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主 論 文 の 要 旨

論文題目　**Analysis of vapor phase reaction by high-resolution mass spectrometry for Group III-Nitrides epitaxial growth (高分解能質量分析によるⅢ族窒化物半導体気相成長の解析)**

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論 文 内 容 の 要 旨

In this thesis, the main objective is to explore specific processes in gas phase reactions of Gallium nitride (GaN) by metalorganic vapor phase epitaxy (MOVPE). As a preeminent candidate for next-generation semiconductor materials, GaN is an ideal material for developing optical and high-power devices, because it has a direct wide bandgap, high dielectric breakdown electric field, and high chemical and thermal stability. For the fine requirements of device structure growth, MOVPE is the main crystal growth method, in which trimethylgallium ($Ga(CH_3)_3$; TMGa) and ammonia (NH_3) are used as Ga and N precursors. The reaction in MOVPE involves two parts: gas phase and surface reactions. Source materials are transported to the heating zone by carrier gas, where the reaction occurs in the gas phase, and finally materials crystallize on substrate surface. The analysis of the gas phase reaction is crucial for clarifying the overall reaction and verifying the theoretical calculations. Therefore, in order to improve the research on the principle of crystal growth, the reaction of the source materials in the gas phase must be the first object that should be explored. The typical flow speed of up to a few meters per second in MOVPE corresponds to gas residence

times in the hot zone in the order of seconds rather than minutes. Therefore, *In situ* monitoring of gas phase reactions under non-equilibrium is required. Moreover, several components with similar masses occur during the growth process of GaN. For example, N_2 and C_2H_4 have masses of 28.006 and 28.031 u, respectively. A high resolution and high sensitivity measurement method is necessary. There are many test methods regarding the monitoring of normal gas phase reactions, such as chemical titration, Fourier transform infrared spectrometry (FTIR), and quadrupole mass spectrometry (QMS), have been commonly used in the previous studies. Due to the particularity of MOVPE growth mode mentioned above, however, it is very challenging to observe the gas phase reaction in a real reactor. Our approach is to introduce a high-resolution (about 0.002 u) time-of-flight mass spectrometry (Tof-MS) system to analyze the gas phase reaction.

First, in Chapter 1 and 2, the research background and experimental methods are explained in detail. The MOVPE system used for the preliminary measurement of gas phase reaction in this study is first introduced. At first, ToF-MS proved to be suitable for the analysis of complicated MOVPE gas-phase reactions through the monitoring results of a conventional quadrupole QMS. A TOF-MS system (infiTOF-UHV, MSI.TOKYO, Inc.) employed in our study has a high resolution of beyond 0.002 u. By using the experimental setup of the MOVPE reactor coupled to the TOF gas monitoring system, the reliability of the monitoring system was tested. In this system, two gas sampling lines were affixed on the reactor, and an *in situ* monitoring line was installed at the center of the wafer's upper surface. The microtube for the other line was aligned with the exhaust line just behind the reactor. All mass values (in u units) are accurate to three decimal places, which is sufficient to distinguish the components in various gas phases. In order to perform gas phase reaction analysis more conveniently. we designed a simple reactor. The reactor included an externally heated quartz tube (inner diameter: 30 mm; heated length: 30 cm). Gases were sampled via another thin quartz tube (tip inner diameter: 1 mm) and passed through a 0.1 mm inner diameter fused silica capillary connecting the gas tube to the entry of the TOF-MS system. All gas lines were

heated at 80°C to prevent gases from adhering to the surfaces. The pressure inside the reactor was set to 99 kPa (almost atmospheric pressure), while the internal pressure of the thin quartz tube was 30 kPa lower than the pressure of the reactor to ensure rapid transport of gases to the TOF-MS system. To obtain the actual temperature distribution inside the reactor, the temperature was measured at the center of the reactor tube using a thermocouple inside a thin quartz tube with a sealed apex.

From Chapter 3 to Chapter 6, the reactions between TMGa and ammonia in the sample reactor are discussed. The actual reaction in the MOVPE reactors are mostly in a non-equilibrium state with local heating at high flow rates. Decreasing the reaction time at high flow rates will reduce the rate of gas-phase reactions, making it difficult to observe the reaction. This experiment focuses on the reaction process in the state of near equilibrium. Therefore, we conducted the experiments at a low flow rate of 1 l/min, which resulted in a flow speed of about 0.03 m/s at RT. And, since the commonly used carrier gases are hydrogen and nitrogen respectively, this experiment mainly discusses the reaction under hydrogen (H_2) and nitrogen(N_2,). Because of the large differences in heat capacity and thermal conductivity between H_2 and N_2, the actual gas phase temperatures in the reactor can deviate considerately from the wall temperature. To obtain the actual temperature distribution inside the reactor, we utilized a thermocouple.

The decomposition process of NH_3 was investigated first. Although the thermodynamic analysis of ammonia shows the possibility of complete decomposition at 400°C, in fact ammonia decomposition is a sluggish reaction. Even at the high temperature of 1200°C (Flow rate: 0.03m/s), only 26% of NH_3 decomposed in a clean metal-free reactor under N_2 atmosphere, whereas a higher ratio of NH_3 decomposition was realized in the presence of stainless steel. It is even more obvious that NH_3 exhibits completely different decomposition rates under different carrier gases. As shown, the decomposition rate of NH_3 in nitrogen atmosphere is significantly higher than that in hydrogen atmosphere. According to the literature, the decomposition of NH_3 is a process of gradual dehydrogenation. However, H_2 carrier gas can produce active H* owing to

thermal dissociation above 350°C, which can be attributed to the high-energy tail of Maxwell distribution. Therefore, Hydrogen suppresses the decomposition of ammonia. We also compared the decomposition of ammonia in different carrier gases in the presence of TMGa. Due to the presence of TMGa, the decomposition of NH_3 in the high temperature region is significantly accelerated, even under hydrogen atmosphere. According to current experimental conditions (V/III ratio is 100), only 1% of NH_3 is consumed even if the decomposition from NH_3 is due to the reaction with TMGa. Therefore, in the presence of TMGa, the reason for the accelerated large amount of NH_3 decomposition is due to the Ga metal catalyst. It can also be seen that even under the catalyst effect, the inhibitory effect of H_2 influences the decomposition of NH_3. At a high temperature of 1000°C, NH_3 decomposition rate is only about 10% in a hydrogen atmosphere, while the decomposition rate in a nitrogen atmosphere is as high as 70%.

Most foundational studies of $Ga(CH_3)_3$ were completed in the 1980s. However, because of their aim of growing GaAs, these studies focused on the temperature range of 300 – 700°C which is considerably below the growth temperature of GaN in the range of 1000 – 1100°C. We thus investigated the decomposition of $Ga(CH_3)_3$ in different carrier gases (H_2 and N_2) at temperatures ranging from room temperature (RT) to 1200°C. $Ga(CH_3)_3$ begins to decompose in hydrogen (H_2) and nitrogen (N_2) at 375°C and 520°C, respectively. In contrast to the almost inert N_2, H_2 participates in the reaction and produces active H* owing to thermal dissociation above 350°C associated with the high-energy tail of the Maxwell-Boltzmann distribution. Therefore, $Ga(CH_3)_3$ is not decomposed by thermal collision in H_2 atmosphere instead active H* attaches to the CH_3 groups of Ga(CH3)3 and forms the main product of CH_4 above 400°C. In contrast, the strong signal of CH_3 suggests the $Ga(CH_3)_3$ loses CH_3^* via thermal decomposition in N_2 atmosphere. Specifically, in the nitrogen atmosphere, with the decomposition of TMGa, we observed high-intensity signal of hydrocarbons compounds such as ethane (C_2H_6) and ethylene (C_2H_4). Finally, by introducing pure C_2H_6, TMG was proved preferentially generates C_2H_6 during the thermal decomposition process. We also observed that C_2H_6 will continue to decompose into C_2H_4 and acetylene (C_2H_2) at high

temperatures. However, In the presence of NH_3, hydrocarbon compounds (even CH_4) will react with NH_3 to form HCN. This type of reaction mode was first reported to occur during the gas phase reaction of nitrides. HCN is not only highly toxic but can also be used as a carbon doping material for GaN. In addition to paying more attention to safety for all operators of nitride crystal growth, whether HCN is the main source of unintentional carbon doping needs to be carefully explored. However, by comparing the reactions at different flow rates, it was found that unintentionally doped carbon sources were more likely to come from undecomposed metalorganics.

The simple reaction experimental system we set up can carry out experiments very conveniently. As a result, most of the reaction modes in the gas phase and the found new reaction paths could be figured out. Using such basic data, further theoretical analysis and optimization of nitrides can be developed. The significance of this study has been achieved. We explore the gas phase reaction as the beginning of the entire crystallization and provide accurate and detailed theoretical data for the subsequent development of nitrides.