



Improve CVD/ALD Performance with Advanced Liquid Source Delivery

1. Abstract

Many of the advanced gas-phase processes used in state-of-the-art microelectronic fabrication place higher demands on vapor delivery solutions. Vaporization challenges include a diverse range of liquids with unique material properties, the use of liquids with low vapor pressure, the use of liquids with a small window between thermal decomposition and vaporization, and growing need for high vapor concentrations. The growing implementation of short pulse processing also creates a need for faster response times. The MSP Turbo II™ (T2) Vaporizer Liquid Delivery System presents a new alternative for liquid vaporization.

2. Introduction

Liquid precursors must be used for many CVD/ALD applications. Liquids with high vapor pressure and high decomposition temperatures can be vaporized relatively easily at low to moderate vapor concentrations; however, care must be taken to ensure that; there are no particulate byproducts formed during vaporization, the vapor concentration output is steady, there is 100% vaporization to prevent persistent clogging and reliability issues, and response times are fast enough for short pulse processing (ALD or short pulse CVD).

Advances in high κ , low κ and metal barrier/interconnect thin films have required the use of more difficult to vaporize precursors. Liquids that have a narrow thermal window between vaporization temperature and thermal decomposition (TEMAZr/TEMAHf, CCTBA), and/or have low vapor pressure can be problematic to vaporize. Additionally, higher vapor concentrations often lead to faster deposition rates [1]; so even for easy to vaporize liquids, there may be a need to vaporize higher concentrations than conventional techniques allow.

3. Traditional Liquid Vapor Delivery Solutions

Traditional liquid vaporizer solutions include vapor draw, bubblers, flash vaporizers, and direct liquid injection (DLI) valves. A vapor draw solution uses an ampule of heated liquid. The temperature and volume of the ampule determine the

amount of vapor (assuming saturation). The vapor created over the liquid can then be introduced into the chamber using a fast-acting valve; often referred to as an ALD valve. This method features an easy control scheme and works well for small concentrations of thermally stable liquids. However, the vapor concentration varies with the liquid level, heating the liquid over time can cause thermal decomposition, and vapor concentration is limited. A bubbler is similar to an ampule, but there is the addition of a carrier gas which has two functions: increase the vapor concentration and speed the vapor delivery to the chamber. An added difficulty with a bubbler is the development of large liquid bubbles which can escape the bubbler and become particle contamination downstream. In both the vapor draw and the bubbler solution, the liquid flow rate is not directly controlled, and the precise concentration of vapor introduced into the chamber can be difficult to determine.

A flash vaporizer or a direct liquid injection (DLI) valve (a type of flash vaporizer) both use a 'push gas' to move the liquid through a liquid flow controller (LFC). This enables precise control of the liquid mass concentration. In a flash vaporizer and DLI valve, the liquid is passed through a heated throttling valve to force a pressure reduction causing the liquid to 'flash' into vapor. A direct liquid injection valve is similar to a flash vaporizer. In a DLI valve, the liquid is metered through a small control valve where local heat is also applied. Both the flash vaporizer and DLI valve work well for low concentrations of thermally stable materials. Higher concentrations can be difficult to achieve, clogging can be problematic, there is potential for incomplete vaporization (liquid entering downstream tubing) and thermally sensitive materials can break down and potentially create solid particulate contamination.

The Turbo II liquid vapor delivery system utilizes a novel direct liquid injection, droplet atomization method as an alternative to conventional techniques. The vaporizer provides a wider process window; enabling vaporization at high and low concentrations, vaporization of thermally stable and thermally sensitive materials, as well as vaporization of liquids with low vapor pressures.

4. Heat Exposure & Thermal Decomposition

Vaporization using excess heat can cause thermal decomposition. Temperature has an exponential effect on the decomposition reaction rate as shown in Equation (1).

Equation 1

$$R = ke - \frac{\Delta H}{RT}$$

Where:

R = Reaction rate

k = Rate constant; dependent on specific reactions and temperature, independent of concentration)

ΔH = Enthalpy of reaction

R = Gas Constant

T = Temperature

Decomposition % increases with time at temperature. Axiomatically, TEMA Zr (Tetrakis(ethylmethylamido) zirconium) a common precursor used to create ZrO₂ thin films, decomposes at ~1.4% per hour at 150 °C [2], and has a half-life of ~1.8 hours at 200 °C [3]. This drives a need for a vaporization method that uses the lowest heat possible and exposes the liquid to heat for as short a time as possible.

The primary method of vaporization is convective heat transfer to the liquid. Convective heat flow rate is directly proportional to the contact area, the conductive heat transfer coefficient of the fluid temperature of the surface and temperature of the fluid.

Equation 2

$$\frac{Q}{\Delta T} = hA(\Delta T)$$

Where:

Q/Δt=Amount of heat transferred per unit time

h=the heat transfer co-efficient

A=cross-sectional surface area

ΔT=temperature difference between fluid temperature and surface temperature

To heat a body of liquid, contact is typically made at the sides and bottom of the heated container. The T2 Vaporizer utilizes a droplet atomization direct liquid injection technique to vaporize liquids.

5. Turbo II™ Vaporizer Atomizer

There are two components of the T2 Vaporizer, the atomizer and the heat exchanger. The atomizer creates a spray of droplets from a liquid – drastically increasing surface area. As the diameter of the droplet size decreases, the total surface area of the liquid increases proportionally. More surface area results in faster heat transfer, faster vaporization, and less time exposed to heat.

Table 1

Surface Area Comparison					
Liquid Volume mm ³	Liquid Mass* mg	Droplet Diameter	Number of Droplets	Total Surface Area mm ²	Total Specific SA mm ² /mg
0.524	0.524	1mm	1	3.14	6
0.524	0.524	1μm	10 ⁹	3141	6000
0.524	0.524	500nm	8x10 ⁹	6283	12,000

*assuming specific gravity of 1g/cm³

The droplet size distribution from an atomizer is a complex function of the liquid and carrier gas orifice design, the liquid and carrier gas push pressure, flow rates and the surface tension of the liquid.

The new Turbo II vaporizer has a size adjustable liquid orifice and a factory adjustable carrier gas orifice, allowing the device to be fine-tuned to specific liquid and carrier gas flow rates. This allows the droplet size to be minimized for each application. The nanometer sized droplets generated with the T2 Vaporizer enable extremely fast vaporization without the need to preheat the liquid or carrier gas. Additionally, there is a precision flow control Piezo valve directly on the atomizer which improves flow control, drastically reduces dead volume, and suppresses liquid bubble formation.

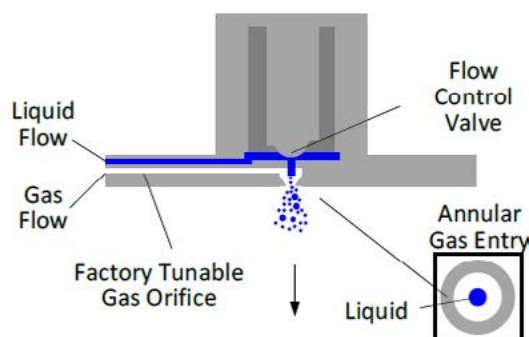


Figure 1. Turbo II vaporizer atomizer schematic.

Less liquid heat exposure leads to a lower risk of thermal decomposition. Efficient heating of the liquid leads to faster and more complete vaporization at lower temperature set points and higher liquid concentrations – closer to theoretical maxima. This enables the successful vaporization of liquids with a small window between thermal decomposition and vaporization.

The highly efficient heat transfer also makes it possible to generate high vapor concentrations versus most conventional techniques. Greater than 6000g/hr for high vapor pressure liquids is easily achievable.

6. Turbo II Vaporizer Heat Exchanger

The heat exchanger of the T2 Vaporizer is directly downstream of the atomizer and is essentially a heated zone with ideally enough energy and residence time to fully vaporize the desired liquid at the desired concentration range.

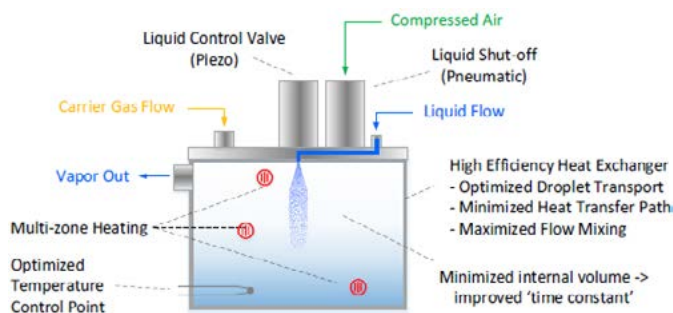


Figure 2. Surface Area to Volume Ratios for Different Heating Approaches.

There heat exchanger on the T2 vaporizer was the result of focused research on optimizing heat transfer efficiency to micro-droplets. Key design characteristics include:

- Multi-zone heating to more effectively control the heat throughout the heat exchanger.
- Optimized temperature control point to provide faster heater response and minimized temperature differentials.
- Improved droplet transfer through the heat exchanger to maximize liquid surface area and speed up heat transfer, as well as reduce risk of internal deposition and clogging.
- Minimized heat transfer path to ensure heat gets to the liquid droplets quickly resulting in faster evaporation and higher capacity.
- Maximized flow mixing to improve heat transfer to the liquid.
- Minimized internal volume so the vapor travels through the vaporizer more quickly contributing to faster vapor response times.

In the Turbo II heat exchanger, the vaporization occurs by mixing the atomized droplets with the gas flow. Heat transfer occurs indirectly through the gas to the suspended droplets, eliminating liquid to hot surface contact. Carrier gas flow surrounds the droplets, largely eliminating direct liquid-to-hot metal contact and helping to keep the internal vaporizer surfaces clean to prevent clogging and reduce maintenance intervals. Droplet temperature remains low due to evaporative cooling, and thermal decomposition is largely eliminated or greatly reduced.

The atomizer and the heat exchanger combine to form the Turbo II vaporizer. Additionally, a mass flow controller is needed to control the carrier gas flow, a liquid flow controller is used to control the liquid flow, and a temperature controller is used to control the heat exchanger temperature. Argon and Nitrogen are the most frequently used carrier gases in T2 vaporizers. The use of Helium as a carrier gas is not recommended due to expense and global shortages; however, it can be used if the process requires it. A temperature limit controller is typically used to provide flexibility in overtemperature protection; however a thermostat can also be used. A vapor filter can be used downstream of the vapor delivery system to provide risk mitigation for any particulates that could be in the line upstream of the vapor delivery to the chamber.

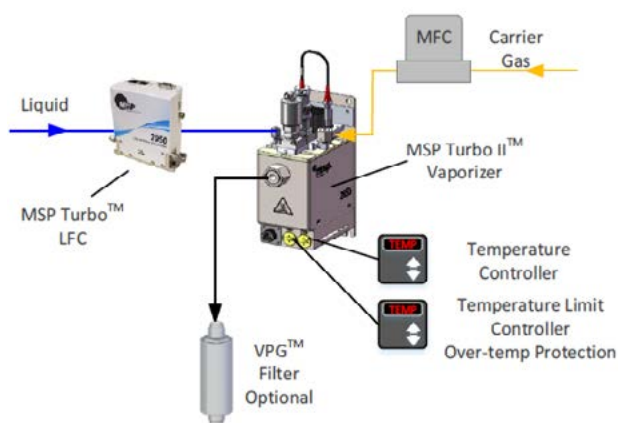


Figure 3. Turbo II™ Vaporizer system schematic.

7. Saturation Vapor Pressure, Enthalpy Of Vaporization & Molecular Weight

Saturation vapor pressure, enthalpy of vaporization and molecular weight are important parameters to consider when optimizing vaporization. The saturation vapor pressure determines the maximum amount of liquid in a defined volume which can be in the gas phase at a given temperature. Fig. 4 shows saturation vapor pressures as a function of temperature for several different liquids commonly used in CVD/ALD applications.

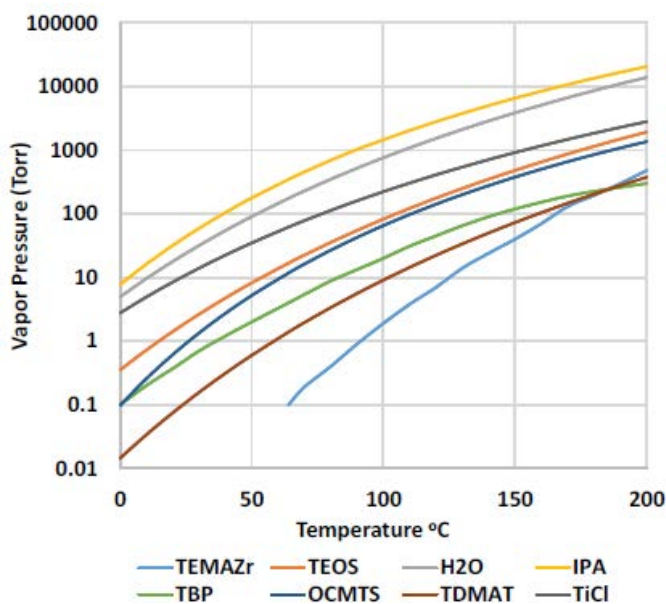


Figure 4. Saturation vapor pressure curves.

If the saturation vapor pressure is limiting the desired precursor concentration range, the volumetric flow rate of the carrier gas can be increased while leaving the liquid flow rate fixed; effectively reducing the system vapor pressure.

Low saturation vapor pressures also mean low evaporation rates making vaporization at high vapor concentrations challenging. Increasing the surface area of the liquid and increasing heat transfer efficiency significantly increase evaporation rates; making the Turbo II vaporizer a good fit for low vapor pressure precursors.

The heater power needed for complete vaporization can be calculated using the liquid enthalpy of vaporization, liquid and carrier gas heat capacity and molecular weight, and the operating temperature differential – ensuring that the vaporizer used will have enough energy to completely vaporize the desired liquid flow rates. Table 2 details enthalpy of vaporization and molecular weight values for TEOS, IPA and H₂O, showing the wide range of energy needed to vaporize 1 gram of different liquids.

Table 2

Energy Needed to Vaporize			
Liquid	Enthalpy of Vaporization (kJ/mol)	Molecular Weight (g/mol)	Energy to vaporize 1 gram (J)
TEOS	54.8	208.3	263
IPA	44	60.1	732
Water	40.62	18.02	2254
OCMTS	47.6	296.62	160
TDMAT	53.8	224.19	240
TiCl	39.8	189.679	210
TBP	61.4	266.32	231
TEMAZr	85	323.63	263

The Turbo I™ vaporizer provides enough energy and residence time for a wide array of applications. Even and efficient heating of the liquid (a combination of increased liquid surface area and uniform heat distribution) leads to faster and more complete vaporization at lower temperature set points and higher liquid concentrations – closer to theoretical maximums.

8. Stable Concentration Output

The Turbo II Vaporizer provides highly stable concentration output which several key design features.

1) Direct Liquid Injection. Mass flow rate is metered using a high precision liquid controller like the 2950 Turbo™ LFC which provides extremely stable mass flow rates along with precise mass delivery control and repeatability. This prevents the mass concentration drift over time that is typically unavoidable in bubbler and ampule systems.

2) More complete vaporization. Incomplete vaporization can lead to mass concentration drift over time in DLI systems, as well as result in persistent clogging. Using a vapor delivery system that is specified for the application to ensure there is enough energy and residence time for 100% vaporization results in stable vapor output over time with reduced maintenance requirements.

3) Liquid bubble suppression. Bubbles in the liquid line can cause vapor concentration and downstream pressure variability. The Turbo II vaporizer suppresses liquid bubble formation and also has an adjustment which can prevent bubbles from forming upstream of the vaporizer.

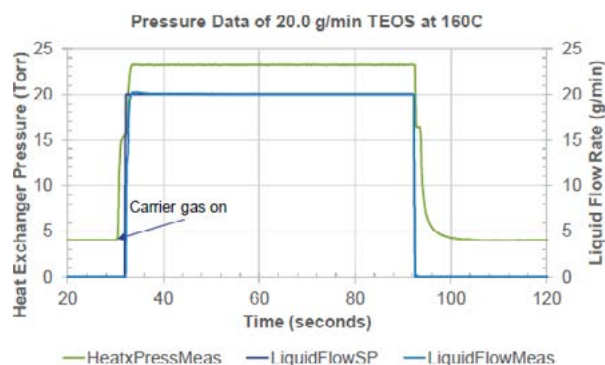


Figure 5. 2950 Turbo™LFC/Turbo II™ Model 2855PE Vaporizer liquid flow and downstream pressure stability (TEOS). 2950 Full Scale is 30g/min.

Figure 5 is an example of a liquid mass flow delivery stability and pressure stability immediately downstream of the T2 vaporizer. Mass flow and downstream pressure stay within $\pm 1\%$ of set point. Depending on downstream configuration, chamber pressure variability will be 10 to 100x less than pressure fluctuation directly downstream of the vaporizer.

9. Response Time

Response time is becoming more and more important especially for short cycle applications like ALD and pulsed CVD. In vaporization, there are two distinct response times. 1) Response time of liquid flow controller, and 2) response time of vapor output.

In many designs, the response time of the LFC is primarily a function of the LFC sensor and electrical design combined with the liquid flow control valve; which in the case of the PE Turbo Vaporizers is the Piezo valve on-board the vaporizer. However, some vaporizer designs can slow the LFC response time if there is a threshold pressure requirement, a valve sequencing issue, or if the vaporizer cannot handle even a small overshoot – creating the need for a slow-rise conservative PID value.

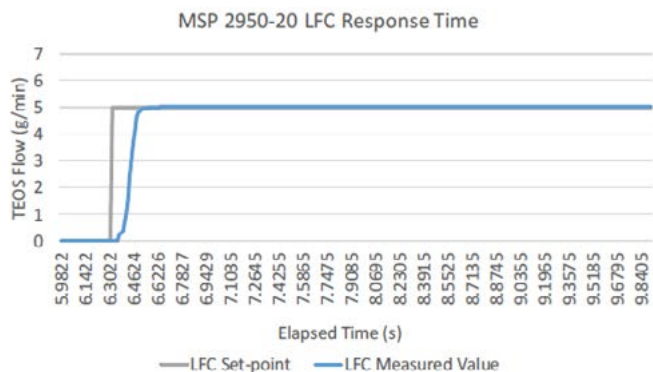


Figure 6. 2950-20 Turbo™ LFC response time (TEOS). 2950 Full Scale is 20g/min TEOS.

Figure 6 is an example of a liquid response time curve using a 2950 Turbo™ LFC and a Turbo II Vaporizer. For specification purposes, the liquid flow response time is defined as time to $\pm 1\%$ of Set Point. In this case, the LFC liquid response time is ~250ms.

The vapor response time is a function of dead volume, pressure differential, carrier gas flow rate, vaporizer design, and operating temperature. The Turbo II™ vaporizers were designed to almost completely eliminate dead volume. There is almost no space between where the liquid is controlled, and the outlet of the atomizer.

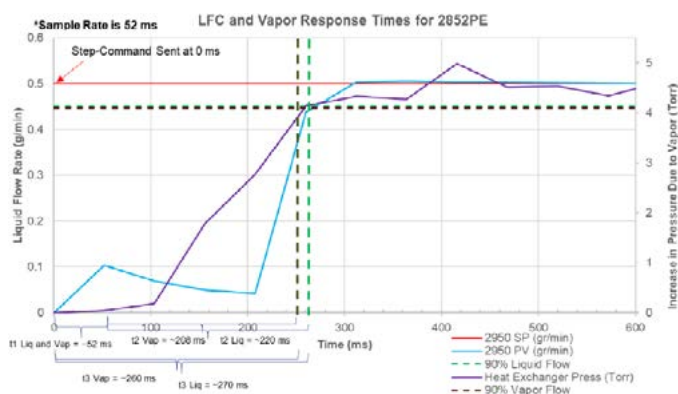


Figure 7. 2852PE Turbo II vapor response times. Liquid flow rate of 0.5g/min, carrier gas of 1.4 SLPM Ar, downstream pressure ~24 Torr, vaporizer temperature set-point 180C.

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The vaporizer response time decreases with lower downstream pressures and higher carrier gas flows. At very low pressures (<10 Torr), even very small carrier gas flow results in vapor response times <0.1s.

Fig. 7 and Table III below detail the vapor response time of the Model 2852PE Turbo™ Vaporizer.

Table 3

Value	Liquid	Vapor
t1	52 ms	52 ms
t2	208 ms	220 ms
t3	260 ms	270 ms

t1 = initial response after step-command

t2 = time from initial response to 90% flow

t3 = total time from step-command to 90% flow or 90% of pressure increase from vapor

10. Field Proven Low Maintenance Solution

While still a newcomer compared to the more conventional vapor delivery techniques like ampules, bubblers and liquid injectors, the Turbo II™ vaporizer has been extensively used in 300mm fabs across the globe for over a decade. While much of the installed base is fitted in CVD or ALD tools running more challenging processes using low vapor pressure, highly thermolabile, or very high flow liquids; the bulk of the installations are used for easy to vaporize liquids with modest liquid flowrates. For these processes, the Turbo Vaporizer is chosen due to its highly stable concentration output and its field proven, low maintenance, clog-resistant design; enabling the CVD tool it is installed on to run for years without issues due to vapor delivery.

11. Conclusion

The Turbo II vaporizer utilizes micro-droplet atomization combined with a highly efficient heat exchanger to provide improved vaporization of liquid precursors for a diverse range of applications. The T2 Vapor Delivery System can be used to provide a highly stable, low maintenance solution for relatively easy vapor delivery applications; or it can enable the use of harder to use liquid precursors by providing lower levels of thermal decomposition, vapor concentrations closer to the theoretical limits, and fast response times necessary for efficient short pulse processing.

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