Ga and N2 at the melting point. GaN crystal can be melted in 6 GPa and 2200 ℃ environments [2]. But traditional process methods cannot meet the acquirement. Because of this reason, GaN single crystal production is hard and costly.

With the rising demand for all kinds of GaN products and the high preferment GaN products acquiring, GaN is becoming increasingly important to make high current density devices such as lasers and high withstand voltage devices. For example, long-life high-power laser sources acquire a dislocation density that cannot be higher than 10^5 cm^{-2}. Because of the shortage of heterogeneous epitaxy such as lattice mismatch, high dislocation density due to thermal expansion coefficient mismatch, mosaic crystal structure, biaxial stress and wafer warpage, the preference of products are limited by the quality of the substrate structure. Therefore, cutting on a large and high-quality piece of GaN is a better

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solution [1]. The main production processes of the single crystal GaN are the ammonothermal method, hydride vapor phase epitaxy and Sodium-flux growth method.

As the crystal growth technology develops, combining two or three methods can be a better choice than using a single method to grow the GaN crystal. And we found that combining ammonothermal and HVPE methods may reduce the cost in the growth period.

2. Hydride Vapor Phase Epitaxy (HVPE)

HVPE is a chemical vapor deposition technology, using hydride (AsH_3, PH_3, NH_3) and chloride (GaCl, $GaCl_3$, InCl) as material. The reaction chamber can be divided into low-temperature areas and material areas. As shown in Figure 1, the reaction is the high purity HCl (850 ℃) and liquid Ga to form GaCl and a small number of by-products, and the N_2 or other gas will carry these gases to the high-temperature growing area (~1050 ℃). At the high-temperature area, the GaCl gas and the NH_3 gas react to produce GaN and deposit it on the substrate (commonly sapphire, silicon carbide, silicon, gallium arsenide) to form thin films.

Main reaction at low-temperature area:

$$Ga(l)+HCl(g)\Leftrightarrow GaCl(g)+1/2H_2(g).$$

Main reaction at high-temperature area:

$$GaCl(g)+NH_3(g)\Leftrightarrow GaN(s)+HCl(g)+H_2(g)\ [3].$$

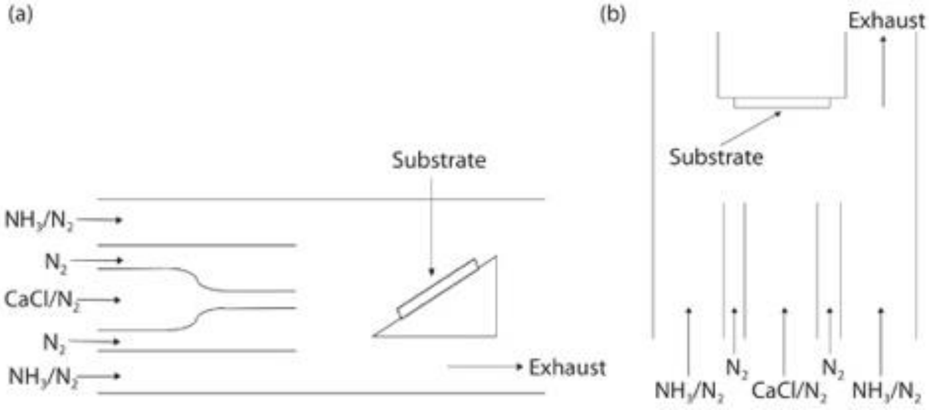


Figure 1. Schematic view of (a) horizontal HVPE reactor and (b) vertical HVPE reactor [3].

The high growth rate of the HVPE (100 μm/h) [4] is an advantage of this method. The purity of the GaN produced by this method is high and the overall impurity concentration can be lower than 10^{14} cm^3 [4]. But the exfoliation technology of the GaN crystal is a problem of the HVPE method. The laser exfoliation technique uses the laser with energy between the band gap of GaN (about 3.4 eV) and band gap of sapphire (about 9.9 eV) to decompose the GaN at the interface of the substrate to separate the GaN crystal and the sapphire substrate. By adjusting the spot and scanning rate, it is possible to separate the 4-inch GaN crystal from the sapphire substrate.[1] Kim with his team realized the separation of the 30*30 mm^2, 400-450 μm thick GaN sheets with sapphire [5]. And it is possible to produce GaN crystal at 175 mm diameter using the stitching HVPE method [6].

2.1. Oxide Vapor Phase Epitaxy (OVPE)

The OVPE method is a way to form GaN crystal using Ga_2O (g), which is created by H_2O (g) and Ga (g) and NH_3 (g). This method can prevent NH_3 and HCl from forming NH_4Cl to increase the purity of the GaN crystal. But because of oxygen impurities, the resistivity of GaN crystal grown by this method is usually lower than that of GaN crystal grown by another method.

$$2Ga(l) + H_2O(g)\rightarrow Ga_2O(g) + H_2(g) \quad (1)$$

$$Ga_2O(g) + 2NH_3(g)\rightarrow 2GaN(s) + H_2O(g) + 2H_2(g) \quad (2)$$

Recently, a team reduced the Ga metal particles by adding N_2O to the gas flow. At the same time, adding N_2O can reduce the creation of polycrystals, and compared to using the H_2O (g), using N_2O can increase the speed of crystal growth [7].

3. Ammonothermal

Although HVPE is a great method to produce GaN crystal, there are also some shortages of HVPE, such as high cost and high curvature of crystal. The basic theory of the ammonothermal method of growing GaN crystal is to dissolve all material required for GaN crystal growth into a mineralizer (such as KNH2) to form a supercritical ammonia fluid. The fluid becomes a saturated solution. This saturated solution is then transformed into a sub-stable supersaturated solution by taking appropriate technical measures to crystallize and grow GaN single crystals on seed crystals [8]. The process will heat all material, seed crystals, and mineralizer solution in a high-pressure container. Then it will create a temperature difference between the material area and seed crystal area, and it can increase the speed of convection of the solution to encourage seed crystal growth. When the material has a positive solubility temperature coefficient, the seed crystal should be placed at the top of the container, which is the low-temperature area, and the material should be placed at the bottom of the container, which is the high-temperature area. It is suitable for negative solubility temperature coefficient material by putting the material at a low temperature and putting the seed crystal at a high-temperature area [8].

For example, KNH_2.

In an alkaline mineralizer system, firstly, the GaN material reacts with the mineralizer to form the intermediate compound. Then the intermediate compound is transmitted to the crystal seed growth area, which is controlled at a suitable temperature by convection, and then the solution reaches supersaturation. Because growing on the GaN seed crystal does not need nucleation energy and the required energy is lower than spontaneous nucleation, the GaN will grow on the seed crystal first. Therefore, the reaction occurring at the dissolution area and growth area are counter-reactions to each other. The example reaction in the dissolution area with the KNH_2 mineralizer is as below:

$$KNH_2+GaN+2NH_3 \rightarrow KGa(NH_2)_4 \quad (3)$$

The following reaction occurs at the growth area:

$$KGa(NH_2)_4 \rightarrow KNH_2+GaN+2NH_3 \quad (4)$$

If use $NaNH_2$ as the mineralizer, the intermediate compound(shown in Table 1) will be $Na_2Ga(NH_2)_5$, and the chemical reaction equation is as below

$$GaN+2NaNH_3+2NH_3 \Leftrightarrow Na_2Ga(NH_2)_5 \quad (5)$$

Table 1. Intermediate compounds formed by acid mineralizers [9].

Number of coordinated NH_3 ligands	Complex unit	Halide in-vestigated
1	${}^{0}[Ga(NH_3)X_3]$	Br
1	${}^{1}_{\infty}[Ga(NH_3)XX_{4/2}]$	F
2	${}^{2}_{\infty}[Ga(NH_3)_2X_2X_{2/2}]$	F
3	${}^{0}[Ga(NH_3)_2X_4]^-$	F
5	${}^{0}[Ga(NH_3)_4X_2]^+$	Cl
	${}^{0}[Ga(NH_3)_5X]^{2+}$	
6	${}^{0}[Ga(NH_3)_6]^{3+}$	Br, I

In addition to GaN polycrystal as the raw material, Ga metal can also be used as the material.

The chemical reaction equation is as below (take the KNH_2 as the example): [7]

$$KNH_2+Ga+NH_3 \rightarrow KNH_2+GaN+1.5H_2 \quad (6)\ [9].$$

Andrew P. Purdy and others synthesized GaN crystals using NH4X (X = Cl, Br, I as a mineralizer for acidic mineralizers and studied the growth of GaN crystals at different temperatures [10].) (The figures are shown in Table 2).

Table 2. Temperature for different acidic mineralizers [8].

Temperature/℃	350-375	375-400	425-450	450-475	475-500	500-525	525-550
NH_4Cl	h&c:10	-	-	h:20	-	h:40	h:70
NH_4Br	-	c:20	c:70	-	-	h:80	h:100
NH_4I	-	c:25	c:95	-	-	c:95	h:100

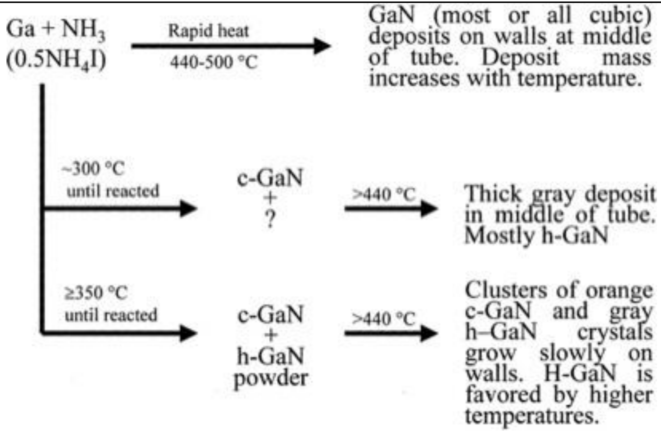


Figure 2. GaN deposit situation in different temperatures [10].

In this studying, the researchers found that,

(1) The lattice deformation of the GaN crystal becomes more severe with the increase of acidity.

(2) The length of the GaN crystal’s vector A increased with the temperature (shown in Figure 2), but the length of the vector C of the GaN crystal was almost unchanged, probably due to the impurity increase along the a-axis.

(3) Whether the seed is polished greatly influences the crystalline quality of the grown GaN crystals. The crystalline quality of the crystals is very poor when the seed GaN crystal is directly grown by the HVPE method without any polishing. But when the crystals are chemically and mechanically polished, the crystalline quality can be significantly improved [8].

Note: P refers to the physical phase, h refers to the hexagonal phase, c refers to the cubic phase; h&c refers to the simultaneous generation of both hexagonal and cubic phase GaN; h refers to the generation of only hexagonal phase GaN, c refers to the generation of only cubic phase GaN, - refers to the generation of no GaN [8].

Dirk Ehrentraut and others cultivated GaN crystals and 2-inch GaN crystals using the ammonothermal method at 750 ℃ and 600 MPa [11] (as shown in Figure 3).

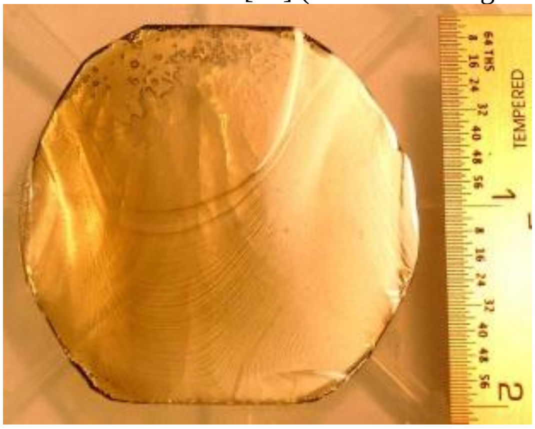


Figure 3. Photographs of SCoRA-grown bulk GaN crystals: 2-in. c-plane with macro-steps [11].

4. Sodium-flux method

The sodium-flux method is a method that adds Na to melted Ga to increase the solubility of N to meet the reaction requirement between Ga and N. Under a certain temperature and pressure, the ion Na will ionize nitrogen at the gas-liquid interface to form N^{3-}. Therefore, the density of the N^{3-} in the melt increases a thousand times compared to the nitrogen gas, and it can exist stably. The N^{3-} is transported to the temperature gradient or concentration gradient downward area. Then when the concentration is above the critical value, GaN will form spontaneous nucleation or liquid phase epitaxy (LPE) growth on GaN seeds [9].

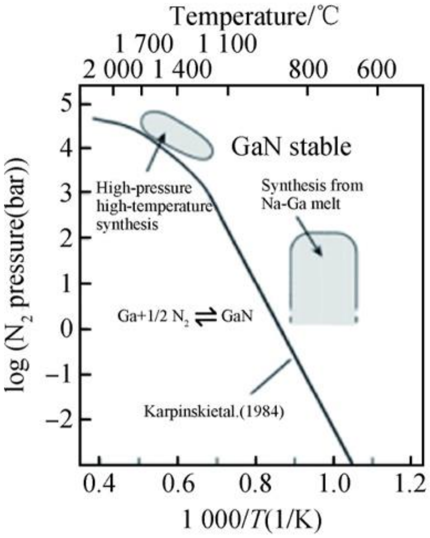


Figure 4. GaN Phase diagram [9].

In the experiment (shown in Figure 4), the growth temperature and pressure can be managed to achieve the supersaturation condition and control the growth progress to obtain continuous and effective crystal growth. Compared to the high-pressure capacitive growth conditions (temperature >1500 ℃, pressure >1 GPa), this method can grow the GaN crystal in a relatively mild condition (~800°C, <5 MPa) [9]. Compared to the high-pressure solution method without using Na (~ 1-2 μm/h) [4], the flux method can effectivity speed up the GaN crystal growth progress (20 μm/h) [4]. But this method has disadvantages either. When the local GaN saturation is high, it is easy to form multinuclear [1] spontaneously.

Masanori Morishita et al. studied the effect of Li and Ca on N and GaN generation in the N-GaN system. The data in this experiment demonstrates that adding Li and Ca to the system increases the solubility of N in the system to different degrees and increases the ratio of N to Ga content (shown in Figure 6). Increasing the ratio of N to Ga can reduce the vacancies of N in GaN crystals and improve transparency (shown in Figure 5) [12].

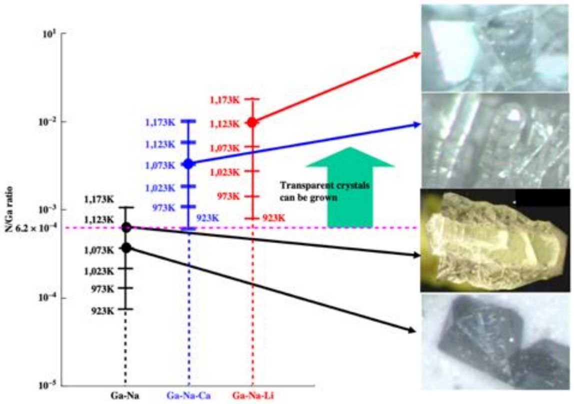
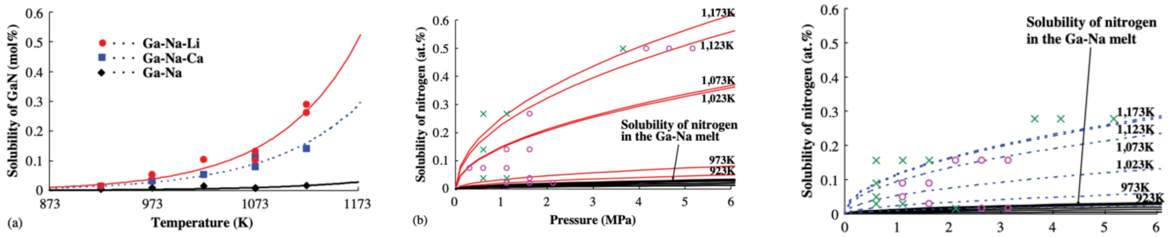


Figure 5. Relationship between the coloration of GaN crystals grown under various conditions and the N/Ga ratio at the onset of the period of growth [12].



(a) (b) (c)

Figure 6. The Ca and Li affect the solubility of N. (a) Solubility curves of solid GaN in Ga–Na, Ga–Na–Li, and Ga–Na–Ca melt. (b) Solubility of gaseous nitrogen in Ga–Na–Li and Ga–Na melt. (c) Solubility of gaseous nitrogen in the case of Ga–Na–Ca and Ga–Na melt [12].

5. Conclusion

In the commercial view, the ammonothermal method is the most promising; the ammonothermal method can improve transparency by adding different elements to reduce N vacancy. Compared to the HVPE method, the ammonothermal method can reduce process costs and require mild production conditions. Compared to the flux method, it can speed up the growth progress and has a low possibility of forming polycrystals. Growing GaN crystal on a GaN substrate can avoid the difficulty of stripping in the HVPE method. And its dislocation density is also the lowest among the three methods. The large GaN crystal block can be grown to cut into small blocks.

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