Cp$_2$Mg in-situ monitoring in a MOVPE reactor using a quantum cascade laser

Daisuke Hayashi$^{1*}$, Yoko Sato$^1$, Masakazu Minami$^1$, Noboru Muramatsu$^2$, and Motoaki Iwaya$^2$

$^1$HORIBA STEC, Co., Ltd., Kyoto 601-8116, Japan
$^2$Meijo University, Nagoya 468-8502, Japan

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We performed in-situ monitoring of bis-cyclopentadienyl magnesium (Cp$_2$Mg) vapor pressure supplied into a metal-organic vapor phase epitaxy reactor. As a light source we adopted a quantum cascade laser (QCL) of 12.9 $\mu$m, which is the wavelength of Cp$_2$Mg infrared absorption. We directly configured a laser path in the reactor to construct the Cp$_2$Mg in-situ monitoring system. We streamed Cp$_2$Mg and measured the vapor pressure in the reactor to evaluate it and its saturation and purge times in comparison with their calculated values which were determined from the measured values in the supply line. Next, we streamed Cp$_2$Mg and other gas species used in gallium-nitride processes one by one to investigate their saturation times with the same QCL. Characteristic features of Cp$_2$Mg such as the largest saturation time ratio and its large fluctuation were observed. These results indicate the importance of Cp$_2$Mg in-situ monitoring in the reactor. © 2019 The Japan Society of Applied Physics

1. Introduction

The formation of p-type layers is crucially important for gallium-nitride (GaN) devices. The p-type GaN is commonly accomplished by magnesium (Mg) doping into a GaN layer and its activation.1–4 The concentration of doped Mg in p-GaN layer is a decisive parameter for its electric properties. The target value of Mg concentration is different depending on the kind of GaN device. In the case of light emitting diodes or laser diodes, a concentration of $1 \times 10^{19}$ cm$^{-3}$ or more is necessary to obtain high conductivity. However, excessive doping leads to a reduction in conductivity due to the hole compensation effect.5–8 Although the mechanism of the hole compensation effect has been well studied,9–15 conductivity tuning in p-GaN layers continues to be difficult.16,17 In the case of normally-off vertical GaN-based transistors, both heavily doped and lightly doped p-GaN layers are simultaneously required.18 In all cases, the precise and well repeatable control of Mg concentration in metal-organic vapor phase epitaxy (MOVPE) is required. Especially, in industrial mass productions for GaN devices, an establishment of the control method has been crucial. Nevertheless, as is well known, Mg has a strong memory effect,19–22 and controlling the concentration is difficult. One promising control method is to monitor the vapor pressure of bis-cyclopentadienyl magnesium (Cp$_2$Mg) in the MOVPE reactor. In-situ monitorings of Cp$_2$Mg vapor pressure have been already performed in supply lines thus far by using the acoustic method33 or the non-dispersive infrared (NDIR) spectroscopy method.34 In the latter case, the consistency between Cp$_2$Mg mass consumption calculated from monitored results and bottle weight loss was confirmed. However, generally the sufficient control of Mg concentration has not been achieved yet in mass production processes. One of the reasons is that the state of Cp$_2$Mg after supplied into the reactor has not been clarified. To overcome the issue, the technology of in-situ monitoring in the reactor has been desired.

For in-situ monitoring in a MOVPE reactor, laser spectroscopy methods are useful because the high directivity of laser beam enables us to construct an effective measurement system even for the reactor size. To date, in-situ monitoring in the reactor using visible lasers has been performed to investigate the surface roughness and incorporation of indium (In) in InGaN layers.25 For monitoring the precursor vapor pressure, a mid-infrared (MIR) laser absorption spectroscopy using a quantum cascade laser (QCL) is preferable because metal organic (MO) precursors have infrared absorptions in the MIR region that are associated with their molecular motions. Since the first demonstration of QCL in 1994,26 the performance has been constantly improved. Today, room-temperature lasing or lasing at wavelengths over 10 $\mu$m are available.27–31 Thus, QCLs have been widely adopted as light sources for gas sensing in recent years.32–35 Some examples of semiconductor process monitoring with QCLs include in-situ monitoring of gas temperature,36 concentration of carbon-fluoride radicals,37 and concentration of etching products38,39 in plasma etching processes. However, in-situ monitoring of precursor vapor pressures in the MOVPE reactors with the QCL has not been reported. In this work, we performed in-situ monitoring of Cp$_2$Mg vapor pressure in the MOVPE reactor using the QCL.40 We directly configured a laser path in the reactor to measure Cp$_2$Mg vapor pressure based on its MIR absorption.

2. Experimental methods

2.1. Calibration of Cp$_2$Mg monitoring system

Although the infrared absorption of Cp$_2$Mg is extremely weak compared with that of other MO precursors, it has a relatively strong absorption in the fingerprint region associated with the C–H bending motion.31 We measured the infrared absorption spectrum of Cp$_2$Mg using Fourier Transform Infrared (FTIR) spectroscopy (HORIBA, FG-100) in the fingerprint region (Fig. 1). An absorption peak was clearly observed at 12.9 $\mu$m. As the infrared absorbance is proportional to the vapor pressure due to the Lambert–Beer’s law, the vapor pressure of Cp$_2$Mg can be monitored based on infrared absorbance at this wavelength.

We constructed an experimental bench including a distributed-feedback type 12.9 $\mu$m QCL (Hamamatsu, LE0945QCL) as shown in Fig. 2. The QCL was installed on the driver board, and the wavelength was adjusted to...
12.9 $\mu$m by tuning the applied current and device temperature. The laser beam emitted from the QCL was reflected by plane mirrors and then injected into the gas cell through one of zinc-selenide (ZnSe) windows. The windows were shaped like a wedge to avoid optical interference due to multiple reflections. The gas cell had inlet and outlet ports to flow Cp$_2$Mg vapor. The length of the gas cell was 200 mm. The laser beam coming out through the window on the other side was reflected by a parabolic mirror and received by a mercury-cadmium-telluride (MCT) detector (Teledyne Judson Technologies, J15D). The detector signal was converted to the infrared absorbance, which is defined as

$$ A = \log \left( \frac{I_0}{I_1} \right). $$

Here, $I_0$ is the baseline signal intensity and $I_1$ is the intensity with Cp$_2$Mg vapor present in the gas cell.

We made a calibration curve, that is, the relationship between the Cp$_2$Mg vapor pressure and its infrared absorbance by using this experimental bench. We extracted pure Cp$_2$Mg vapor from the bubbling bottle into the vacuumed gas cell. We measured the infrared absorbance varying the Cp$_2$Mg vapor pressure in the gas cell. The resulted calibration curve is Fig. 3, which shows a good linearity with a determination coefficient of $R^2 = 0.998$.

2.2. Installation to MOVPE reactor

We installed the QCL and the MCT detector into the MOVPE reactor (Taiyo Nipponsanso SR2000HT) and constructed the Cp$_2$Mg in-situ monitoring system. In the reactor, a quartz flow channel shown in Fig. 4(a) was laid. The detailed structure of the flow channel is explained in Refs. 42, 43. The injection nozzle part of the flow channel had three gas flow layers as shown in Fig. 4(b). Cp$_2$Mg was supplied into the middle layer, and delivered to the susceptor. On the way to the susceptor, it was mixed with other gas species at the two junctions. The middle layer was joined with the bottom layer at the first junction, and then joined with the top layer at the second junction. The flow channel was surrounded by a stainless outer frame, and the space between the flow channel and the outer frame was constantly purged by nitrogen (N$_2$). The QCL and the MCT detector removed from the experimental bench were respectively attached on the sides of the outer frame as shown in Fig. 4(c). The laser beam emitted from the QCL entered through the ZnSe window and reached the flow channel. On both sides of the flow channel, pin holes with diameters of 2 mm were formed. The beam passed through the flow channel via the pin holes and was received by the MCT detector after coming out the frame. The length between the pin holes was 80 mm. Therefore, the infrared absorbance could be converted to the Cp$_2$Mg vapor pressure in the reactor by using the conversion factor that was the proportional coefficient in Fig. 3 multiplied by 200/80. The location of the path was upstream of the susceptor by 70 mm.

The gas flow system of the reactor is displayed in Fig. 5. Besides Cp$_2$Mg, other gas species used in GaN processes such as trimethyl-gallium (TMGa), trimethyl-aluminium (TMAI), trimethyl-indium (TMIn), and ammonia (NH$_3$) could be supplied into the reactor. Bubbling bottles of the four MO precursors were equipped in thermal baths, and the levels of temperature were fixed. In the Cp$_2$Mg supply line between the bubbling bottle and the reactor, we placed another Cp$_2$Mg monitor of the NDIR (HORIBA STEC, IR-400) to compare with the measured Cp$_2$Mg vapor pressure in the reactor.

3. Results and discussion

3.1. Cp$_2$Mg vapor pressure in the reactor

We bubbled Cp$_2$Mg by carrier hydrogen (H$_2$) and measured the vapor pressure with the NDOR monitor placed just after the bubbler bottle in the supply line. After that, Cp$_2$Mg vapor was mixed with dilution gas (H$_2$ or N$_2$) and delivered to the reactor, where the vapor pressure was measured again with the QCL. On the way to the laser path in the reactor, it passed...
through various flow regions in the pipe and the flow channel whose volumes and temperature were different. We summarized the details of pipe diameters, lengths, volumes, temperatures, flow rates, and the saturation times of the flow regions together with their definitions in Table I.

Figures 6(a), 6(b) show the rises and falls of Cp2Mg vapor pressures measured in the supply line and in the reactor. The horizontal axes show the elapsed time after the bubbling bottle was opened. We defined the saturation and purge time as the elapsed times when the vapor pressure reached 90% and 10% of the saturated value, respectively. In Table II, we summarized the measured and calculated values of saturation and purge time delays and saturated vapor pressure in the reactor. The saturation (purge) time delay means the...
The difference between saturation (purge) time measured with the NDIR monitor and the one measured with the QCL. The calculated saturation and purge time delays were sum of the saturation times listed in the lowest row of Table I. The measured saturation and purge time delays were significantly larger than the calculated ones. We believe that these large delays were due to adsorption and desorption of Cp2Mg with the inner walls of the pipe and the flow channel.

The saturated vapor pressure measured in the reactor was 1.5 Pa. Although it was a little smaller than the calculated value, which was determined from the value measured in the supply line (5.9 Pa) and dilution rate (1.0/2.8), it can be regarded as reasonable considering that the mixing mechanism of supplied vapor is highly complicated in the flow channel.

Table I. Detail of each flow region from NDIR gas cell to the laser path in the reactor.

| Definition of region | Start | NDIR gas cell | Pipe 1 | Pipe 2 | Flow channel |
|---------------------|-------|---------------|--------|--------|--------------|
|                     |       | NDIR gas cell inlet | NDIR gas cell outlet | Run/Vent valve | Flow channel inlet | First junction | Second junction | Laser path |
| End                 |       | NDIR gas cell inlet | NDIR gas cell outlet | Run/Vent valve | Flow channel inlet | First junction | Second junction | Laser path |
| Inner diameter (mm) | 23.00 | 4.35           | 4.35   | —      | —             | —             | —             | —          |
| Length (mm)         | 200   | 1894           | 2650   | —      | —             | —             | —             | —          |
| Volume (ml)         | 83.1  | 28.1           | 39.4   | 31.9   | 12.7          | 22.4          | —             | —          |
| Temperature (°C)    | 60    | 50             | 50     | 50     | 50            | 50            | 50            | 50         |
| Flow rate (slm)     | 1.00  | 1.00           | 1.60   | 1.60   | 2.20          | 2.80          | —             | —          |
| Saturation time (s) | 4.1   | 1.4            | 1.3    | 1.0    | 0.3           | 0.4           | —             | —          |

Table II. Comparison of measured and calculated time delays of saturation and purge and saturated vapor pressures in the reactor.

| Measured | Calculated |
|----------|------------|
| Time delay (s) | Saturation | 33.0 | 8.5 |
|           | Purge     | 30.0 | —   |
| Vapor pressure (Pa) | 1.5 | 2.1 | —   |

Fig. 6. (Color online) Rises (a) and falls (b) of Cp2Mg vapor pressures measured in the supply line and in the reactor. Dashed lines show saturation and purge time on each monitoring point.

Fig. 7. (Color online) Infrared absorption spectrum of gas species tested in the reactor. Dashed line shows the wavelength of 12.9 μm.

3.2. Comparison of saturation time with other gas species

We streamed Cp2Mg and other gas species one by one and investigated their saturation times. Figure 7 shows the FTIR spectra of other gas species tested in the reactor. As all of them had infrared absorption at 12.9 μm, we could measure their saturation times in the reactor using the same QCL.

In this experiment, we set the start point as the time when the run/vent valves in Fig. 5 were switched to the “run” line, and we measured the saturation time in the reactor. As the line lengths (from the run/vent valves to the reactor) and the flow rates were different depending on the gas species, we could not simply compare the measured saturation times. To get a fair evaluation, we defined the saturation time ratio as follows:

\[ R_t = \frac{\tau_{\text{meas}}}{\tau_{\text{cal}}} \]  

where \( \tau_{\text{meas}} \) is the measured saturation time and \( \tau_{\text{cal}} \) is the calculated time which was determined from the volumes of pipe and the flow channel and the flow rate. In Table III, we listed the calculated saturation times together with the lengths and/or volumes of the pipe and the flow channel, and flow rates. The inner diameter of pipe and the definitions of region 1–3 in the flow channel are the same as described in Table I. The pipe temperature was 24 °C for NH3 line and 50 °C for MO precursors’ lines. The temperature of the flow channel was 50 °C. Pressure in the line and the flow channel was 101.3 kPa. The resulting \( R_t \) values are summarized in Table IV. The \( R_t \) of Cp2Mg was the largest among the gas species. This means Cp2Mg takes the longest time if these gas species are streamed through the same line length under the same flow rate. The \( R_t \) became smaller in the order of TMIn, TMAI, TMGa, and NH3.
of Cp2Mg. This means that the production processes.

Finally, we investigated the behavior of $R_\tau$ when we repeated the five cycles of three-minute stream and one-minute purge for each gas species. Figure 8 shows the results. Throughout the five cycles, the order of $R_\tau$ did not change from the one in Table IV. However, a remarkable fluctuation was observed for only $R_\tau$ of Cp2Mg. This means that the saturation time of Cp2Mg can widely vary on each process even under a fixed condition. This unstable behavior of Cp2Mg can lead to the variation of Mg concentration in mass production processes.

4. Conclusions

In this work, we directly configured a laser path in the MOVPE reactor and performed in-situ monitoring of Cp2Mg vapor pressure. Throughout the experiments, we observed the characteristic features of Cp2Mg. In the experiment where we streamed Cp2Mg and monitored the vapor pressure in the supply line and in the reactor simultaneously, we found that the saturation and purge time delays of Cp2Mg measured in the reactor was significantly larger compared to the calculated ones. In the other experiment where we streamed Cp2Mg and other gas species one by one and compared their saturation times, we found that Cp2Mg showed the largest saturation time ratios and a large fluctuation of it. It was not until we performed the Cp2Mg in-situ monitoring in the reactor that these characteristic features were observed. Therefore we emphasize that not only monitoring Cp2Mg vapor pressure in supply line but in-situ monitoring in the reactor is extremely important for the precise and well repeatable control of Mg concentration.

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ORCID iDs

Daisuke Hayashi © https://orcid.org/0000-0002-7204-2491

Table III. Lengths and/or volumes of pipe and flow channel, flow rates, and calculated saturation times.

| Gas species | Length (mm) | Volume (ml) | Flow rate (slm) |
|-------------|-------------|-------------|-----------------|
| NH3         |             | 3940        | 1.60            |
| TMGa        |             | 5080        | 0.75            |
| TMAI        |             | 4980        | 0.95            |
| TMIn        |             | 4880        | 1.65            |
| Cp2Mg       |             | 2650        | 1.60            |

Table IV. Saturation times in the reactor.

| Gas species | $R_\tau$ |
|-------------|----------|
| NH3         | 1.4      |
| TMGa        | 2.5      |
| TMAI        | 2.9      |
| TMIn        | 3.7      |
| Cp2Mg       | 5.2      |

Fig. 8. (Color online) Behavior of saturation time ratio. Five cycles of three-minute stream and one-minute purge were repeated.
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