How to stabilize the epitaxial growth process?

Gas delivery for MOCVD

Abstract

Vapor concentration control of precursors provide substantial improvement in stabilizing MOCVD processes. By measuring a precursor partial pressure in a downstream line with a Non Dispersive Infrared (NDIR) technology and controlling its total pressure, a precursor concentration can be kept constant. This precursor concentration control is validated as a practical method against a temperature fluctuation of a cylinder bath and a failure of reaching a saturation pressure in a cylinder.

Introduction

MOCVD is essential for epitaxial growth technologies in III-V compound semiconductor industries, including LEDs, LDs and high speed devices. Because most liquid or solid metal organic precursors for III-V semiconductor growth have relatively high vapor pressures even below 100°C, it’s easy to deliver the precursors in a gaseous state, leading to suitableness for mass production systems.

There are some vaporizing methods, in which bubbling is widely used for III-V MOCVD. In the bubbling method, a carrier gas flows through a bubbler cylinder filled with a precursor and the generated mixture of the carrier gas and the precursor is delivered to a growth chamber.

Usually, epitaxial growth is conducted under a gas transport limited condition, where reaction speed on a substrate surface is much higher than gas transport speed. Precursor molar flow ratio is, therefore, directly related to thickness and solid composition of the growth films.

Problems

Under an ideal vaporizing condition, an upper space inside a cylinder is always at equilibrium with a precursor, and the temperature inside a cylinder is the same as the controlled temperature of a stabilization bath. If a bubbling system satisfies the above conditions, stable molar fraction ratios can be obtained by a Mass Flow Controller (MFC) set at the upstream side of the cylinder.

Actual bubbling cylinder condition, however, is not ideal because of the following reasons: 1. Some cylinder’s temperature is different from a temperature of the carrier gas, which would cool off or heat the inside of the cylinder during bubbling. 2. Recent enlarging MOCVD chambers requires an increase in bubbling flow rate to increase molar flow ratio, which would cool off the precursor temperature due to the vaporization heat and would also increase the pressure in the cylinder. 3. Vaporizing characteristics differ depending on cylinder suppliers even under the same condition due to the difference in the internal structure of the cylinder. 4. The amount of residual precursor is changing over the life of the cylinders especially in solid precursors, which would affect the molar flow ratio. Cylinders should be replaced even when an adequate precursor remains in order for a stable condition.

A solid composition of growth films are usually investigated after epitaxial growth by

X-ray diffraction, photoluminescence and electrical measurements. It takes time and costs money to modify growth parameters when some abnormalities in thickness, solid composition, emitted wavelength and doping level are detected.

Solution

Most precursors absorb IR light by the vibrations or rotations within the molecule. HORIBA has developed NDIR technologies for half a century for measuring gas concentrations in many industries. For the semiconductor industry, IR-300 series have been launched and are used to measure precursor concentration at the downstream side of the bubbling cylinder.

Monitoring a concentration is considered to be important for checking a process condition. The next step for a next generation gas delivery system will be to automatically adjust the precursor concentration, which we call Vapor Concentration Control / Controller (VCC).

HORIBA has two different VCC concepts, flow-based and pressure-based ones. The latter is suitable for III-V MOCVD systems because a bubbling system should have a pressure controller valve (PV) at the downstream of a cylinder and a PV can be readily replaced by a pressure-based VCC module with compact design.

The precursor concentration in a downstream pipe of a cylinder is given by

$$\text{Conc.} = {}^{P_v}\!/_{P_t} \qquad (1)$$

where P_v is the precursor partial pressure and P_t is the total pressure in the pipe. As for a usual gas delivery method by bubbling, P_t is set to constant and is controlled by the PV. It looks reasonable as long as P_v is stable. As mentioned above, P_v is, however, susceptible of bubbling conditions. In the VCC system, P_t is continuously controlled in such a way that P_v/P_t should be constant by using the NDIR signal and the pressure sensor inside the VCC module. For example, when a measured precursor concentration is larger than a set one, the piezo valve starts to tighten the flow path to increase P_t.

Since a MFC, set at the upstream side of a cylinder, ensures a constant mass-flow, the VCC system achieves an output with constant molar flow ratio. The schematic diagram of a bubbling system is shown in Fig. 1.

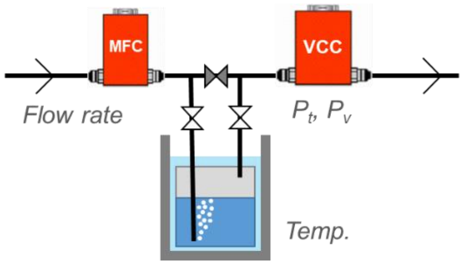


Fig. 1. Schematic diagram of a bubbling system with a MFC and a VCC module.

Examples

Although trimethylindium (TMI) is commonly used for growth of Indium contained III-V compound semiconductor films, the vapor pressure of TMI differs depending on the literature [1], indicating that the vapor pressure of solid precursors such as TMI is easily affected by experimental conditions. Therefore VCC is preferable to be adopted.

TMI concentration control by the VCC module is performed under conditions in which the bath temperature is intentionally changed from about 28°C to 34°C (Figure 2). The N_2 flow is set to 400 sccm as a bubbling gas and the precursor concentration in the pipe is set to 0.1 vol. %. As expressed by the Antoine equation, the logarithm of the vapor pressures relates to the reciprocal temperature. Regarding TMI, the vapor pressure varies by about 50% between the temperature of 28°C and 34°C. Without VCC, the carrier concentration would increase under the normal bubbling control.

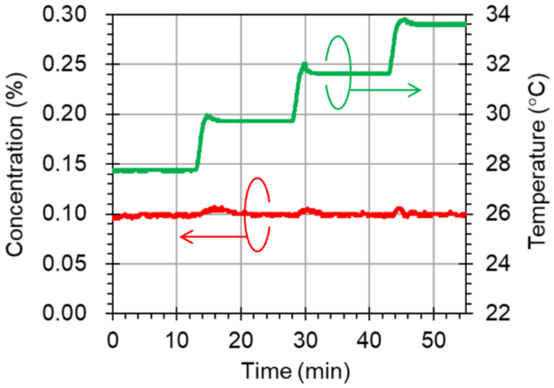
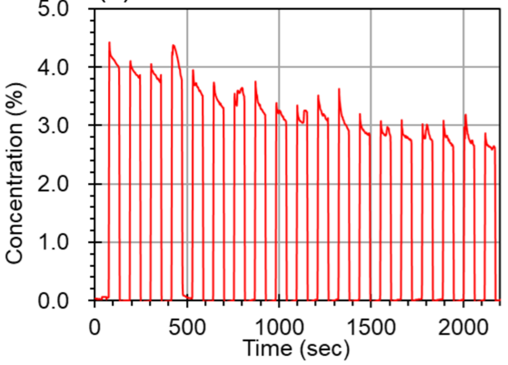


Fig. 2. Bath temperature dependence of TMI concentration with VCC.

Isopropyl alcohol (IPA) concentration measurements were made to study the behavior during the bubbling processes. The temperature of the IPA cylinder was not controlled intentionally and the flow rate of the Nitrogen as a carrier gas is set to a high of 50 slm. The Nitrogen gas flow alternate between the bypass line and the bubbler once every 60 seconds. Figure 3(a) shows the measured IPA concentration without VCC. As the cycle time increases, IPA concentration in the downstream line of the bubbler decreases. This phenomena is presumably attributed to heat of evaporation, which remove heat of surrounding area. As a result, the IPA temperature decreases, leading the vapor pressure decreases. By contrast the stable IPA concentration of about 2.5% is observed under the VCC control shown in fig. 3(b). Although the IPA temperature should also decrease in a condition such as a bubbling gas flow rate is 50 slm, the VCC control makes it possible to maintain at a constant level of precursor concentration by controlling P_t.

(a) without VCC



(b) with VCC

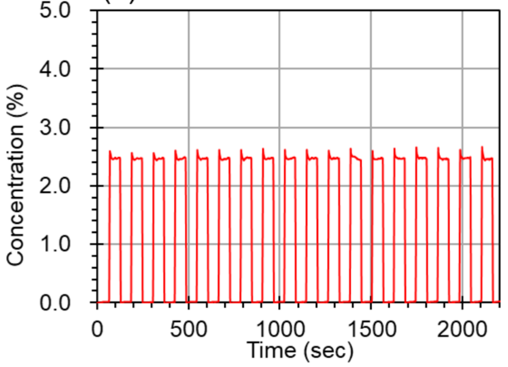


Fig. 3. IPA concentration during intermittent bubbling processes (a) with VCC, (b) without VCC.

Conclusion

A new concept stabilizing precursor delivery against a fluctuation of a bubbling condition is proposed. Although bubbling is a convenient method for vaporizing precursors for III-V MOCVD growth, how much concentration of a precursor that a bubbling system generate strongly depends on process and environmental condition. VCC has potential for use in one of the stabilizing methods of the gas delivery, which allows better quality control of MOCVD growth processes.

References

[1] Deodatta V.Shenai-Khatkhate et al., Journal of Crystal Growth 310 (2008) 2395.