Article

Development of $GaCl_3$ Supply Technology for Mass-Production Halide Vapor-Phase Epitaxy System

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Silicon carbide (SiC), gallium nitride (GaN), and gallium oxide (Ga_2O_3), which have wide band-gap and big Baliga's Figure of Merit compared with silicon (Si), are required to improve the power conversion efficiency of power devices for the low carbon society. Especially, Ga_2O_3 is good material because of low cost substrate can be manufactured. Reduction of the growth cost is a major issue for the spread of Ga_2O_3 devices, and we think that development of a mass-production system using HVPE method with capability of high-speed and high-purity growth is necessary for reduction of the growth cost of Ga_2O_3.

In this paper, we report on the trial production and evaluation of the $GaCl_3$ generator that supplies metal chloride ($GaCl_3$) as source material for mass-production HVPE system. As a result of generating $GaCl_3$ using two-step reaction with Ga metal and chlorine gas, it was confirmed that the amount of $GaCl_3$ reaches more than 7000 μmol/min required for Ga_2O_3 growth in the HVPE system (6 inches x 7). By optimizing the structure of the container filled with Ga metal and gas flow conditions, we succeeded in increasing the reaction efficiency between Ga metal and chlorine gas to 99% or more.

1. Introduction

Japan's power consumption reaches one trillion kWh annually and power, illumination, and communications equipment account for a high percentage of this consumption. Developments in power electronics technology are needed to promote energy savings in these areas, and the spotlight is on wide band-gap semiconductor devices using SiC, GaN, and Ga_2O_3 in addition to the current mainstream Si devices.[1-8)]

There are various deposition methods for these next-generation semiconductor materials, such as molecular beam epitaxy (MBE), sublimation, pulse laser deposition (PLD), metal-organic chemical vapor deposition (MOCVD), and halide or hydride vapor phase epitaxy (HVPE). MOCVD is mainly used for the production of optical devices, such as LEDs, laser diodes, and electronic devices for amplifiers used in cell phone base stations. Due to the rapid development of the IT society in recent years and the promotion of energy conservation, there is increased demand for higher performance, lower cost, and higher efficiency semiconductor devices. As a result, the focus is on HVPE, the growth method shown in Figure 1, that has been adopted for GaN substrate production devices for its fast growth speed.[9) 10)]

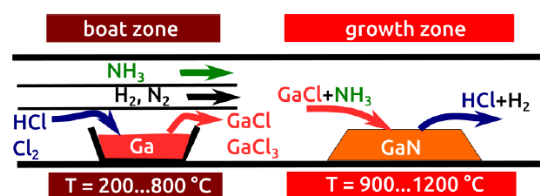

Figure 1 Schematic diagram of conventional HVPE reactor.

The advantages of HVPE as a growth method are that it uses metal chlorides (GaCl, $GaCl_3$, $AlCl_3$, $InCl_3$, etc.) for lower source material costs than other methods, high purity growth is possible, and its growth speed is fast (100 μm/hr or more) in case of GaN and gallium arsenide (GaAs). However, only practical methods for single smaller diameter (2 inch or 4 inch) units have been developed. To reduce growth costs, a practical mass-production HVPE system for larger diameter (6 inch or 8 inch) units is required.

The difficulty in fabricating mass production HVPE system is caused by the source material internal supply method in which both the metal chloride generation unit and

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the growth unit are located in the same reactor. [10] In order to correspond to large diameter substrates in conventional HVPE system, it is necessary to scale up the complex metal chloride generator unit that is made up of quartz parts and gas nozzles. However, fabricating larger quartz parts is difficult and impractical. Therefore, the external metal chloride supply method has been proposed in which the metal chloride generator and growth unit are separated. [11] In fact, there are reports of GaN growth based on the HVPE method that supplies vaporized $GaCl_3$ from an external supply of solid $GaCl_3$. [12] However, solid $GaCl_3$ is more expensive than Ga metal. Moreover, it is highly moisture absorbent so that when filling source material water gets mixed in. As a result, this method has not been used for mass-production system. Also, conventional $GaCl_3$ generators that generate $GaCl_3$ with a two-step reaction using Ga metal and chloride gas cannot produce amount of $GaCl_3$ required for mass-production system because the reaction between the Ga metal and chloride gas is not enough. In addition, because a horizontal flow is used, the increased reaction area creates a larger footprint which in turn leads to a larger system. A $GaCl_3$ generator for a mass-production HVPE system requires a more reaction efficiency to produce a higher supply of $GaCl_3$ and a smaller generator.

Schottky barrier diodes consists of single-layer structures that use the HVPE method to grow Ga_2O_3 layers on 2 inch or 4 inch single substrates, have been verified and produced by Novel Crystal Technology [13]. But unfortunately, reducing the growth cost is required for mass-production.

Therefore, to produce a practical mass-production HVPE system for growing Ga_2O_3, we developed a more compact $GaCl_3$ generator that can produce large quantities of $GaCl_3$. We made a prototype $GaCl_3$ generator for commercial use that can generate $GaCl_3$ from a reaction between Ga metal and chloride gas, and this paper reports on the generated amount of $GaCl_3$ and the reaction efficiency.

2. Development of the $GaCl_3$ Generator

For the $GaCl_3$ generator, we used the two-step reaction method to generate $GaCl_3$ by causing a reaction between Ga metal and chloride gas (Cl_2 or HCl) at more than 800℃. [14] GaCl was generated in the first step (Zone 1) and in the reaction in the second step (Zone 2), highly pure $GaCl_3$ was generated.

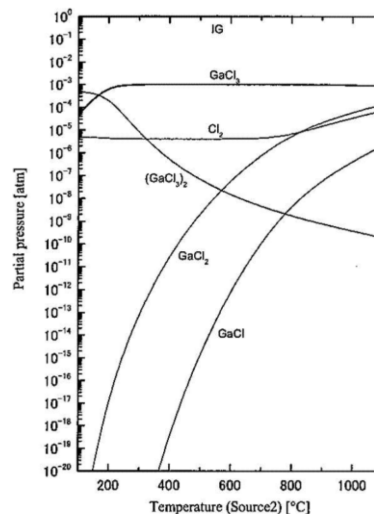

Figure 2 Equilibrium partial pressures of gaseous species in $(Ga\text{-}Cl_2)\text{-}Cl_2$ reaction.

Figure 2 shows the reaction temperatures and equilibrium partial pressures in the $(Ga\text{-}Cl_2)\text{-}Cl_2$ reaction. [14] In the $(Ga\text{-}Cl_2)\text{-}Cl_2$ reaction, highly pure $GaCl_3$ can be generated over a wide temperature range. This is because there is no Ga metal in Zone 2 and the GaCl generated in Zone 1 selectively reacts with the Cl_2 supplied in Zone 2. Additionally, because $GaCl_3$ is stable at approximately 200℃, another advantage of using $GaCl_3$ is that it can be transferred to the growth reactor through pipes at a relatively low temperature.

Figure 3 shows a photo of the exterior of the $GaCl_3$ generator that we developed for the aforementioned $(Ga\text{-}Cl_2)\text{-}Cl_2$ reaction and a cross-sectional view. Table 1 shows the main specifications of the $GaCl_3$ generator. The interior of the quartz tube can set one to four vessels (called boats) that can be charged with Ga metal. There is a mantle heater installed for heating on the exterior of the quartz tube. We have used multi-series boats in which the introduced gas flows from the top boat to the bottom boat. In Zone 1 which is filled with Ga metal, the Ga metal-Cl_2 gas reaction generates GaCl and that is transferred to Zone 2. By re-adding Cl_2 to the boat in Zone 2, the GaCl-Cl_2 gas reaction occurs and $GaCl_3$ is generated. The generated $GaCl_3$ gas is supplied through pipes to the growth reaction furnace.

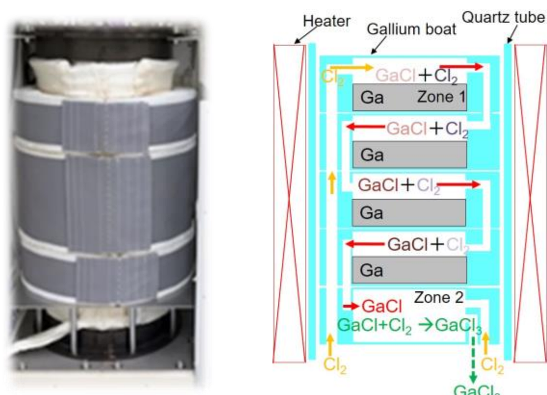

Figure 3 Photo and cross sectional view of the $GaCl_3$ generator.

Because multi-series boats are used, the footprint of the $GaCl_3$ generator is 500 x 500 mm which is only about half the footprint of the horizontal flow $GaCl_3$ generator using the two-step reaction method that was adopted for experiments. By fabricating the $GaCl_3$ generator smaller, this also makes it possible to install multiple gas supply units inside the growth system. In order to acquire contact time between the Ga metal and Cl_2 gas, we installed multiple diffusion plates inside the boats. A patent is currently pending for the $GaCl_3$ generator that we developed.

Table 1 Specifications of the $GaCl_3$ generator.

	Specification
Reaction	Ga +1/2Cl_2 → GaCl (Zone 1) GaCl + Cl_2 → $GaCl_3$ (Zone 2)
Source zone	Multi series graphite boat
Reactor	Vertical quartz reactor
Heater	3-zone electric furnace
Amount of Ga metal	3 kg/boat
Size	500×500×1300(H) mm

3. Experiment

The following is a description of the experiment conducted with the $GaCl_3$ generator that we developed. Figure 4 shows the system diagram for the $GaCl_3$ generator. The gas supply system consists of the Cl_2 line for GaCl generation, the Cl_2 line for $GaCl_3$ generation, the quartz tube purge line, and the H_2 line for Ga cleaning. The flow rate of the various gases are controlled by the mass flow controller and the gases are supplied to the interiors of the boats.

First, we measured the temperature distribution in the $GaCl_3$ reactor. We inserted a K-type thermocouple into the upper flange and we confirmed the vertical temperature distribution in the quartz reaction tube by changing the position of the thermocouple. Next, we generated $GaCl_3$ by using a boat filled with Ga metal for GaCl generation and another one for $GaCl_3$ generation. Ga metal (purity 7N, made by DOWA Electronics) and Cl_2 gas (99.999%, made by JFP) were used to generate $GaCl_3$. Table 2 shows the generating conditions. The flow rate of Cl_2 for $GaCl_3$ generation was two times that of Cl_2 for GaCl generation (the theoretical optimum value). We prevented the disproportional reaction of the initially generated GaCl (3 GaCl → $GaCl_3$ + 2 Ga) in the exhaust pipe by starting the flow of Cl_2 for $GaCl_3$ generation followed by the flow of Cl_2 for GaCl. The generated $GaCl_3$ was passed through piping that was heated to 200℃ and collected in a trap cooled to room temperature or less. Also, a rotary pump was installed for nitrogen/vacuum cycle-purge before the $GaCl_3$ generator was opened to the atmosphere.

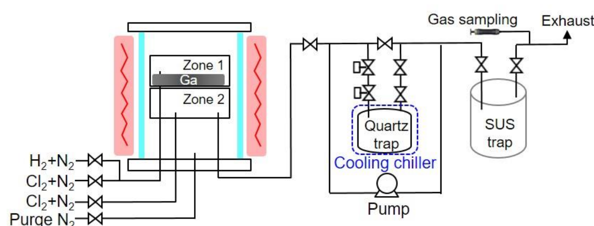

Figure 4 Experimental system diagram of the $GaCl_3$ generator.

We estimated the generated amount of $GaCl_3$ from the Ga metal weight change and input Cl_2 flow rate. We calculated the Ga metal and Cl_2 gas reaction efficiency from the estimated generated amount of $GaCl_3$ and the theoretical generated quantity. We confirmed the generated amount of $GaCl_3$ against the total gas flow rate (N_2 + Cl_2) above Ga metal, and the input Cl_2 flow rate.

To visually confirm the generation of $GaCl_3$ gas, the generated $GaCl_3$ gas was flowed to the interior of the cooled quartz trap. The powder solidified in the quartz trap was measured by XRD measurement for substance identification. While $GaCl_3$ was generated, a detector tube (measurement range of 0.5 to 8 ppm, made by Gastec) was used in the exhaust pipe for direct sampling and the unreacted Cl_2 concentration was confirmed. We also simulated the gas flow

in the boats filled with Ga metal to visualize it and verify the effectiveness of the diffusion plates.

Table 2 Process condition of the $GaCl_3$ generator.

Parameter	Setting Value
Reaction Pressure	Atmospheric Pressure
Reaction Temperature	850ºC/boat temp.
Reaction Time	60 min.
Total Gas flow	Cl_2 : 25 – 200 sccm N_2 : 950 – 2975 sccm
Purge Gas in quartz tube	N_2 : 2000 sccm

4. Results and Discussion

4.1 Temperature characteristics of the $GaCl_3$ generator

Before conducting the $GaCl_3$ generation experiment, we measured the temperature distribution of the interior of the $GaCl_3$ generator (see Figure 5). We inserted a thermocouple into the $GaCl_3$ generator and measured the temperature distribution in the vertical direction. At the boat interior temperature at 850℃, the temperature distribution of the area where the Ga metal boat was located (the reaction area) was approximately Δ 5 ℃. This is a good temperature distribution. From this result, we determined that the insulation was functioning as designed and the reaction area had a sufficiently wide stable temperature range so that we could increase the number of boats filled with Ga metal and further increase the generated amount of $GaCl_3$.The advantage of this $GaCl_3$ generator is that by using multi-series boats, we can increase the Ga metal surface area without increasing the installation area.

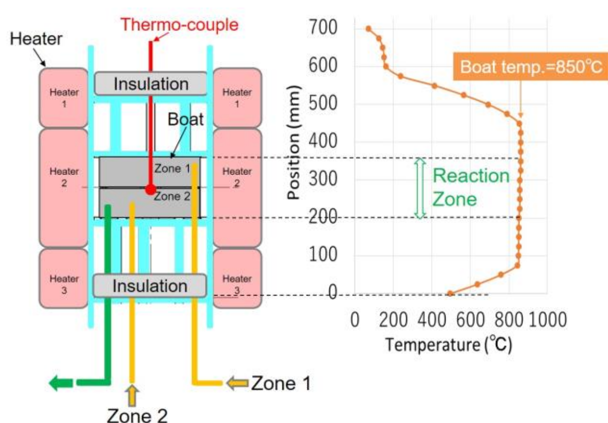

Figure 5 Temperature distribution of the $GaCl_3$ generator.

4.2 Confirmation of $GaCl_3$ generation

Figure 6 shows $GaCl_3$ being collected in the quartz trap. We visually confirmed that $GaCl_3$ gas formed as a white powder at the bottom of the quartz trap. We believe that all of the generated gallium chloride was $GaCl_3$ due to the fact that we did not visually confirm Ga metal in the powder at pipes located outside the $GaCl_3$ generator or in the quartz trap. After conducting XRD measurements of the collected powder (see Figure 7), the measurement result was a good match with the diffraction pattern calculated from the crystal structure and the powder was identified as $GaCl_3$.

Figure 6 Photos of $GaCl_3$ solidified in a quartz trap.

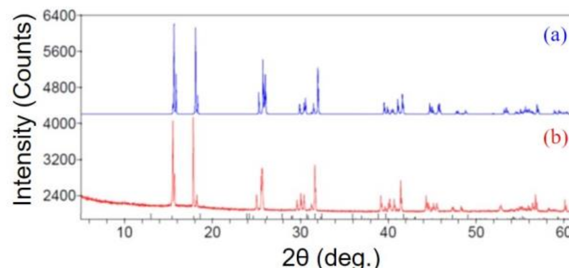

Figure 7 XRD data of solidified powder in a quartz trap.
(a)Calculated $GaCl_3$ data from crystal structure.
(b)Measurement result of powder trapped in quartz trap.

4.3 Generation characteristics of the $GaCl_3$ generator

We examined the relationship between the total flow rate of the Cl_2 and N_2 into Zone 1 and the Ga metal-Cl_2 gas reaction efficiency (Figure 8). At this time, we fixed the Cl_2 flow rate for GaCl generation to 25 sccm and set the Cl_2 flow rate for $GaCl_3$ generation to two times that (the theoretical optimum value). We only used one boat for GaCl generation at this time. When the total flow rate was 3000 sccm, the Ga metal-Cl_2 gas reaction efficiency was approximately 80%, but when the total flow rate was reduced to 1000 sccm, the reaction efficiency improved to over 99%. When we sampled the exhaust gas from the $GaCl_3$ generator with a gas detector tube during $GaCl_3$ being generated with a total flow rate of 1000 sccm, the unreacted Cl_2 concentration was extremely small at less than 1 ppm. Considering that reaction efficiency of the conventional horizontal flow $GaCl_3$ generators is approximately 80 to 90% [15], the $GaCl_3$ generator that we developed is extremely good efficiency.

Figure 9 shows the results when we fixed the total flow rate in Zone 1 to 1000 sccm, 1500 sccm, and 3000 sccm and examined the relationship between Cl_2 flow rate and generated amount of $GaCl_3$. The Cl_2 flow rate and generated amount of $GaCl_3$ have a proportionate relationship and we were able to attain good control when the Cl_2 flow rate was increased. By increasing the Cl_2 flow rate, it is likely that we can secure amount of $GaCl_3$ reaches more than 7000 μmol/min required for Ga_2O_3 growth in the HVPE system (6 inches x 7). It can especially be seen that the total flow rate over the Ga metal is reduced, the generated amount of $GaCl_3$ is high. It is believed that this result because when the total flow rate over the Ga metal is reduced, the flow speed is also reduced and the Cl_2 residence time increased. By improving the reaction efficiency between Ga metal and Cl_2 gas, increases the generated amount of $GaCl_3$ and unreacted Cl_2 gas is not supplied to the growth reactor.

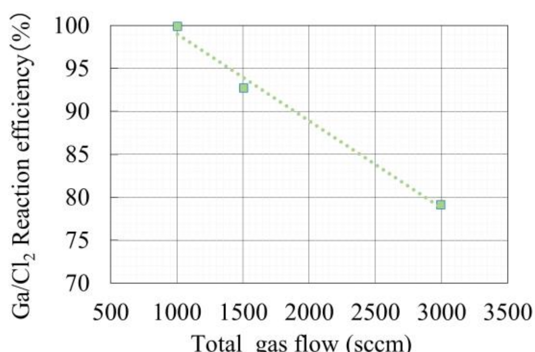

Figure 8 Reaction efficiency of Ga metal and Cl_2 gas.

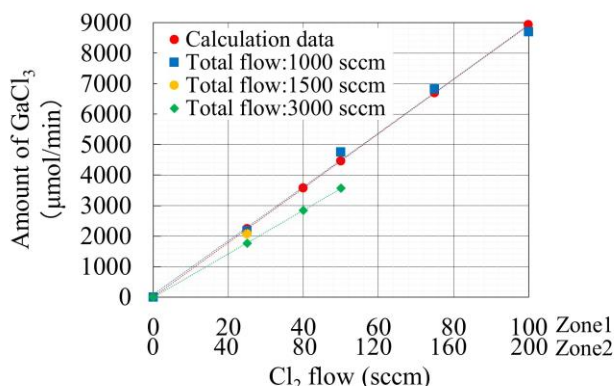

Figure 9 Relationship between Cl_2 flow rate and amount of $GaCl_3$ generation.

In the unit we developed, the boats in the $GaCl_3$ generator have numerous diffusion plates that improve the reaction efficiency of the Ga metal-Cl_2 gas. Figure 10 shows the simulation results of gas flow when diffusion plates are installed. By installing diffusion plates with bent ends into the boats, it can be seen that gas circulates vertically. By creating circulation, the generated GaCl is prevented from staying on the surface of Ga metal, thereby improving the reaction efficiency between Ga metal and Cl_2 gas [16].

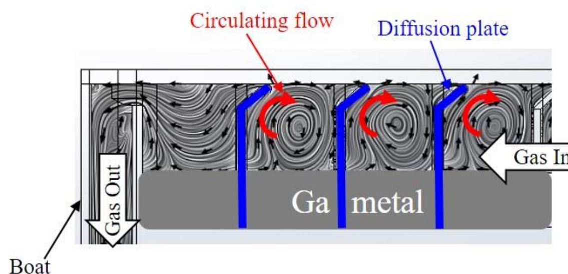

Figure 10 Structure of diffusion plate and simulation result of circulating flow in Ga boat.

5. Summary

In this project, we developed and assessed a prototype external supply $GaCl_3$ generator for mass-production HVPE system. This prototype used a "two-step reaction process using Ga metal and Cl_2 gas" that we believed could provide an inexpensive supply of highly pure $GaCl_3$.

In our examination of the generated amount of $GaCl_3$ using the $GaCl_3$ generator, we found that we could acquire amount of $GaCl_3$ reaches more than 7000 μmol/min required for Ga_2O_3 growth in the HVPE system (6 inches x 7). When measuring unreacted Cl_2 concentration by examining Ga weight reduction and using a gas detector tube, we found that the Ga metal and Cl_2 gas reaction efficiency was extremely high to 99% or more. The vertical $GaCl_3$ generator for which we adopted multi-series boats saves considerable space when compared with horizontal generators used in experiments, and we found that it was possible to add it to the gas supply system of mass-production Ga_2O_3 HVPE system. We will continue development to establish $GaCl_3$ supply technology for the reactors of mass-production HVPE system and to further reduce the size of $GaCl_3$ generators. We will also work to make the generator more versatile and standardized so that it can be used to generate $AlCl_3$ which is a growth source material in the HVPE method. We also plan to design, manufacture, and release a mass-production HVPE system using the external supply method that is similar

to the large diameter multi wafers growth reactor and generator in Figure 11.

Our company has also started the development of Ga_2O_3-MOCVD system which is a material with the potential for low loss and energy savings [17]. Power devices require transistors and other devices that have complicated structures and shapes, and MOCVD is suitable for their production because of its thin film interface steepness. We shall fabricate Ga_2O_3 mass-production growth system using HVPE and MOCVD to contribute to the spread of Ga_2O_3 power devices and to promote energy conservation.

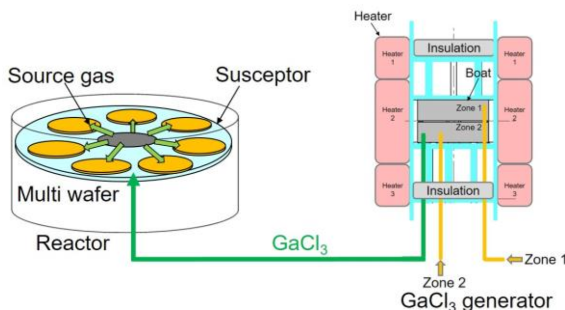

Figure 11 System of mass-production HVPE using external source supply.

6. Acknowledgment

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