

## TECHNOLOGY TOPIC

# Liquid-injection system based on mass flow controllers

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In chemical vapor deposition (CVD) processing, there is a growing tendency to use liquid precursors instead of gases. The popularity of liquid precursors is based in part on physical properties that render them less harmful, flammable, corrosive, and poisonous than gaseous ones. One of the more common liquids used in fabricating semiconductor devices is tetraethylorthosilicate (TEOS), which is frequently substituted for silane. With TEOS, conformal SiO<sub>2</sub> films with no detectable carbon can be deposited with better step coverage and with far less hazard than silane. In metal-organic CVD (MOCVD) processes, liquid precursors for metals such as copper are often used because gaseous ones are not available.

The integrity of deposition systems depends on accurate regulation of the distribution of gas, vapor, or liquid. A vapor is a gas at below the critical temperature. Gas mass flow controllers (MFCs) can easily control the flow of gases. Liquids must first be converted to vapor for the reaction process to occur, but controlling vaporization is a delicate matter. Bubbler delivery systems are commonly used, but their performance is poor.

The liquid-precursor delivery system described in this article is based on an injection technique in which the liquid is measured and controlled by a mass flow controller. This system has a faster response time, better stability, and a lower working temperature than conventional bubbler systems (Fig. 1).

### Bubbler-based systems

A variety of bubbler configurations are conventionally used in vapor delivery systems (see Fig. 2). A bubbler consists of a liquid-containing vessel that is shrouded with a temperature-controlled heater jacket. MFCs are used to control either the vapor out or the input carrier gas.

In all configurations, the flow of vapor is directly related to the vapor pressure in the vessel, which varies with temperature, according to the characteristics of the liquid. The relationship between temperature and vapor pressure dramatizes the large excursions in the vapor pressure caused by small temperature variations (Fig. 3). The sensitivity to temperature changes contributes to the main problems with bubbler systems: poor repro-

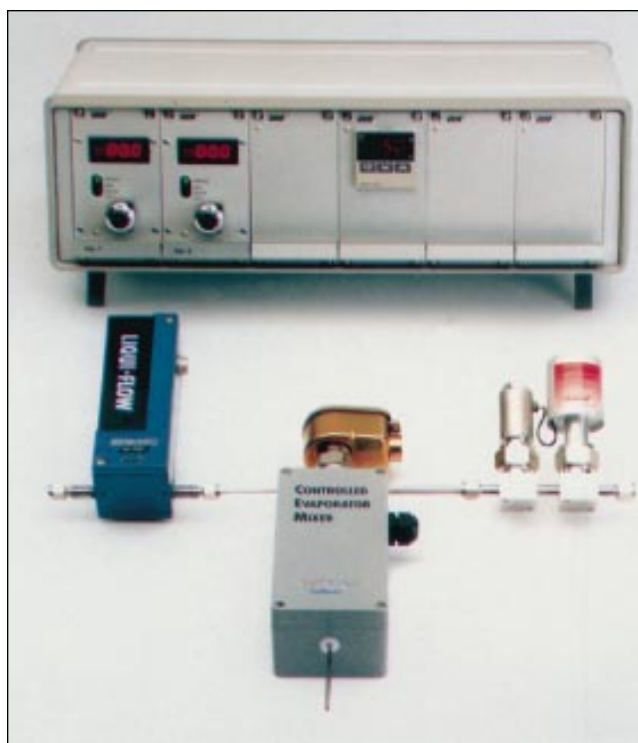


Figure 1. Components of a CEM system include a liquid flowmeter (left), a gas MFC, and the liquid mixing valve (middle) on top of the vaporization chamber. The control electronics for the MFCs and the temperature are in the box (back). (Photo courtesy of Bronkhorst High-Tech)

ducibility and instability of the vapor flow.

Different bubbler configurations have been designed to overcome the sensitivity problem and achieve stable vapor flow. The flow can be controlled with a manual restriction or by an MFC at the outlet (Fig. 2a). In the no-carrier-gas configuration, an MFC manages the flow of vapor, and achieves stable and flexible flow control with good precision. The precursor must be at an elevated temperature to achieve high vapor pressure, and concurrently

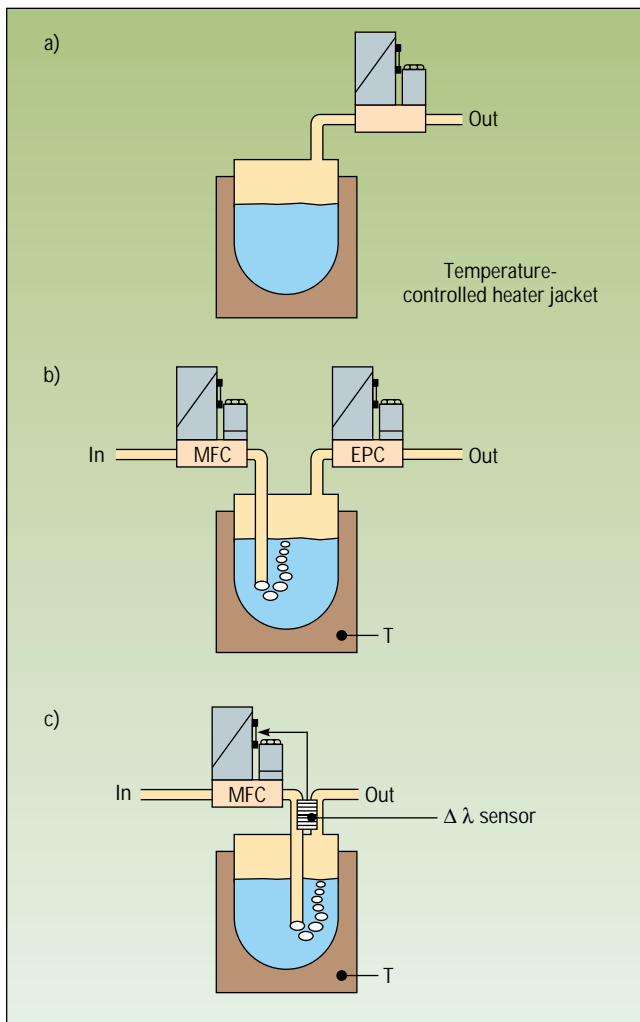


Figure 2. Bubbler configurations: a) vapor control by a MFC; b) bubbler with carrier gas with pressure held constant by an EPC; and c) vapor content is sensed by the thermal conductivity sensor and controlled by the MFC.

the MFC temperature must be high to prevent condensation. The resulting flow of vapor, therefore, depends on vapor-pressure characteristics.

The high temperatures for the liquid and for the mass flow controller cause reliability and system design problems. A precursor can break down when kept at high temperatures for extended periods. Mass flow controllers for high temperatures are expensive, delicate, and not very precise or repeatable. The electronics must be isolated from the heated zone.

Other bubbler system configurations use a carrier gas. In the simplest one, the flow of vapor is controlled by the carrier gas flow. This system can be improved by holding the pressure constant in the bubbler. As a consequence, the ratio between the carrier gas and vapor is fixed, stabilizing the output (Fig. 2b). More sophisticated systems use a sensor to measure the vapor content in the carrier flow (Fig. 2c). The flow of vapor can then be kept constant by controlling the carrier gas flow, based on the sensor signal.

### Liquid injection

Dispensing systems based on liquid injection differ fundamentally from bubbler systems. In liquid injection, vapor delivery depends on control of liquid flow, as opposed to vapor control. The precursor is controlled in its natural (liquid) state, at ambi-

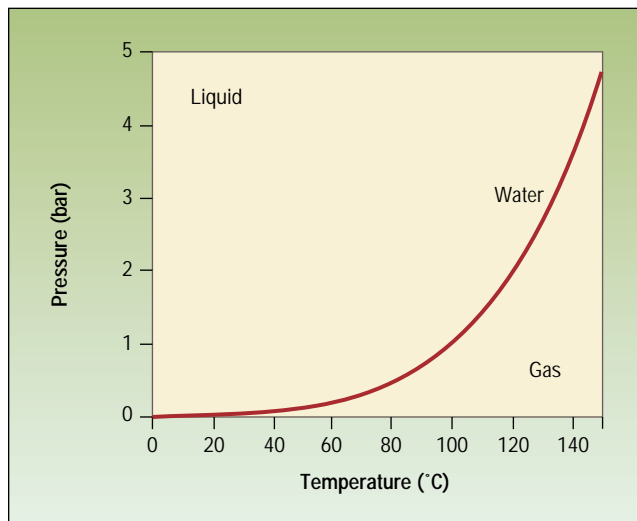


Figure 3. Vapor pressure lines of some fluids on a linear pressure scale. The relationship between temperature and vapor pressure dramatizes the large excursions in the vapor pressure caused by small temperature variations.

ent conditions, and subsequently evaporated.

Although liquids can be controlled by pumps [1, 2, 5], MFCs for liquids are more attractive and have been used in our controlled evaporating and mixing (CEM) system (Fig. 4). A thermal mass flow sensor, which unlike most gas mass flow sensors does not need a by-pass line, measured liquid flow. The thermal sensor had a hot-spot temperature of only a few degrees above ambient [3].

The liquid, controlled by the liquid flow controller, is transported with a carrier gas into the evaporator-mixer where vaporization takes place. The heater can provide vapor temperatures between ambient and 200°C. The inner volume of the mixing

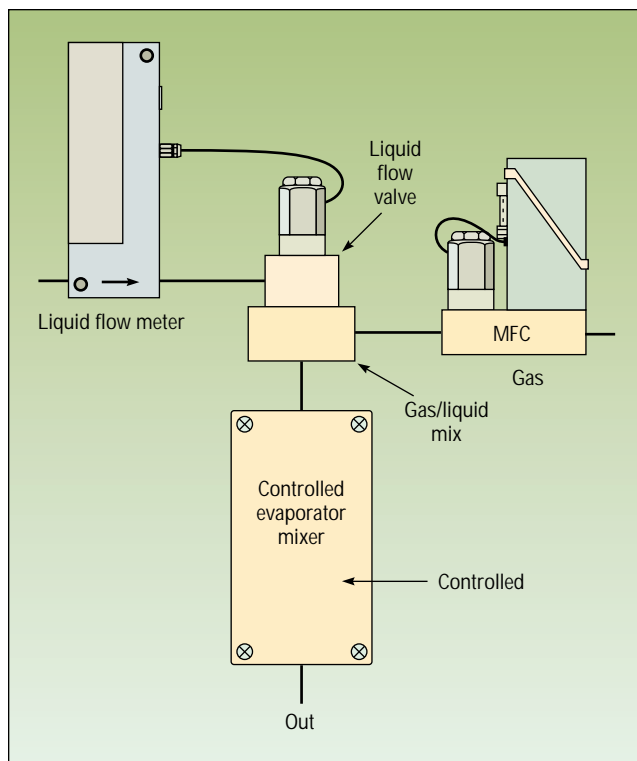


Figure 4. Schematic layout of the CEM system. The liquid, controlled by the liquid flow controller, is transported with a carrier gas into the evaporator-mixer where vaporization takes place.

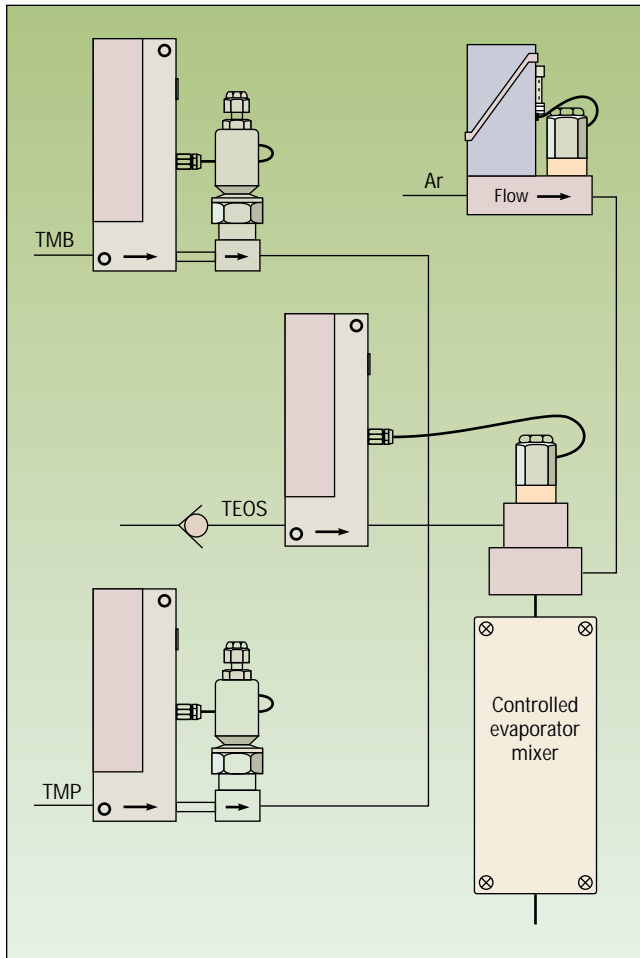


Figure 5. The setup for the BPSG process. TMP, TMB and TEOS are mixed "in situ" and consequently evaporated and mixed with Argon.

chamber was minimized, so that the response of the system is defined mainly by the response of the liquid and gas MFCs [4].

Temperature and pressure are only boundary conditions. The temperature of vaporization, for example, is not critical as it is in bubbler systems. The only criterion is that the partial pressure of the fluid must be lower than the vapor pressure at that temperature to prevent condensation.

The instrument can control flows in the range of 250 mg/h to 1 kg/h, corresponding to vapor flows (based on water) from 5 sccm to 20 slm. Most CVD processes use vapor flows in these ranges. The flow of vapor is limited by the maximum power (1000 W) available in the heater. The system always needs a minimum flow of gas to carry the liquid into the heated evaporation zone. Flows are stable, repeatable, and easily adjustable via the flow controllers.

The ratio of the vapor to carrier gas (the pick-up rate) is usually higher in the CEM than in bubbler systems. In the CEM, this ratio can be chosen from 0 to 100% (saturation), while typical ratios for bubbler systems have a maximum of 90–95%. Comparing the responses of bubbler and CEM systems is difficult because of the variety of configurations. Nevertheless, the typical response time of a bubbler without a run/vent mode is minutes, while the response time of the CEM is seconds. In a CEM system, a run/vent line is not necessary, in contrast to bubbler systems. With a low working temperature (0 to 200°C), the CEM allows the liquid to remain at room temperature.

## Applications

The CEM liquid injection technique opens new processing opportunities, such as evaporation of liquid mixtures. In a bubbler-based system, co-evaporation is not possible because the fluid with the highest vapor pressure will evaporate first. Solids dissolved in a solvent have also been vaporized successfully in the CEM system [6]. Evaporation at pressures much higher than atmospheric is possible, as long as the pressure conditions are not violated.

In many applications, such as those for silicon oxidation, DI water is evaporated. With a liquid injection system, the water supply is not limited, while in classic bubbler systems, the bubbler must be refilled. Trichloroethane (Trans-LC) for scrubbing a quartz reactor in an interdeposition CVD processing step has also been delivered with a CEM system. The resulting pick-up rate was much higher than in a bubbler system.

Many metal-organic liquids break down when held at high temperatures for a long period. Therefore, the classic bubbler system is not a viable approach. CEM liquid injection for dosing Cupra-select during a CVD process has been used [7].

For applications involving BPSG planarization processes with TEOS, TMB (trimethylboron), or TMP (trimethylphosphite), a special design has been developed. The system consists of three liquid MFCs and only one evaporation unit. The mixture can be created "in situ," and adjusted even during the process (Fig. 5).

## Conclusion

Vapor flows in liquid injection systems depend on controlled liquid flow. Fast response, high repeatability, good stability, and low working temperatures are the main advantages of the CEM liquid injection system. New procedures such as evaporation at high pressures and evaporation of mixtures are possible. While bubbler system technology is simple and mature, CEM techniques can have better performance. ■

## Acknowledgment

Trans-LC and Cupra-Select are both registered trademarks of Shumacher.

## References

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HENDRIK JAN BOER received his MS degree in physics from the State University of Groningen in the Netherlands. He is a research and development engineer at Bronkhorst High Tech. He has experience in the development of mass flow sensors for gases and liquids and did research in the field of thermodynamical properties of gases and liquids. *Bronkhorst High-Tech B.V., Nijverheidsstraat 1a, 7261 AK Ruurlo, The Netherlands, e-mail: hjboer@bht.nl.*