In situ monitoring of $Ga(CH_3)_3$ reaction with HCl on nitride semiconductor Metal-Organic Vapor Phase Epitaxy (MOVPE) by using “infiTOF-Pro”

Keywords：semiconductor, gas analysis, monitoring, rimethylgallium, MOVPE

Overview

- Using infiTOF-Pro, in-situ monitoring of the reaction of TMG with HCl on nitride semiconductor MOVPE was performed.
- The products formed by the reaction of TMG with HCl were detected and identified.
- The experimental results are useful to validate theoretical calculations of the reaction of TMG with HCl.

Introduction

Nitride semiconductors are candidate materials for high-power transistors. To achieve high breakdown voltage performance, the GaN drift layer must be grown with the lowest amount of impurities possible. To improve device performance, several researchers have focused on reducing the carbon, silicon, and oxygen impurities in GaN. Reducing the carbon concentration is especially difficult under conventional growth conditions, because using trimethyl gallium (TMG), which provides a methyl group needed in the production process, also results in carbon impurities. Metal-organic halide-vapor phase epitaxy (MOHVPE) can effectively reduce carbon incorporation by replacing the carbon-based methyl groups with chlorine using HCl. Previous reports on GaN growth by MOHVPE have focused on high growth rate of the GaN bulk crystal without considering the effects of impurity incorporation. However, Amano et al. reported on the impurity concentration in GaN grown by MOHVPE and concluded that chlorine replacement cannot sufficiently reduce the carbon concentration and that the direct reactions must be monitored in the vapor phase.

In this application note, we present the in-situ monitoring of the reaction of TMG with HCl in a conventional horizontal MOVPE reactor using “infiTOF-Pro”.

Experimental

Figure 1 shows the experimental setup of the MOVPE reactor coupled to the infiTOF-Pro. In the figure, all gases flow from left to right and then out the exhaust port. TMG reacts with HCl on the wafer surface. The gas products are sampled by the line installed at the center of the wafer's upper surface, and introduced into the electron ionization (EI) source of the infiTOF-Pro by a microtube (I.D. 0.1mm, L50mm) heated at 120 °C in order to prevent sample gases from adsorbing to the tube. The size of the quartz flow channel in the reactor was designed for a single 4-inch wafer. The number of turns for the infiTOF-Pro was set to achieve a resolving power of 10,000 or more. Other MOVEP experimental conditions are listed in Table 1.

Table 1 Experimental condition

Wafer surface temperature	RT-1150℃
Wafer material	Sapphire 2"
Channel width	120 mm
Channel height	6 mm
Reactor pressure	200 torr
Flow speed	1 m/sec
Carrier gas	H_2 (+N_2)
TMG	100 sccm

Results and Discussion

Figure 2 shows the mass spectrum of TMG in the absence of HCl supply. Peaks for $Ga(CH_3)_3^+$, $Ga(CH_3)_2^+$, $GaCH_3^+$, Ga^+, and CH_4^+ were observed. The strongest peak was for $Ga(CH_3)_2^+$ while $Ga(CH_3)_3^+$ could almost not be detected at all. The signal intensity ratio of $Ga(CH_3)_3^+/Ga(CH_3)_2^+$ was less than 1%.

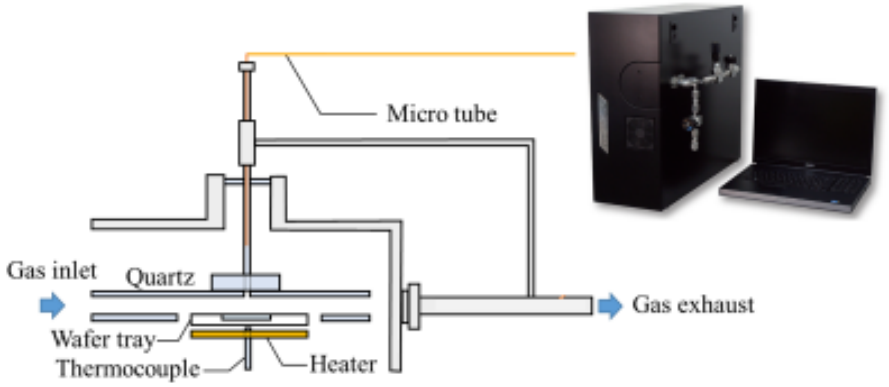

Fig. 1 Experimental setup of MOVPE reactor coupled to the infiTOF-Pro.

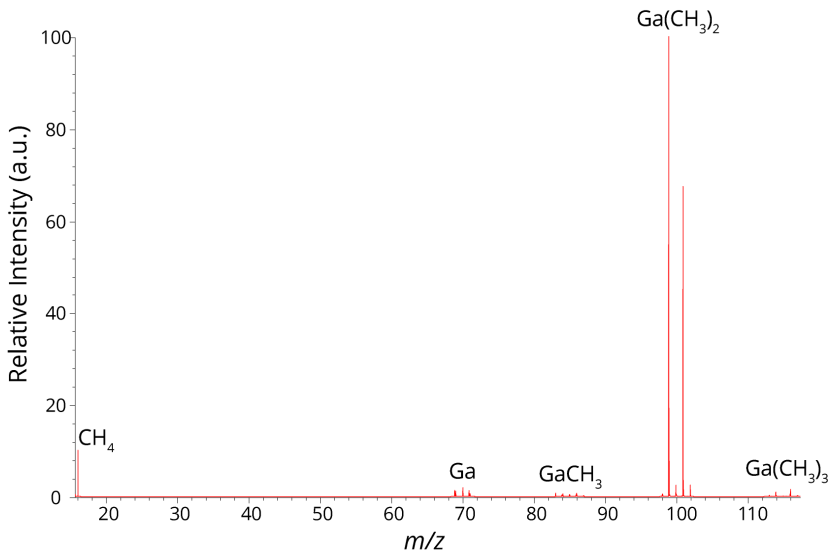

Fig. 2 Mass spectrum of TMG.

Figure 3 shows the mass spectrum observed from the reaction of TMG and HCl. Five reaction products were clearly observed, and were identified by accurate mass measurements (see Table 2) and isotope patterns. Blue arrows indicate isotopes for each respective ion shown. Each measured isotope ratio was well-matched to its theoretical abundance ratio (data not shown).

Table 2 shows the theoretical and calculated values of each component and their associated errors, which were obtained by a post-calibration process using HCl and $Ga(CH_3)_2$ as calibrants. In each component, the mass error between theoretical and calculated values was within 3 [ppm], indicating that there is sufficient mass accuracy to identify the components by exact mass.

Table 2 Theoretical and calculated values of each component and their errors.

	Theoretical	Experimental	u	ppm
$Ga(CH_3)Cl_2$	155.8849	155.8847	0.00025	1.6
$GaCl_2$	140.8614	140.8611	0.00032	2.3
$Ga(CH_3)_2Cl$	133.9414	133.9414	0.00002	0.1
$Ga(CH_3)Cl$	118.9179	118.9179	0.00004	0.3
GaCl	103.8944	103.8946	0.00015	1.4

Regarding the generation of $Ga(CH_3)_xCl_y$ (x = 0, 1, 2. y = 1, 2.) compounds, there are several possibilities besides generation by the reaction of TMG with HCl:

- GaCl resulted from EI fragmentation of $Ga(CH_3)Cl_2$, $Ga(CH_3)_2Cl$, $GaCl_2$, and Ga(CH)Cl.
- $Ga(CH_3)Cl$ resulted from EI fragmentation of $Ga(CH_3)Cl_2$ and $Ga(CH_3)_2Cl$.
- $GaCl_2$ resulted from EI fragmentation of $Ga(CH_3)Cl_2$.

In order to reveal the origin of $Ga(CH_3)_xCl_y$ products, mass chromatograms of each component normalized to HCl signal intensity were measured (Figure 4).

Figure 4 shows that:

(1) The signal intensity of $Ga(CH_3)_2Cl$ and $Ga(CH_3)Cl$ clearly decreased.

(2) The signal intensity of GaCl clearly increased.

(3) The signal intensity of $Ga(CH_3)Cl_2$ and $GaCl_2$ seem to decrease somewhat.

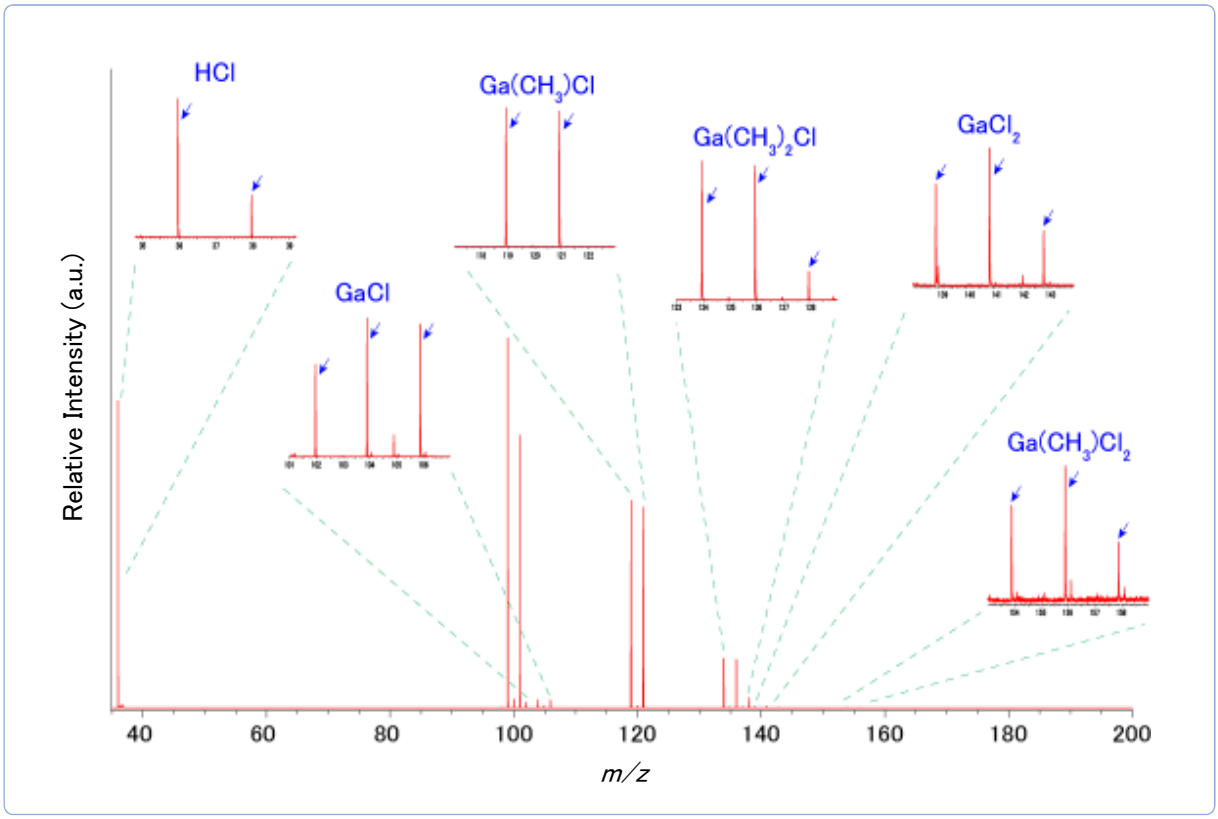

Fig. 3 Mass spectrum of reaction products of TMG and HCl.

Because only GaCl increased, it can be concluded that GaCl was not formed by EI fragmentation of Ga(CH3)Cl2, $Ga(CH_3)_2Cl$, $Ga(CH_3)Cl$, or $GaCl_2$, but by reaction of TMG with HCl. Mass chromatograms of $Ga(CH_3)_2Cl$ and $Ga(CH_3)Cl$ had decreasing trends, so it is possible that $Ga(CH_3)Cl$ was the result of EI fragmentation of $Ga(CH_3)_2Cl$. It is difficult to discuss the origin of $GaCl_2$ and $Ga(CH_3)Cl_2$, because the associated mass chromatograms do not exhibit a concrete trend. Since the origin of $Ga(CH_3)_xCl_y$ products is based only on experimental results, it is necessary to supplement the results with theoretical calculation in order to precisely understand the reaction of TMG and HCl.

Conclusion

In-situ monitoring of the reaction of TMG with HCl on nitride semiconductor MOVPE was performed using infiTOF-Pro. Several reaction products such as GaCl, $Ga(CH_3)Cl_2$, $Ga(CH_3)_2Cl$, $Ga(CH_3)Cl$, and $GaCl_2$ were observed. Results indicate that GaCl resulted from reaction of TMG with HCl, and $Ga(CH_3)Cl$ resulted from EI fragmentation of $Ga(CH_3)_2Cl$. It is necessary to compare experimental results with theoretical results in order to understand the true nature of the reaction of TMG with HCl in the MOVPE reactor. Results also indicate that infiTOF-Pro is useful for investigating MOVPE reactions.

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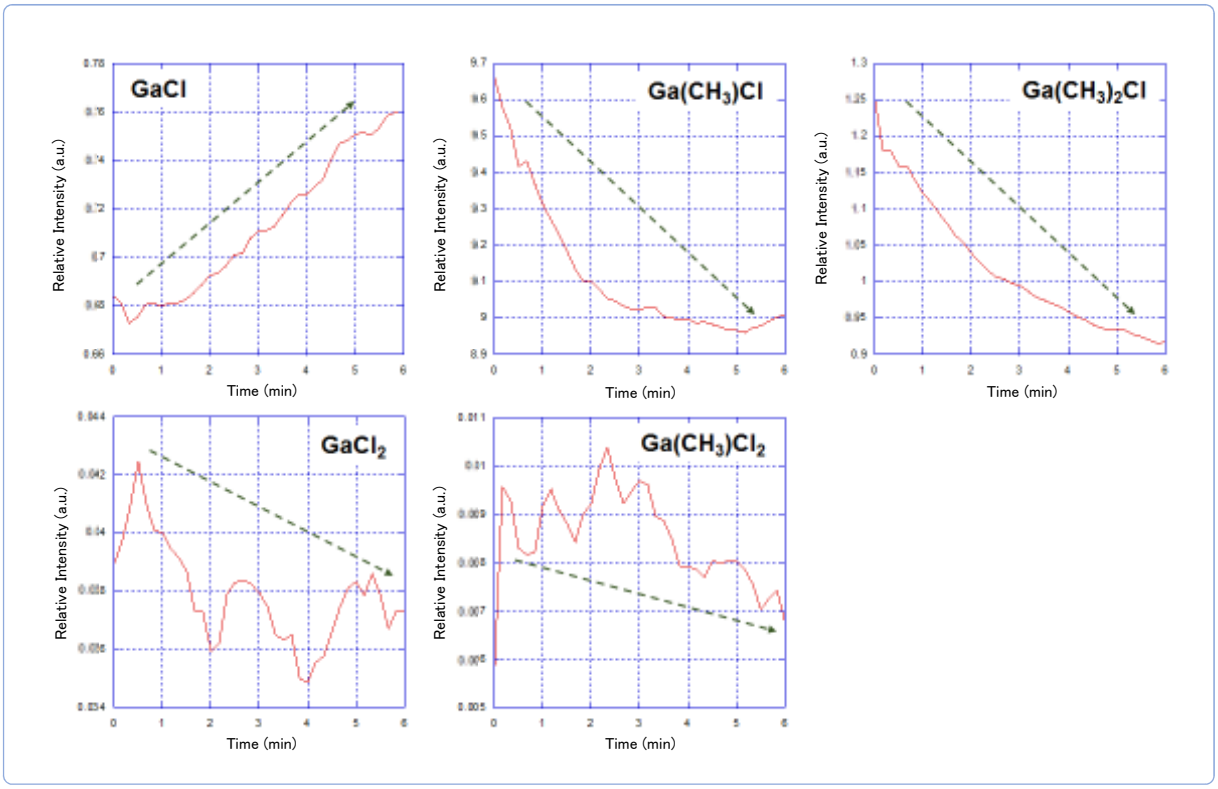

Fig.4 Normalized mass chromatograms of chlorine adducts.

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