FEATURE ARTICLE

The Evaluation of Liquid Material Vaporization and Supply System for CVD

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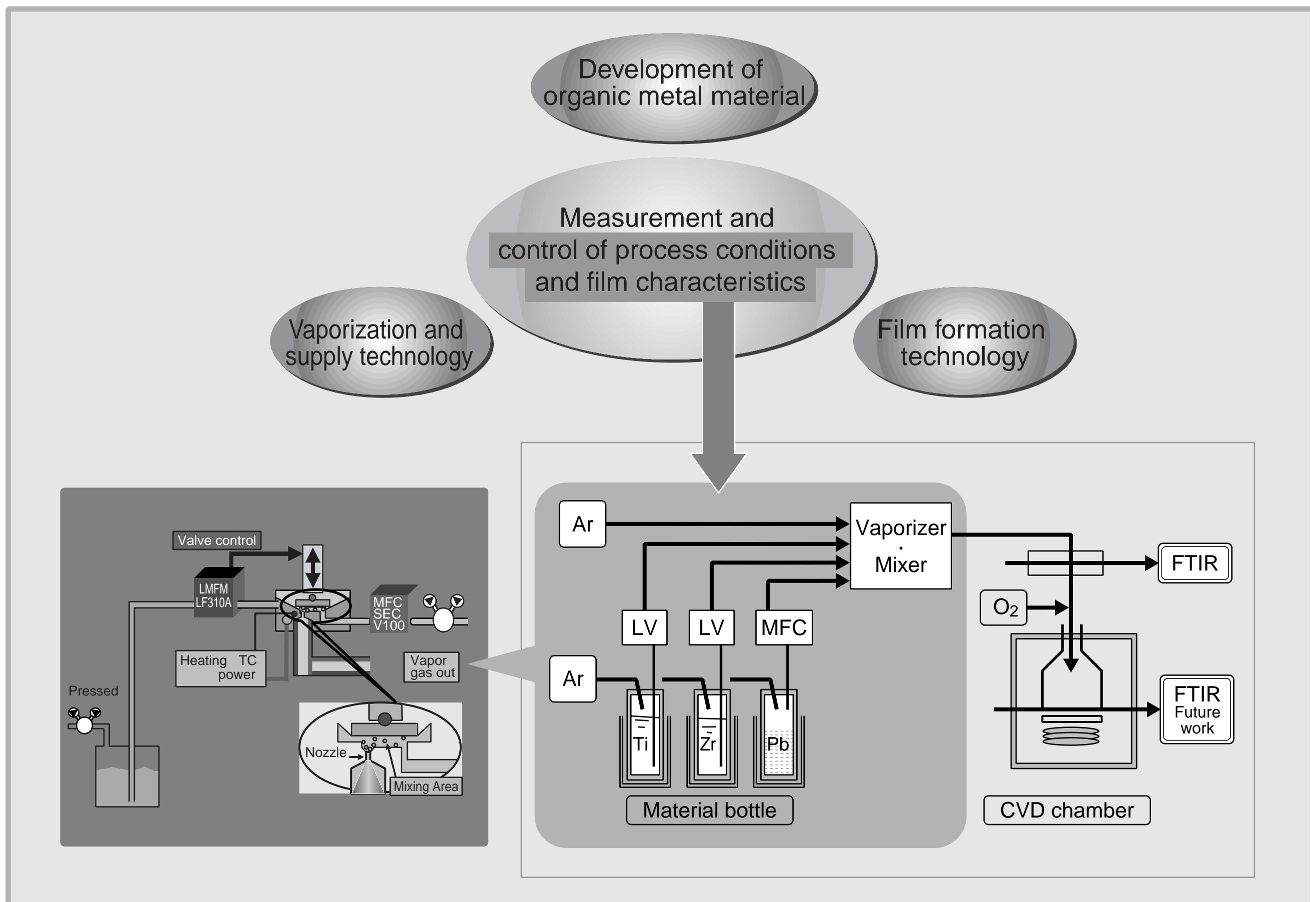


Abstract

Semiconductor manufacturing technologies are diverse and fast-changing, and none more so than thin film formation technology. The MOCVD is one of the most feasible thin film formation technique for ferroelectrics thin film for FRAM, capacitor film, insulating films and other high-functional thin film. Currently various substances are proposed as source materials for thin film. As these materials become more diverse, the technology in which the liquid material efficiently and stably vaporizes becomes very important. This paper reviews the various liquid material vaporization and supply methods, and presents the vaporization test results for some material using the direct injection method. And automatic tetra etoxy silan delivery system that developed by STEC Inc. is introduced.

1 Introduction

Semiconductor devices are structured by laminating many thin films and there are many film formation methods including chemical vapor deposition (CVD) and physical vapor deposition (PVD). As semiconductor devices become more miniaturized and denser, the requirements of film formation become more diversified and more precise. In particular, CVD allows forming a variety of film so far as source gas can be prepared, and provides better step coverage and high controllability. Therefore, CVD will become one of the important techniques that support the progress of semiconductor technologies. This paper discusses a liquid material vaporization and supply system for CVD.

2 Raw Material Compounds for CVD Film Formation

As shown in Table 1, the raw material compounds for CVD are roughly classified into inorganic compounds and organic metallic compounds.

Inorganic compounds are further classified into hydrides and halides. Hydrides and halides show high vapor pressure and are gas or liquid at room temperature. For CVD, therefore, they can be easily supplied in a state of gas.

As organic metallic compounds, alkoxy compounds, alkyl compounds, and complex compounds are mainly used. All of them show low vapor pressure and are liquid or solid at room temperature. For this reason, they must be vaporized when used for CVD. If you look for any new material for CVD, there will be no appropriate hydride or halide. Even if one is found, it will be unstable. For the CVD raw material supply system, therefore, it is an issue how efficiently these organic metallic compounds in a state of liquid are gasified and supplied stably.

Inorganic compound	Hydride	SiH_4, PH_3, B_2H_6, AsH_3
	Halides	SiH_2Cl_2, $SiCl_4$, $TiCl_4$
Organic metallic compound	Alkoxy compound	TEOS, TEPO, TMB, PETa
	Alkyl compound	TMP, TMAI
	Complex compound	$Sr(DPM)_2$, $Bi(DPM)_3$

Table 1 Typical Raw Materials for CVD

3 Liquid Material Vaporization and Supply Methods

The vaporization and supply method for liquid materials is classified into the bubbling method, baking method, and injection method. These methods have their own features, but the injection method is becoming the mainstream as semiconductor manufacturing equipment becomes more precise, lower in price, and more compact. The features of each method are as described below:

3.1 Bubbling Method

The configuration of this method is illustrated in Fig.1. The liquid material is maintained at constant temperature and pressure and the flow rate of carrier gas controlled to send a constant amount of material to the CVD chamber. When the liquid material is mixed with the carrier gas until the saturated state, the supply flow rate Q_m of the material can be expressed with the following equation:

$$Q_m = Q_c \times P_1/(P_1 + P_0)$$

where Q_c is the flow rate of the carrier gas;
P_1 is the vapor pressure of the material; and P_0 is the pressure in the bubbler.

However, as heat of vaporization is removed, the temperature of the material might decline resulting in decreased vapor pressure, or changes in the bubbler pressure might cause changes in the supply amount of the material. Therefore, a mass flow meter (MFM) or a heat conduction type concentration sensor (TCD) must be installed on the secondary side to compensate for the above possible changes.

Recently, however, the bubbling method has not been used frequently because control accuracy is limited and a high flow rate of supply cannot be achieved for materials of low vapor pressure.

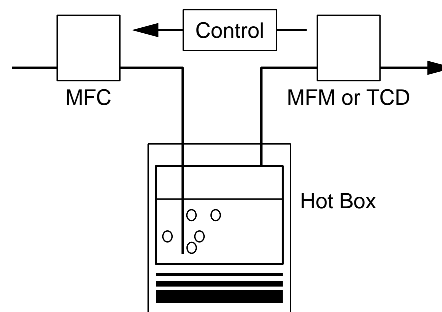


Fig.1 Bubbling Method

3.2 Baking Method

The configuration of the baking method is illustrated in Fig.2. The material is heated to increase the vapor pressure. The flow rate of the vapor is controlled with a mass flow controller (MFC) for high temperature, which has been directly heated. Since the vapor generated from the material is directly controlled with the MFC, the flow rate can be accurately controlled and the interfusion of impurities can be minimized.

Because of these features, the baking method is frequently used mainly to control tetra etoxy silan (TEOS), an alkoxy compound of silicon. However, it has some drawbacks including (a) it is not suitable for materials of low vapor pressure and atmospheric pressure processes, (b) the equipment is large-scaled and expensive, and (c) the footprint is large because the entire raw material supply system must be put in a constant temperature bath.

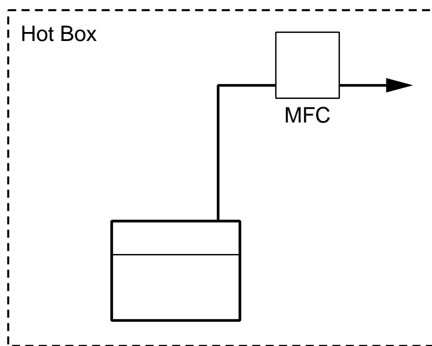


Fig.2 Baking Method

3.3 Injection Method

The injection method directly controls the flow rate of a liquid material in the state of liquid and carries out the vaporization and supply of only the necessary amount. This method is classified into the column method in which the material is vaporized in a column and the direct injection valve method in which the material is vaporized directly in a control valve.

(1) Column Method

The configuration of the column method is illustrated in Fig.3. The carrier gas and liquid are mixed in the heated column so that the liquid vaporized. The column is charged with metallic particles to increase the contact area with the liquid and thereby effectively vaporize the liquid. The equipment can be downsized because it is only necessary to heat the column and subsequent line. In the pressure reducing process, however, cavitation or the like can cause unstable generation of vapor.

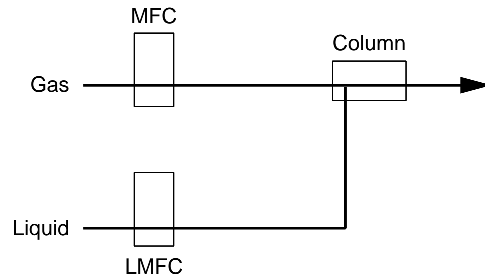
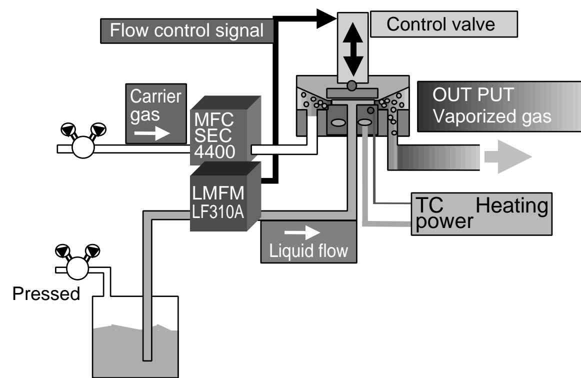


Fig.3 Column Method

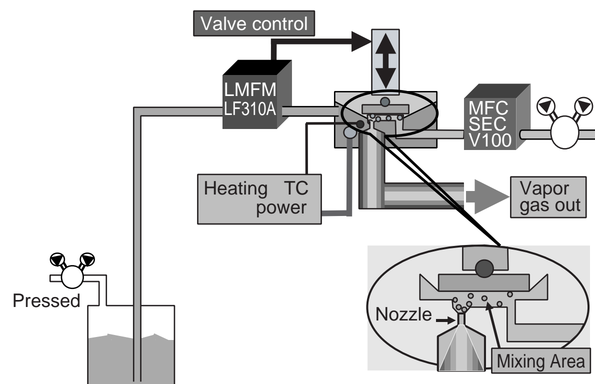
(2) Direct Injection Method

The direct injection method vaporizes liquid by mixing the liquid with carrier gas while heating the flow control valve for the liquid. Since the vaporizer also serves as the control valve, the equipment can be downsized and low-priced. The gas-liquid interface is formed at the seat of the control valve, enabling rapid rising and falling of material supply.

The direct injection method is still classified into the liquid injection method in which mixing with the carrier gas and vaporization are simultaneously carried out and the mixing injection method that has been improved to increase the vaporization efficiency. The configuration of each method is illustrated in Fig.4.



(a) Liquid Injection Method



(b) Mix Injection Method

Fig.4 Direct Injection Method

4 Evaluation of Characteristics of Vaporization by Direct Injection Method

4.1 Evaluation of Vaporization Characteristics of PETa

Tantalum oxide (TA_2O_5) is high in dielectric constant and used as a capacitor material instead of SiO_2 in next-generation semiconductor devices. Pentaetoxy tantalum (PETa) is used as material for Ta_2O_5 film, but its vapor pressure is approximately 20 Pa at 170°C. Vaporization of liquid material becomes more stable as the vaporizer temperature or the flow rate of carrier gas becomes higher. However, if the vaporization temperature is too high, thermal cracking might occur in the material. For this reason, the optimal temperature must be obtained.

The equipment illustrated in Fig.5 was used to conduct an evaluation test for the vaporization characteristics of PETa.

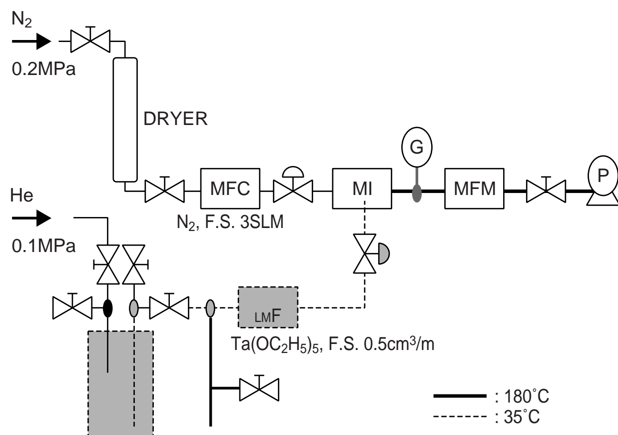


Fig.5 Testing Equipment for Evaluating Vaporization Characteristics

4.1.1 Test Procedure

The flow rate of carrier gas was maintained at 300 to 700 SCCM and the secondary side in a vacuum state of approximately 2.7kPa. The temperature of the vaporizer was changed in a range between 150°C and 180°C to change the generated amount of PETa in a range between 0.1 and $0.5cm^3$/min, and then the state of vaporization was evaluated. The stability of vaporization was evaluated by observing the stability of output from the MEM for high temperature, which was put in the piping on the secondary side of the vaporizer, and the internal state through the transparent window provided on the vaporizer.

4.1.2 Test Results

The output from the MFM and the internal state of the vaporizer are shown in Fig.6. The output from the MFM was unstable at $0.4cm^3$/min when vaporization was insufficient with droplets noted. The output was stable at $0.2cm^3$/min when vaporization was sufficient. Some droplets were observed in the vaporizer at $0.3cm^3$/min, an intermediate level, when the output from the MFM showed tailing at the falling part.

The above test results demonstrate that the state of vaporization can be estimated from the output from the MFM on the secondary side.

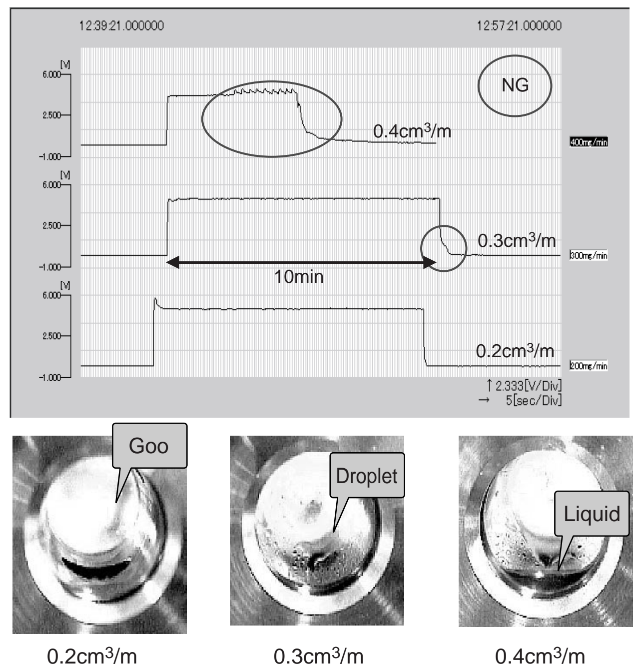


Fig.6 Output from MFM and Internal State of Vaporization

4.1.3 Influence of Vaporization Temperature

Fig.7 shows the changes that occurred in the outputs from the MFM for liquid and gas when the temperature and flow rate of the vaporizer were changed. The rising and falling characteristics, and the stability of the MFM for gas during vaporization show that the state of vaporization become more stable as the generated amount of PETa decreases. When the temperature of the vaporizer is 180°C, PETa can be stably vaporized at 0.5cm^3/min.

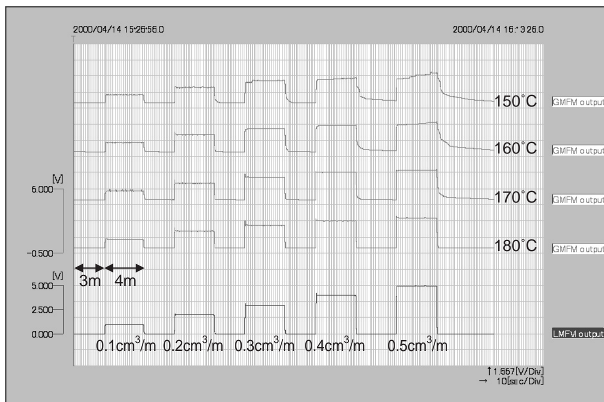


Fig.7 Influence of Vaporization Temperature

4.2 Evaluation of Vaporization Characteristics of TEPO

As the silicon wafer size change to 300 mm, it will be necessary to increase the flow rate of materials for the purpose of boro-phospho silicate glass (BPSG) film formation. The same flow as in the vaporization test of PETa was used to conduct a TEPO[$P(OC_2H_5)_3$] generation test by the liquid injection and mixing injection methods.

The evaluation results based on the MEM on the secondary side of the vaporizer are shown in Table 2 and 3. Although the pressure condition is slightly different, the vaporization efficiency is greatly improved by the mixing injection method. This indicates that a high flow rate can be achieved under the same condition.

Flow rate of carrier gas (N_2)	Amount of TEPO vaporization : 0.05(g/min)
9.0SLM	○
8.0SLM	△
7.0SLM	×

Condition: Vaporizer temperature 100°C
pressure 93kPa

○ : Good △ : Slightly bad × : Bad

Table 2 Characteristics of TEPO Vaporization by Liquid Injection Method

Flow rate of carrier gas (N_2)	Amount of TEPO vaporization :(g/min)				
	0.15	0.125	0.1	0.075	0.05
2.0SLM	○	○	○	○	○
1.5SLM	△	○	○	○	○
1.0SLM	×	×	△	○	○

Condition: Vaporizer temperature 100°C
pressure 80kPa

○ : Good △ : Slightly bad × : Bad

Table 3 Characteristics of TEPO Vaporization by Mixing Injection Method

5 Automatic Delivery System for Liquid Materials

To continuously use the vaporizer for the baking method or injection method in the commercial production line for semiconductors, it will be necessary to automatically feed liquid material. As an example, our TEOS automatic delivery system is introduced below. The appearance and flowchart of this system are shown in Fig.8 and 9.

Fig.8 Automatic Delivery System for Liquid Material

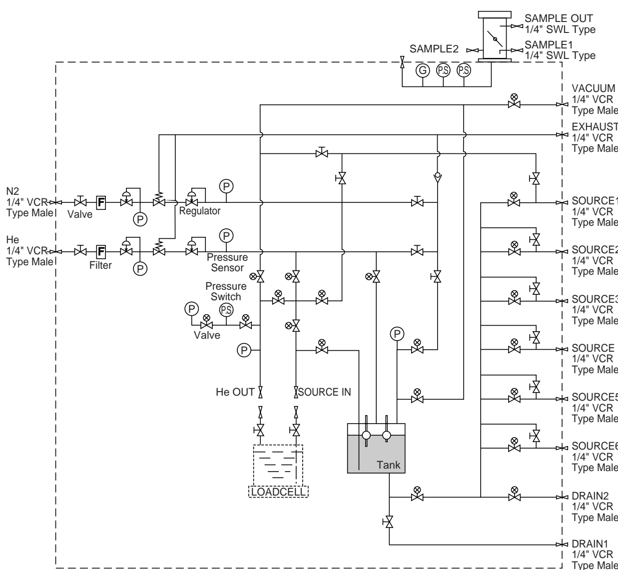


Fig.9 Flow of Automatic Delivery System for Liquid Material

This system provides the following features:

1. Conforming to safety regulations [CE marking/SEMI STANDARD(S2)]
2. Minimize footprint
3. Safety design with automatic monitoring system
4. Easy operation by using two way communication
5. Non stop recharging at replacement of source tanks
6. Best compatibility with LSC/VC system

6 Conclusion

In the semiconductor manufacturing process, liquid material will become more or more important. On the other hand, the vaporization and supply system has some problems in complying with new materials and increasing the flow rate to handle 300mm wafers. In order to settle these problems, the users' needs must be grasped accurately. We wish to take this opportunity of making information exchange with our customers more frequent, and hope that we will play a part in further development of the semiconductor industry.

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