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# 主　論　文　の　要　旨

論文題目　**Study on High Quality bulk GaN Single Crystal Growth by Halide Vapor Phase Epitaxy**
**(ハライド気相成長法による高品質バルク GaN 単結晶成長に関する研究)**

氏　　名　**劉　強**

## 論　文　内　容　の　要　旨

High quality freestanding GaN wafers are in strong demand to improve state-of-the-art III-Nitride optoelectronic, electronic and RF devices. However, growth of bulk GaN from liquid is extremely difficult unless under high pressure over 6 GPa and high temperature over 2200 °C. Hence, alternative fabrication methods of freestanding GaN wafers of were developed. Among all these methods, Halide Vapor Phase Epitaxy (HVPE) is considered as the most promising technique for mass production. This is mainly because that HVPE is the most cost-effective method due to its favorable growth conditions, namely, low pressure and relatively low growth temperature, high growth rate and ability to high purity material. In this dissertation, the bulk growth related topics have been survived.

In Chapter 2, to obtain a higher Ga conversion rate, a higher growth rate and less influencing by parasitic deposition, the conditions in the pre-reaction zone, during mass transportation and in the growth zone were optimized. Thermal dynamic calculation was applied to help optimize the growth condition at pre-reaction zone and growth zone. The mass transportation of reactant gas through the advection and diffusion of flow was studied by solving a stagnation point flow model in cylindrical coordinates and by simulation study. In the pre-reaction zone, a higher GaCl conversion rate will result in a higher Ga yield and a higher growth rate. To obtain a higher GaCl conversion rate, the total flow rate was fixed to ensure the reactant gas stay long enough time in the Ga tank. The carrier gas is fixed to pure $H_2$ to improve the GaCl conversion rate. The pre-reaction zone temperature was set to a fixed value to take a balance point between heating time and GaCl conversion rate. The mass transportation reactor can be simplified to a stagnation point flow model in cylinder coordinates. From the analytical solution of the model, input flow speed (total flow rate), input source concentration and the distance from wafer to nozzle are the variables. Ga yield (the ratio source gas reaching on wafer surface) and growth rate (the amount source gas reaching on wafer surface per unit time) are the key parameters. Firstly, a smaller distance from wafer to nozzle will result in a higher Ga yield and higher growth rate at the same time, but this will trade off the mixing distance. Because the source gas in HVPE reactor usually mixed after inject out from nozzles, so there is always a limitation for the minimum value of this distance. Secondly, by keeping the distance from wafer to nozzle, the growth rate and Ga yield is a pair of trade-offs by changing the input flow speed. Thirdly, by increasing the input source concentration, only the growth rate will increase but the Ga yield will remain. To prevent the parasitic deposition on the nozzles, the design with three concentric nozzles was used, barrier gas flow from the middle nozzle to separate GaCl flow in the middle and the $NH_3$ flow from outermost. The flow speed of barrier gas is preferred to be always faster than the rest two to ensure the source gas mixing is delayed from the nozzle outlet. Three different flow conditions with different input flow speed ratio (GaCl:barrier:NH3) of 1:2:1, 1:1.7:1 and 1:1.5:1 and different total flow of 8.925 slm, 11.903 slm and 13.892 slm were studied by experiment, calculation and simulation. By considering the parasitic deposition on the nozzles and the epilayer thickness uniformity, flow condition 2 was selected as the optimized flow condition. In growth zone, the chemical reaction near wafer surface was studied by fitting the thermal dynamic calculation result and the experiment result with a proper fitting coefficient k (which can eliminate the difference due to difference between the calculation model and the actual fact). Both of the growth rate dependence on input GaCl concentration with either a constant V/III ratio or a constant input $NH_3$ concentration, and the growth rate dependence on input $NH_3$ concentration with constant input GaCl concentration, fit well between the calculation and the experiment. For the growth rate dependence on temperature, the experiment result deviate from the calculation below 1050 °C. This indicates that the growth on the wafer surface below 1050 °C is rather depend on surface kinetic model rather than thermal dynamic model. To ensure the growth is under source gas controlled regime with a high growth rate, i.e., in thermal dynamic controlled regime but close to surface kinetic controlled regime, the growth temperature was set to 1050 °C.

In Chapter 3, key factors that influence the thick epitaxial growth were surveyed. These factors include seed selection, edge protection, seed fixation, long time growth and regrowth. For seed selection, homoepitaxial crystal growth on seeds fabricated by different methods were proceeded. The morphology, crystallinity, radii of curvature, dislocation density and dislocation propagation at interface were evaluated. Three facts are key to thick epilayer growth. Firstly, the epilayer can succeed the crystallinity from the substrate, i.e., epilayer on the substrate with higher crystallinity will also result in a better crystallinity. Secondly, the stress for all the seeds will increase after epilayer growth regardless of the substrate is under compressive stress or tensile stress. Thirdly, the dislocation bundles generated at interface will worsen the epilayer quality. Considering the above three facts, ammonothermal substrate was finally selected for thick epilayer owning to its supreme advantages in high crystallinity, flat lattice bow and no dislocation bundle generation at interface. For seed edge protection, protection rings made of four kinds of different material were tested in the growth experiments. W ring was selected for long time growth owing to its catalytic effect in preventing parasitic deposition. For seed fixation and backside protection, different methods were tested including seed fixation by sugar or AlN ceramic cement, backside protection by SiN thin film. None of these methods work out well. Finally, W ring was temporarily used to fix the seed because the growth time is below 10 hours and seed fixation is not yet a serious problem. Long time growth on ammonothermal substrate was proceeded with W ring protecting the edge. The growth rate of 250 μm/h and thickness of 2.3 mm were finally achieved after 8 hours growth. And regrowth technic showed there is a limit thickness for the epilayer with the current configuration, epilayer thicker than this critical value will result in the crack in the epilayer

In Chapter 4, the reactor for large wafer growth was introduced, the optimized growth condition was obtained which can achieve film with good uniformity on large wafer area. W catalyst effect to decompose GaN can be enhanced by cycles of aging procedure. Simulations were performed to study the flow in a vertical HVPE reactor with inner/outer flow independently controlled showerhead configuration. The flow field in the reactor become more complex with extra input flow, but both growth rate and Ga yield can be improved at the same time without compromising the uniformity by controlling the balance between the two input flows. Besides, Area ratio of inner to outer region was optimized to 0.943, and showerhead version II was designed based on the result. The experiment result fitted with the simulation result with a fitting coefficient of 0.44. Besides, based on the SIMS result of the epilayer grown 10mm distance away from W plate, it shows that there are no extra impurities from W metal.

In this dissertation, three contributions have been made. Firstly, an approach which is most promising to obtain true bulk GaN crystal has been proposed. Secondly, by analyzing the stress generation mechanism and excluding the impossible reasons, various edge effects ranging from spurious growth on the edges or formation of facets is considered as the main cause of stress during thick epilayer growth, and a tungsten ring was used to decompose lateral growth in non-polar and semi-polar directions. Thirdly, parasitic deposition was prevented by extra barrier flow and by using W metal owning to its catalytic effect to decompose GaN, furthermore, the catalyst effect of W can be improved after several cycles of aging. Fourthly, a prototype reactor with showerhead configuration was introduced, by employing the design of independently controlled inner and outer flow, uniformity can be optimized by changing the flow balance. The area ratio of inner region and outer region can be further optimized to 0.94 by simulation.

In the future, a "growth cannel" configuration has been proposed to further improve the critical thickness, and the stress at edges during growth should be further studied. Besides, further optimization of showerhead configuration design and flow condition is also expected. Eventually, large size (4-inch even 6-inch) bulk crystal with uniform thickness distribution, with thickness in centimeter level, and dislocation level lower than $10^4$ $cm^{-2}$ is expected.