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e-Readout
HORIBA Technical News Letter

The e-READOUT is a technical newsletter designed to help our readers to understand our proprietary technologies and our products. Our experts in different fields, from all over the world write the content with the spirit of sharing our know-how in developing solution to solve the challenges we face in this rapidly changing world.

InGaAs-layers growth by MOCVD via vapor concentration control

- HORIBA's novel proposal for controlling TMIn gas delivery

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Precursor delivery via bubbling presents technical challenges on the production stability of MOCVD, especially in the case of solid precursors. A precursor concentration controller, VCC-100, has been installed on a commercial MOCVD system to control Trimethylindium concentrations. Instead of changing the carrier gas flow ratio, precursor concentration adjustment proved to be a practical approach to obtain epitaxial layers with the desired composition. In addition, VCC-100 can contribute to the long-term stability of precursor delivery to the process chamber.

Introduction

Recently there have been remarkable advancements in infrared emitting / receiving devices for remote sensing applications including Lidar, face recognition and non-destructive inspection technologies. Many of these new applications have become more familiar. Quantum cascade laser technology has made spectacular progress in the past 20 years, the progress of which has allowed us to utilize compact mid-Infrared light sources for gas analysis applications.

Most infrared semiconductor devices are based on indium containing materials, such as InGaAs. Because solid composition and thickness control of each layer in a ternary or quaternary compound are directly linked with device characteristics, precise MOCVD precursor delivery control from a bubbler to a chamber has a great importance on epitaxial growth processes and ultimately device performance.

Problems

Trimethylindium (TMIn) is widely used as an indium precursor, which presents a challenge due to its solid state, requiring the sublimated precursor to be delivered by a bubbling process. Different from ordinal liquid precursors, some issues in a TMIn bubbling process are temperature non-uniformity in the precursor material, difficulty in reaching saturation vapor pressure and susceptibility to residual precursor volume.

Indium composition of about 50% are often used for $In_{1-x}Ga_xAs$ layer on InP substrates and for $(Al_xGa_{1-x})_yIn_{1-y}P$ layer on GaAs substrates due to the lattice matched conditions. The vapor pressure of TMIn is more than 100 times smaller than Trimethylgallium (TMGa) at the same temperature, bubbling flow rate settings for TMIn tend to be larger than those for TMGa and therefore TMIn bubbling conditions easily deviate from the ideal settings.

Regardless of whether a precursor is liquid or solid, keeping a precursor temperature constant is of particular importance during the bubbling process if no precursor control methods are utilized. As expressed by the Antoine equation, a 0.5°C change from 20°C target can affect the TMIn vapor pressure by about 4%, this does not support mass-production yield requirements.

Solution

There are some methods for controlling gas delivery from a bubbler, which are broadly classified into two categories based on what parameter is controlled: (i) Flow control and (ii) Concentration control. In the former method, the controlled parameter is a gas flow feedback through a precursor concentration monitor located on the downstream side of a bubbler that maintains the precursor molar flow rate at a precise value. A mass flow controller (MFC) can be installed on either the upstream or downstream side of the bubbler.

The latter is referred to as vapor concentration control (VCC). Instead of controlling a total flow rate of the precursor line, concentration can be controlled by total pressure or dilution ratio control while maintaining the total flow rate.

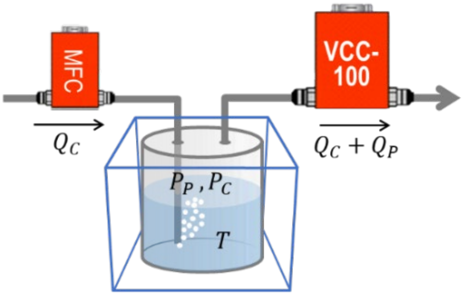

Figure 1: Schematic diagram of a bubbling system with a MFC and a VCC module.

HORIBA STEC has developed VCC-100, a vapor concentration controller which integrates gas sensing technology and valve control in one control loop. Figure 1 shows a schematic diagram of bubbler, piping and components. VCC-100 is based on the concentration control method of adjusting the total pressure. The principle is written in another application note [1]. A precursor molar flow rate in a steady state is given by

$$Q_P = \frac{C}{1-C} \times Q_C \tag{1}$$

where Q_P is the precursor molar flow rate, C is the precursor concentration in the downstream of the bubbler and Q_C is the carrier gas molar flow rate controlled by the MFC. The most important factor in the precursor delivery is to control Q_P. Equation (1) indicates that Q_P can be managed when C can be kept under control, even if C varies according to environmental conditions.

Examples

VCC-100 was installed downstream of a TMIn bubbler line of a MOCVD system in order to compare InGaAs growth results and VCC-100 performances.

1. $In_XGa_{1-X}As$ composition control by VCC

Usually composition of $In_XGa_{1-X}As$ layers are controlled by changing the flow rate, Q_C and therefore the delivered TMIn/TMGa molar ratio can be adjusted. TMIn molar flow ratio, however, is not usually proportional to Q_C because C is not always constant as Q_C changes. In this experiment, Q_C of the TMIn line was kept constant but C was varied by using VCC-100. 0.2 μm-thick five InGaAs layers with different In/Ga compositions were grown after InP buffer deposition on an InP substrate by supplying TMIn, TMGa and AsH_3 as precursors. The chamber pressure and the wafer temperature were set to 50 Torr and 590°C respectively.

Shown in figure 2 are the sequence of TMIn concentrations controlled by VCC-100. The temperature of TMIn bubbler was maintained at around 20°C and H_2 carrier gas flow rate was set to 500 SCCM. The total pressure at the downstream of the bubbler is about 742.5 Torr when the TMIn concentration is set to 0.17 vol.%. Similar to changing Q_C , stabilizing Q_P takes time, which depends on the length of the piping, the size of the bubbler and the bubbling conditions. Because usual MOCVD systems have a valve block just upstream of a chamber in which gases can be switched between flowing into the chamber or into a vent line, the stabilization wait time won't be a major barrier for this application.

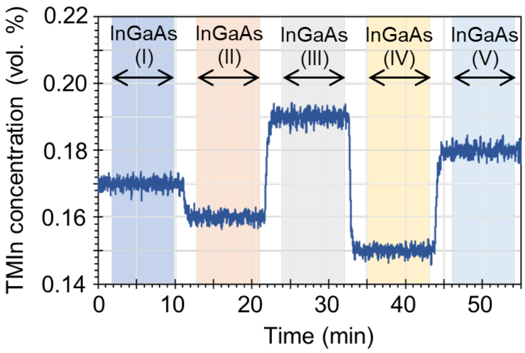

Figure 2: TMIn concentration sequence during the InGaAs layers growth (8 min growth each and 3 min intervals for waiting the stable concentrations).

The X-ray diffraction (XRD) 2θ-ω scan profile in the vicinity of the (004) reflection peaks are shown in figure 3. Other than the main peak from InP substrate, five distinct peaks from epitaxial InGaAs layers were observed, suggesting that VCC-100 was successfully applied to the indium composition control. The reciprocal space mapping in the vicinity of the (224) reflection indicates that the InGaAs layers were grown coherently. The indium composition estimated from (004) XRD peaks, therefore, should take into account the effect of strain.

In order to check the actual indium composition, secondary ion mass spectrometry (SIMS) depth profile analysis was performed on the same InGaAs sample as shown in figure 3. Figure 4 shows the indium molar fraction, X, measured by SIMS as a function of the input TMIn ratio.

Compared to the indium molar fractions estimated from the XRD peak positions, the ones measured from the SIMS result are smaller in the range larger than 0.53 and are larger in the range smaller than 0.53 due to the stress of the films. These results are consistent with the reciprocal space mapping measurement.

The input TMIn ratios do not match the indium molar fractions, since gallium and indium incorporation ratio are independently affected by V/III ratio, growth temperature, surface crystallinity and so on. It is noteworthy that VCC-100 has an embedded concentration control algorithm and only a concentration set point is needed to realize precise composition control.

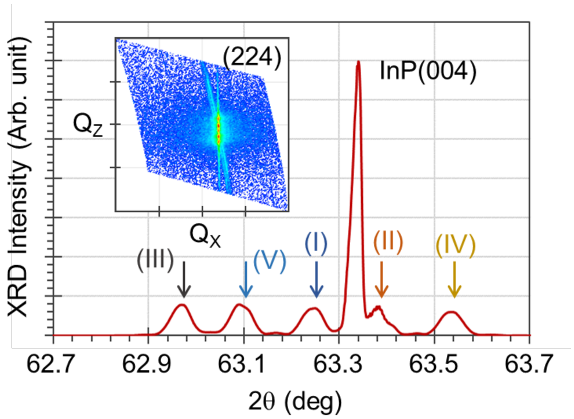

Figure 3: XRD pattern of the five InGaAs layers with different Indium composition. The numbers denoting the InGaAs (004) peaks correspond the ones in figure 2. Insert graph: Reciprocal space mapping around the (224) peaks.

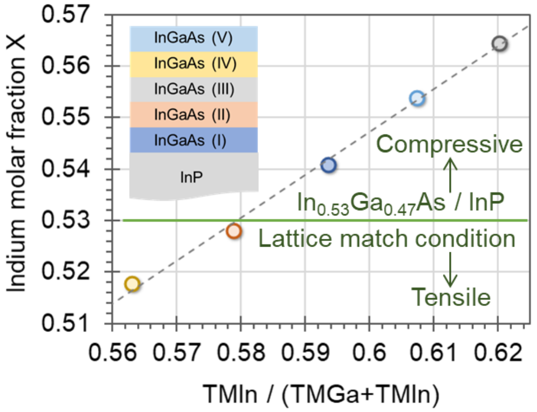

Figure 4: Indium composition of In$_x$Ga$_{1-x}$As layers vs TMIn supply ratio.

2. Stability against bubbler temperature

One of the difficulties of powdered solid precursor vaporization is to maintain the precursor temperature. Even if the bubbler temperature can be kept constant, the precursor temperature will be easily affected by the inside structure of the bubbler, the remaining amount of precursor, the carrier gas flow rate, and the porosity of the precursor. For this reason, the key problem is attaining consistent TMIn delivery.

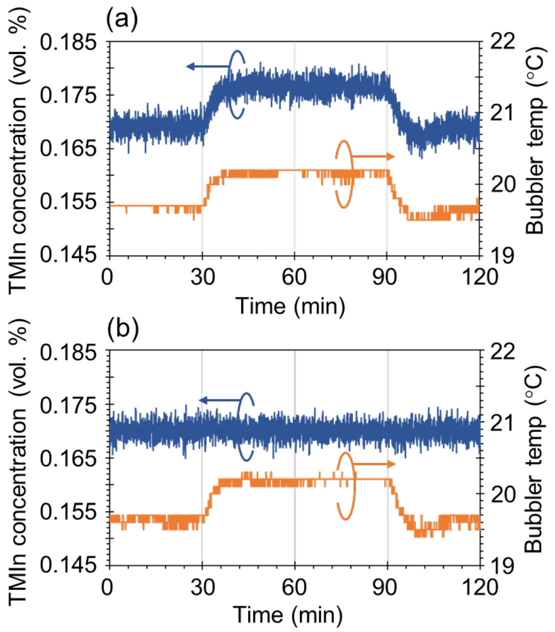

Figure 5: TMIn concentration and bubbler temperature during InAlAs/InGaAs SLs growth (a) under constant pressure control, (b) under constant concentration control.

Here, the bubbler temperature of 0.5°C was intentionally changed during 30 pairs of lattice-matched superlattices (SLs) of InAlAs/InGaAs growth as shown in figure 5. For the first 30 min, the growth was carried out at a set temperature of 20.0°C, and then the set temperature was increased to 20.5°C for 60 min, and finally the temperature setting was lowered again to 20.0°C for 30 min. The bubbler temperature was measured by a thermocouple sensor. The change in TMIn concentration under constant pressure control clearly appears to follow temperature dependence of vapor pressure (Figure 5 (a)), whereas the TMIn concentration under constant concentration control remained constant despite the bubbler temperature changes (Figure 5(b)).

Figure 6 shows the 2θ-ω scan profiles in the vicinity of the InP(004) reflection peaks from the InAlAs/InGaAs SLs samples with the period of 50 nm. The clear XRD satellite peaks are observed in both of the profiles, indicating the excellent interface between each layer. The SLs sample grown under constant pressure control has split peaks at the satellite lines, which can explain that the indium composition and the layer thicknesses are slightly different in the growth time of 30-90 min and in other regions due to the change in TMIn concentration. By contrast, the single sharp satellite peaks are only measured from the SLs sample grown under constant concentration control. It can be seen that a change of only 0.5°C in a temperature bath for a bubbler has significant effect on the device characteristics.

Precursor concentration control can contribute not only to stabilizing film composition during deposition processes but also to long-term production stability and process yield.

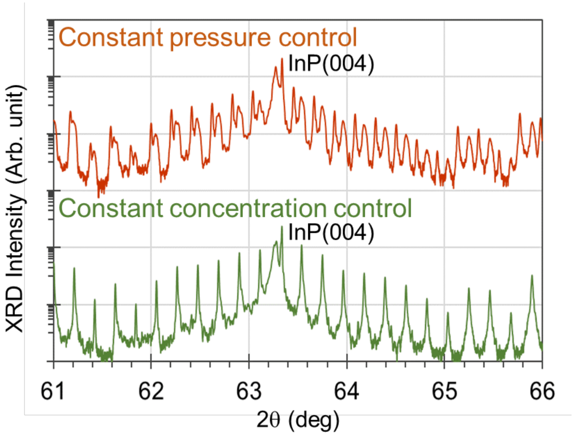

Figure 6: XRD patterns of 30-pairs InAs/InGaAs SLs on InP substrate.

Conclusion

HORIBA vapor concentration controller, VCC-100, was installed onto a MOCVD system. Deposited films obtained by both the usual bubbling process control (total pressure control) and concentration control were compared. If a vapor pressure of a precursor inside a bubbler is at a saturation vapor pressure and stable during a bubbling process, total pressure control will not be a problem. In case of most liquid precursors, vapor pressure of the precursor can be easily maintained if there is enough precursor remaining.

The situation is different for solid precursors, such as TMIn. The amount of precursor delivery is strongly affected by the condition inside of the bubbler, e.g. surface area and positions of the powdered precursor. In this application note, a new method for controlling $In_XGa_{1-X}As$ composition based on the pressure based VCC is proposed and shows promise for a grown film quality comparable to the normal bubbling method. Controlling a precursor concentration while maintaining a constant carrier flow rate is considered to be an advantage for a bubbling process for solid precursors. Moreover, the bubbling process controlled by VCC method has proved to be robust against precursor vapor pressure changes caused by for example temperature changes.

References

[1] HORIBA Semiconductor Application Note No. RD00029190. “Gas delivery for MOCVD” (2020).

Product information

VCC-100 monitors the gas concentration based on the IR-300 technology and feeds back it to the valve to keep it constant. VCC-100 is a product that adds a valve function to IR-300 so that the concentration can be controlled by a single unit. All the user has to do is input the desired concentration, and the internal algorithm will control the concentration to keep it constant.

For more information about VCC-100, please visit: HORIBA

VCC-100
Vapor Concentration Controller

Upcoming Event : **Photomask Japan 2022, 26-28, Apr. (Japan)** **Location: Digital Forum**
https://www.photomask-japan.org/

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