Current methods for GaN synthesis and the limitations

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Abstract. The application of GaN has greatly enhanced the performance of optoelectrical and microelectronic devices. However, the industrial application still faces huge challenges due to the difficulty during the synthesis process. This paper introduces several current methods for GaN synthesis and talks about their advantages and limitations. Four methods are introduced: high pressure nitrogen solution growth process, ammonothermal method, sodium flux process and hydride vapor phase epitaxy. As a result, they are only suitable for specific use like scientific research and can't be used for massive production. This paper reviews main GaN synthesis methods and points out the limitations they have to overcome for commercial applications.

1. Introduction
Gallium nitride (GaN) is a binary semiconductor with a direct band gap as wide as 3.4 eV. It has a Wurtzite crystal structure so this compound is very hard. GaN also has low sensitivity to radiation, as a result, it can be used in space or other extreme conditions. Because of its unique properties, in the past few years, GaN has been widely used for different applications in optoelectronic and microelectronic: light emitting diodes, blue or violet laser diodes, transistors, solar cells and photodetector for communication or guidance.

Using of GaN can greatly improve the device performance. Recent research has shown the power conversion efficiency of violet LEDs grown on bulk GaN substrates reaches a peak value of 84% at 85 °C and maintains high at high current density [1]. The high conversion efficiency of solar cells also observed by using family of GaN[2]. Hosne et al. recently propose an enhancement of 16% in the modulation bandwidth, 6.5 times in linewidth and 7.4 times in SMR improvement on 450 nm GaN blue laser[3]. These are just small part of relevant researches, more work has been done to improve device performance.

However, no matter how many devices are improved by application of GaN, they still can't be seen outside the laboratory. The reason is that GaN is hard to obtain. The melting temperature of this compound is over 2500 °C [4] and the nitrogen pressure required for congruent melting of GaN is expected to be higher than 6 GPa [5]. At a lower pressure, GaN will not melt but decompose. This property is beneficial for high-temperature application. However, it makes melting, Czochralski or Bridgman, methods impossible for crystallization of GaN. As a result, people came up with growth techniques asking for low temperature and pressure.

This paper talks about four processes for GaN growth and their advantages and limitations. Each of them has different properties and can be applied to different fields.
2. Analysis

The high pressure nitrogen solution growth process. In the early 1980s, scientists found great difference between calculation and experiment. The experiment shows nitrogen equilibrium pressure is only 2GPa while the result is 6.5GPa when calculating with ideal gas. [6] Since the previous condition is already achievable at that time, people tried to grow GaN crystal by high pressure nitrogen solution growth process [7].

This method is to converse metallic gallium into gallium nitride in high nitrogen pressure and high temperature condition (1-2GPa, 1400-1500 °C). The crystallization is driven by solid diffusion. A polycrystalline GaN film will first form on the surface of liquid gallium without a seed prepared before. Metallic gallium can help to dissolve the nitrogen molecule into atoms so that GaN can form on the surface of liquid gallium. The GaN will then dissolve and in the melt solution, nitrogen atoms will travel to cold part. Due to the thermal gradient and the characteristic that nitrogen solubility decreases with temperature, nitrogen supersaturation will happen. The schematic ideal of this method is shown in Fig. 1.

![High pressure apparatus diagram](image)

Fig. 1. High pressure apparatus: (1) capillary, (2) screw, (3) plug, (4) 3rd stage of high pressure chamber, (5) cooling system, (6) piston, (7) gas cleaner, (8) press piston, (9) 2nd stage of compression, (10) 1st stage of compression, (11) bottled as, (12) 4th stage of high pressure chamber.

By this process, scientists have grown GaN with very low dislocation density (<100cm-2). However, the size of GaN crystal produced by this technique is dependent on the container volume and reacting time. The size was limited to 1 cm (lateral) and 100 mm (thickness). Even a substrate with this small size can construct lasers with 100-200 mW power reproducibly.

Sodium flux process. This technique was invented at the end of 1990s, some scientists tried to synthesis alkali nitrides but obtained GaN by accident [8]. In this process, sodium azide and gallium
are adding into a tube full of argon that then be sealed and heated. When temperature is over 300°C, NaN₃ decomposed into Na and N₂, supplying raw material for the reaction. The reaction will happen at temperature from 600°C to 800°C and pressure between 5 to 10 MPa. The whole process will last for 24 to 96 hours with a rNA between 0.2 to 0.8 [rNA is the molar ratio of sodium] [9].

Few steps happen in the tube to form GaN crystal. Firstly, on the surface of the melting solution, a GaN crystalline layer will form. After this, the crystal will keep growing below the layer.

The temperature and pressure condition required in this process are lower than those of high pressure nitrogen solution growth and usually nitrogen and gallium won't react under 950°C. One explanation is sodium is a catalyst in this reaction. Sodium is an alkali metal and it can lose electrons easily so nitrogen can fill its first empty orbitals. Due to the two nitrogen atoms with negative charge, thus the bond in the molecules is weakened. Since there is no sodium nitride and nitrogen solubility is low in the melting solution, gallium nitride is the only product. The apparatus used in this method is shown in Fig. 2.

![Fig.2. Gas pressure cell and heater for Sodium flux process.](image)

In this technique, the product is affected by the value of rNA. When it is high, the product will be dark dine powder and when it is high, product is transparent crystal. The size and duration of growth is limited by the pressure. Since the reaction consumes nitrogen, as crystal grows, the pressure will decrease and reaction rate will decrease until stop. The other influence factor is the impurities captured in the flux. This may lead to formation of polycrystalline layer, which significantly reduce the performance of GaN semiconductor devices.

**Ammonothermal method.** The ammonothermal method is one technique invented in the middle of 1990s to provide GaN with high purity and crystallinity at relatively lower temperature (around 400–550°C) and pressure (around 100–500MPa)[10]. The experimental procedure is not complex. Ga metal or GaN powder is usually used as procurer and NH₄Cl is mineralizer. This technique is based on chemical reactions, so adding mineralizers can increase the reaction rate by produce more ions in the supercritical NH₃ solution. That makes the reaction between Ga and NH₃ possible in the condition said before. Adding them into autoclave with Pt covered inner wall, which helps prevent contamination. Introducing NH₃ into the autoclave after evacuation. Autoclave is heated up using tube furnace toward 500°C in 6h and kept at this temperature for 72h. The pressure in autoclave is 120-135MPa, which results from the heating. The whole process lasts about 3.5 days and this is the most important problem of this technique. The apparatus used in this method is shown in Fig. 3.
Fig. 3. Schematic idea of the ammonothermal method.

Ammonothermal method is mostly developed for mass production of GaN crystals. Ammonothermal company can produce GaN on substrates with diameter reaching 2 inches, however, the slow rate and high point defect concentration still limit its application.

Hydride vapor phase epitaxy (HVPE). Another technique is called hydride vapor phase epitaxy (HVPE). Just like silicon wafer, for industrial application, large area of material is necessary. As said before, it’s hard to manufacture GaN directly so in HVPE, a substrate is used for GaN crystal growth and the substrate is usually sapphire. In this technique, GaN is crystalized from gas phase in a reactor. In the low temperature part of the reactor (~800 °C–900°C) metal Ga is reacted with hydrochloride (HCl) and form gallium chloride (GaCl). GaCl will then carried by inert gas travel to high temperature part. At 1000 °C–1100 °C, GaN is formed by reaction between GaCl and ammonia. The last step is to crystallize GaN on the substrate. The driving force for this reaction is supersaturation, which comes from the inconsistence between pressure of GaCl. The schematic ideal of this method is shown in Fig.4.

There are mainly three important limiting factors in HVPE, two of them is parasitic deposition and anisotropy of the growth, they will lead to defects in the crystal. As a result, time for crystallization should be well controlled. Another limiting factor is the substrate. As said before, sapphire is the most common substrate, however, there is a large mismatch between the lattice constant and thermal expansion coefficient of sapphire and GaN. These mismatches will lead to force acting in the lattice. As GaN growing, the force will become larger so more defects happen.
3. Result

Previously, four different techniques for GaN crystal growth have been introduced. Table 1 shows different conditions they need for crystal growth and the size of their product. High pressure nitrogen solution growth process needs the most critical condition: 1-2 GPa of pressure and 1400-1500 °C of temperature. The size is about 1 cm in lateral and 100 mm in thickness. Sodium flux asks for a 5-10 MPa nitrogen pressure, 700-800 °C of temperature and the size of the crystal depends on the pressure. Ammonithermal method needs 200-300 MPa of pressure, only 400-500 °C of temperature and get a product with diameter reaching 2 inches. Hydride vapor phase epitaxy requires a temperature over 1000 °C and no pressure condition is necessary. The crystal has a diameter around 5 mm.

|                     | High pressure nitrogen solution | Sodium flux | Ammonithermal method | Hydride vapor phase epitaxy |
|---------------------|--------------------------------|-------------|----------------------|-----------------------------|
| Pressure            | 1-2 [GPa]                      | 5-10 [MPa]  | 200-300 [MPa]        | No requirement              |
| Temperature         | 1400-1500 [°C]                 | 700-800 [°C]| 400-500 [°C]        | 1000 [°C]                   |
| Size                | 1 [cm] (lateral), 100 [mm] (thickness) | Depend on pressure | 2 inches of diameter | diameter exceeding 5 [mm]   |

The temperature is usually not a serious problem for industrial manufacturing of GaN but the pressure requirement is. Although hydride vapor phase epitaxy doesn't need a high pressure, this technology costs so much that it is only a experimental way for scientists and not be use for commercial application.

The other three methods all ask for a high pressure requirement. To maintain such large pressure, high quality equipment is necessary. However, for mass production, large scale equipment is almost impossible to reach such high quality requirement. Another disadvantage is the need for exact oxygen- and water-control to prevent formation gallium oxide. An isolated production system that is full of inert gas is required. Moreover, the chemical compounds used in the reaction hinder the commercial application of them. For example, storing of sodium requires very strict condition and all the materials have to be highly pure that no contamination is allowed. Therefore, GaN still cannot be producted massively but recently much researches have been done to apply GaN in different areas.

4. Conclusion

The previous four methods are the main methods used for GaN synthesis but none of them can be applied for massive production due to the critical reaction condition like high pressure, high temperature and purity requirement. They do work for some specific purposes like scientific research, which only needs a small amount and doesn't care about the cost.

Using of bulk GaN for massive production is hard but using nanoscale GaN with different shapes like nano-wires or nano-tube is possible. Adding nano scale GaN structure on thin film can also affect the performance of different devices like solar cells and transistors. According to the difficulties of growing bulk GaN, more works can be done to find out how can nano scale GaN improve the performance. Consequently, GaN would be a key material in many applications like opto-electrical and microelectronic devices.

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