GaN-based LEDs using Homo-Epitaxial technology and the Progress and Challenges of HVPE method

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Abstract. GaN and other group III-nitrides are promising materials for optoelectronic devices applications. Currently, sapphire is the most widely used substrate material for GaN LEDs due largely to economic considerations. During the past decade or so, free-standing GaN substrates fabricated via HVPE have gained technological importance and circumventing the shortcomings of sapphire substrates in terms of thermoconductivity and lattice mismatch. This technology, however, does have its own set of challenges. This review summarizes the current state of freestanding GaN substrate technology, the challenges it is facing, and outlook.

1. Introduction
The appearance of blue LEDs based on GaN gave people the chance to create white LEDs, which are more economical, environmental-friendly and have higher efficiency, so they attract a lot of attention and become popular very soon. To make a LED chip, it needs monocrystal substrates as the base and this is the key to decide the quality of a LED. Although using homo-epitaxial technology is the best choice, the growth of GaN monocrystal faces some difficulties, so people tend to let GaN grow on other materials, which is called hetero-epitaxial, and sapphire is the most successful material to make LEDs in business nowadays.

Sapphire has some advantages over other materials. Considering all possible monocrystal substrates materials, we can see that SiC seems to be the one suitable material, due to lower lattice mismatch and smaller difference in the coefficient of thermal expansion. However, it needs a very complex procedure to process properly and the expense is high. Therefore, it cannot be a good choice to use for large-scale production. If the LEDs want to be industrialized, the process to produce substrates should be simple and the expense ought not to be too high. That’s why though the mismatch between sapphire and GaN is up to 10^8 cm^-2[1], it is widely used around the world. Table 1. shows some physical properties of sapphire.

Table 1: The Physical Properties of Sapphire[2]

| Physical Properties                  | Numerical Value | Scope of Application |
|--------------------------------------|-----------------|----------------------|
| The Coefficient of Thermal Expansion / K^-1 | 9.03 x 10^-6 (/c axis) | 20~1000°C            |
| Thermal Conductivity /[W/(m·K)]     | 23 (/c axis)    | 296K                 |
| Energy Gap / eV                      | 8.1~8.6         | 300K                 |
| Tensile Elongation / GPa             | 190             | 300K                 |
| Poisson’s Ratio                      | 0.25~0.30       | 300K                 |
Though the sapphire-substrate LED is produced and sold worldwide, it also has some limitations. The one is the large lattice mismatch between foreign substrates and GaN, this will affect the continuum of lattice. Even on the most suitable film of sapphire, the lattice mismatch is still as high as 13.3%, and this will cause the dislocation density up to $10^{11} \text{cm}^{-2}$[2]. Meanwhile, the mismatch of thermal is also as large as -25.5% [2], which may break the chip in some extreme situations. Besides, low light extraction efficiency (LEE) is also a big problem.

When LEDs are connected with batteries, the carriers, electronics or holes, are recombined in the quantum confinement and emit photons, then LEDs emit light. However, since chips may absorb and reflect some photons, a large bunch of photons cannot arrive at people’s eyes. According to the calculation, the conventional sapphire-substrate LEDs’ LEE is only around 29%[3].

Considering all of the defects mentioned above, people are focusing on looking for other better substrates and free-standing GaN substrate was considered again. Using homo-epitaxial technology can reduce the mismatch between lattice and improve the thermoconductivity. Meanwhile, it can improve the quality of the chip and increase the internal quantum efficiency. What’s more, GaN substrate can fabricate vertical-structure chip, which can enlarge the current expansion scale. Therefore, free-standing GaN substrate is the most valuable research direction for people to devote to.

This passage uses meta-analysis method to analyze the potential technologies which can be used to fabricate GaN substrates and thinks the free-standing technology is the best one to improve the quality of GaN-based LEDs. HVPE is used most to produce free-standing GaN, therefore, the passages focus on discussing this technology and want to make people understand this technology better.

2. Literature review

Many studies have devoted to finding effective ways to improve the quality of LEDs’ substrates, such as new substrates. However, hetero-epitaxial has its own defect, the high lattice mismatch. Thus, more and more groups deter to homo-epitaxial technology, although making GaN substrates has some obstacles that need to be overcome.

There have been many institutions studying the GaN fabricating process all over the world and some discoveries and improvements have been achieved[2]. The Dam’s[3] group found that the shape and size of the reactor influence the rate of reaction a lot. A slice change of the angle of quartz nozzle can have a big effect on the growth rate. Safvi’s[4] group found that the relationship between the growth rate of GaN and temperature is similar to MOCVD technology through contrast tests. The increasement of growth rate is proportional to the partial pressure of GaCl. The partial pressure of NH$_3$ has little effect on the growth rate but affects the quality of the GaN layer. Zellweger’s[5] group found that using N$_2$/H$_2$ instead of purify N$_2$ as the carrying gas can improve the quality of GaN crystals. Meanwhile, some companies in United States and China have been devoted to achieving the pyriform artificial GaN crystals with HVPE then people can attain GaN crystals by using linear saw. The following GaN can continue to grow in the GaN crystals attained before, thus, the dislocation density can drop step by step and people can get perfect material ultimately.

The previous researches mainly focus on the effects of variables during manufacturing process but do not analyze the most popular way to produce the free-standing GaN. Therefore, this passage discusses the HVPE technology thoroughly using meta-analysis method and wants to let people understand the development of free-standing GaN substrates better.

3. Free-standing GaN substrates and its improvement

Traditionally, free-standing GaN substrate means LED chips that they can remove the extra substrate and grow on large GaN monocrystal directly. However, because of the high temperature and pressure required, producing large enough GaN monocrystals as the substrates needs to overcome lots of technology problems. There are still some efforts need to do to arrive at the industrialized goal.

Nowadays, the free-standing GaN substrate is fabricated with another substitutable technology. The widest used fabrication method is that getting GaN thick single crystal layer via hetero-epitaxial technology at first, then stripping the GaN layer from the foreign substrates and doing following
processes to make the substrates be a suitable substrate. Though GaN substrates made by this way cannot be as perfect as ideal large GaN substrates, it still makes an impressive improvement in the quality and efficiency of optoelectronic devices.

In theory, homo-epitaxial is the best way to produce GaN-based chips, but there are still some obstacles that need to be overcome before devoting chips into market. The main challenge is the high cost, due to the difficulty to produce large size bulk of single GaN crystals. People have made large efforts to find useful methods and researchers have made 2 inches GaN single crystals successfully and the dislocation is reduced to $5 \times 10^3 \text{cm}^{-2}$ since now. However, this method achieved success just in the laboratory and cannot be industrialized. Therefore, the common way to produce GaN crystals is to strip the thick GaN layer which grows on hetero-epitaxial substrates, such as sapphire. The following passage will mainly discuss how to produce the large size of GaN single crystals and the sequence process technology.

4. The main methods of making GaN single crystals
There have been some applied methods to produce free-standing GaN substrates, such as ammonothermal crystal growth, Na-flux method, high pressure growth method and HVPE. Table 2 shows the comparisons of some important growing qualities of each method. Among these methods, HVPE is the critical choice, because it costs less and has developed maturely. The following passage will discuss this method.

| Growing Methods | Ammonothermal crystal Growth | Na-flux Method | High Pressure Growth Method | Na-flux Method |
|-----------------|-----------------------------|---------------|------------------------------|---------------|
| Growing Conditions $T_g/\degree \text{C}$ | 1000–1050 | 400–500 | 400–500 | 600–800 |
| Time / h | $<10$ | 170 | 100–200 | 100 |
| Dislocation Density / cm$^2$ | $1 \times 10^5$ | $5 \times 10^4$ | 10–100 | $2 \times 10^5$ |
| $p(N_2)/MP_a$ | Ordinary Pressure | 200–300 | 1–2 | 5–10 |
| FWHM(0002) / arcsec | 100–145 | 15–50 | 20–30 | 55 |

4.1. The development of HVPE
The hydride vapor phase epitaxy (HVPE) method is a very old method for semiconductor’s growth. It has also been the most popular technology for producing free-standing GaN substrates, since it is cheap and the process is simple. Meanwhile, GaN has a very high growth rate over 800 $\mu m/h$, and it can grow evenly on a large scale.

Its manufacturing-system includes furnace stack, quartz reactor, gallium boat and the equipment for gas to flow. The following are the related chemical equations[2].

$$2\text{HCl}(g) + 2\text{Ga}(l) \rightarrow 2\text{GaCl}(g) + \text{H}_2(g)$$
$$\text{GaCl}(g) + \text{NH}_3(g) \rightarrow \text{GaN}(g) + \text{HCl}(g) + \text{H}_2(g)$$

HCl flows into the gallium boat mixing with $N_2$ and reacts with Ga in it to create GaCl; then GaCl and NH$_3$ go into the equipment which is above the substrates to create GaN. HVPE growth reactions usually occurs in the environment where temperature is over 1000$\degree$C and under the normal air pressure. Currently, most companies aim to attain the GaN crystals. Usually, they let GaN thick layer formed on the foreign substrates at first, such as sapphire or GaAs, and then they remove the foreign substrates using physical or chemical methods, like using laser or etching the substrates.

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4.2. The challenge of HVPE technology

Although this technology has many advantages and has been widely used, there are also some problems remained. The main problem is the vice production \( \text{NH}_4\text{Cl} \) appears during the growth process. It will form some corrosive powder below 340℃ and this powder will pollute the pyriform GaN crystals and prevent the current from flowing, so that it will take longer time for GaN to grow and waste a lot of money. People need to find a way to keep the powder away from the reaction areas. One of the possible solutions is to use vertical HVPE reaction chamber, where pyriform GaN crystals are hang on the top of the chamber, so that powder cannot drop on crystals’ surface. This is mentioned by Aixtron Company and used commercially.

4.3. Process of removing foreign substrates

To get native thick GaN crystals, researchers need to strip the GaN substrates from the foreign substrates. The way chosen to strip the foreign substrates is dependent on the chosen foreign substrates. Chemical etching is often used when GaAs is regarded as the substrates and laser lift-off is applied on sapphire-based GaN.

Although this method seems to be perfect, there is great challenge during removing process. Taking the laser lift-off process as the example, as impulse UV lasers irradiating through sapphire substrates, the temperature of the film between GaN and sapphire increases soon. Followed by thermal decomposition of nearby GaN, GaN can separate from sapphire substrate. To apply this technology, the energy of laser should be a little higher than the energy band of GaN (3.4eV)[7]. GaN cannot be stripped totally with low energy while it may be broken if the energy is too high. It is very easy for GaN to break during removing process and because of the limitation of the energy density of lasers, researchers have to find other ways to overcome the challenge.

Some possible solutions have been found. The first one is that the adopted lasers should have moderate energy density. The second way is that researchers can start to scan the substrates from the bounder, so that the gas formed during the decomposition process can emit from the bounder which can reduce the air pressure above the GaN layers. Also, people can stick temporary substrates to GaN crystals, such as Si. The temporary film can support the GaN during the stripping process so GaN substrates keep integrity. Besides these methods, there is also a technology called self-separation. The State Key Laboratory in Peking University has studied it and already had some discoveries [7]. The self-separation technologies include using chemical pre-treatment and pre-thermal treatment on sapphire surface they found have obtained 2-inch GaN crystals successfully. This is also a potential technology.

5. Future outlooks

Free-standing GaN substrates can bring a lot of benefits such as simplifying the fabricating-process sharply. Meanwhile, due to the perfect thermal stability and chemical stability, there is still room for people to explore to find more efficiency epitaxial technology. Plus, there is no lattice mismatch and the dislocation density has been reduced[8]. It has a bright future in LEDs with much higher power.

Homo-epitaxial technology also has big potential in producing vertical structure chips, which can increase the photon emitting efficiency and enlarge the LEDs’ lighting area. What’s more, it can provide high quality non-polarization films, which may reduce the inter-quantum efficiency and can multiple
the lighting efficiency. Seoul Semiconductor Company has released their production, nPola, and its lighting efficiency has reached 500lm/W. This is much higher than LEDs which are available in the market.

6. Conclusion
GaN has several advantages in producing optoelectronics devices and some of them have been used in business all over the world, especially LEDs. However, with the fast development of optoelectronics business, people are asking for high power devices with much higher efficiency and quality but the current technology cannot satisfy people's demands.

Homo-epitaxial technology is mentioned to solve this problem. Free-standing substrates can eliminate the defects like lattice mismatch, and it has high thermoconductivity. Also, it can reduce the dislocation density. Lots of methods have been explored to produce thick bulk GaN crystals and HVPE is a practical one. Since it has a high grown rate and can reduce the cost, this technology has been used in business successfully. However, it still cannot solve the dislocation problem totally and it is easy to break the GaN substrates during stripping process, and this will increase the expense and refine its development.

Although there are many obstacles need to be overcome, the advantages of free-standing GaN have attracted a lot of interests of companies and research groups worldwide. It can multiply the efficiency of inter-quantum and increase the lighting ability sharply. Moreover, it can apply for non-polar or semi-polar substrates and produce vertical structure chips. Thus, free-standing GaN substrates are promising materials for producing high power LEDs or other solid light devices. With the development of technology, the cost of GaN can be reduced and more and more GaN-based LEDs will be applied in business.

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