

Improved Liquid Source Vaporization for CVD & ALD Precursors

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I. INTRODUCTION

Liquid precursors must be used for many CVD/ALD applications. Liquids with high vapor pressure and high decomposition temperature can be vaporized relatively easily at low to moderate vapor concentrations; however care must be taken to ensure there are no particulate byproducts formed during vaporization, that the vapor concentration output is steady, and that response times are fast enough for short pulse processing (ALD). Advances in high κ , low κ and metal barrier/interconnect thin films has required the use of more difficult to vaporize precursors. Liquids that have a narrow thermal window between vaporization temperature and thermal decomposition (TEMAZr, CCTBA) and/or have low vapor pressure can be problematic to vaporize. The Performance Enhanced Turbo-Vaporizer™ utilizes a novel direct liquid injection, droplet atomization method as an alternative to conventional techniques like bubblers and DLI valves.

II. HEAT EXPOSURE AND 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).

$$R = ke^{-\frac{\Delta H}{RT}} \quad (1)$$

R = Reaction rate, k = Rate constant; dependent on specific reactions and temperature, independent of concentration), ΔH = Enthalpy of reaction, R = Gas Constant, T = Temperature

Axiomatically, decomposition % increases with time at temperature. TEMAZr (Tetrakis(ethylmethylamido)zirconium) a common precursor used to create ZrO_2 thin films, decomposes at ~1.4% per hour at 150°C [1], and has a half-life of ~1.8 hours at 200°C [2].

The primary method of vaporization is conductive heat transfer to the liquid. Conductive heat flow rate is directly proportional to the contact area, the conductivity of the fluid and the distance between contact points.

$$\frac{Q}{\Delta t} = -kA \frac{\Delta T}{\Delta x} \quad (2)$$

$Q/\Delta t$ = Amount of heat transferred per unit time, k = the material's conductivity, A = cross-sectional surface area, ΔT = temperature difference between contact points, Δx = distance between contact points.

To heat a body of liquid, contact is typically made at the sides and bottom of the heated container. The Turbo-Vaporizer utilizes a droplet atomization direct liquid injection technique to vaporizer liquids. Droplet atomization 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 droplets 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 gas orifice design, the liquid and gas flow rates and the surface tension of the liquid. Ideally it is best to optimize the orifice size as a function of the desired liquid and carrier gas flow rates.

The Turbo-Vaporizer has a size adjustable liquid orifice and a factory adjustable carrier gas orifice, allowing the device to be fine-tuned to specific processes. This allows for the droplet size to be minimized for each application. The nanometer sized droplets generated with the Turbo-Vaporizer enable extremely fast vaporization without the need to preheat the liquid or carrier gas.

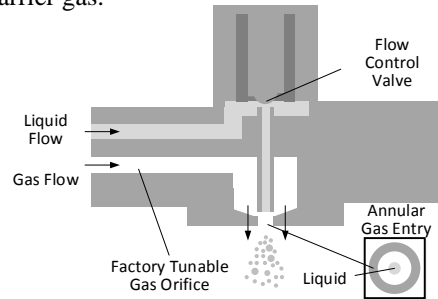


Fig. 1. Schematic of Performance-Enhanced Turbo-Vaporizer atomizer.

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.

III. 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 which can be in the gas phase at a given temperature. Fig. 2 shows saturation vapor pressures as a function of temperature for several different liquids commonly used in CVD/ALD applications.

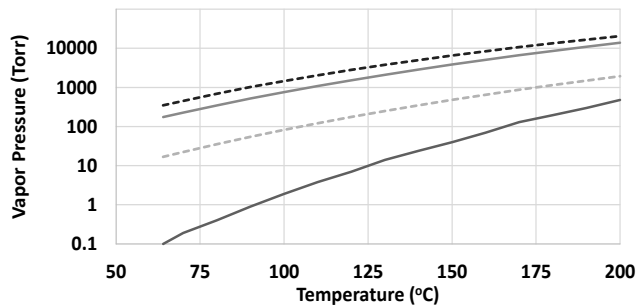


Fig. 2. Saturation vapor pressure curves.

If the saturation vapor pressure is limiting available precursor concentrations for optimal deposition rates; by applying the ideal gas law, the volumetric flow rate of the carrier gas can be increased while leaving the liquid flow rate fixed. Effectively reducing the system vapor pressure.

The heater power needed for complete vaporization can be calculated using the enthalpy of vaporization of the liquid and the carrier gas combined with respective molecular weights – 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 vaporizer 1 gram of different liquids.

TABLE 2

Energy Needed to Vaporize			
Liquid	Enthalpy of Vaporization (kJ/mol)	Molecular Weight (g/mol)	Energy to vaporizer 1 gram (J)
TEOS	54.8	208.3	263
IPA	44	60.1	732
Water	40.62	18.02	2254

The line of Performance Enhanced Turbo-Vaporizers features a variety of heat exchangers designed to provide 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.

IV. 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. Response time of the LFC is primarily a function of the LFC mechanical and electrical design, but also important is the compatibility of the vaporizer to run with an

aggressive PID setting. If the vaporizer can handle liquid overshoot without clogging concerns, a more aggressive start to the control loop can be used. Fig. 3 shows a LFC/Turbo-Vaporizer response time of ~1s.

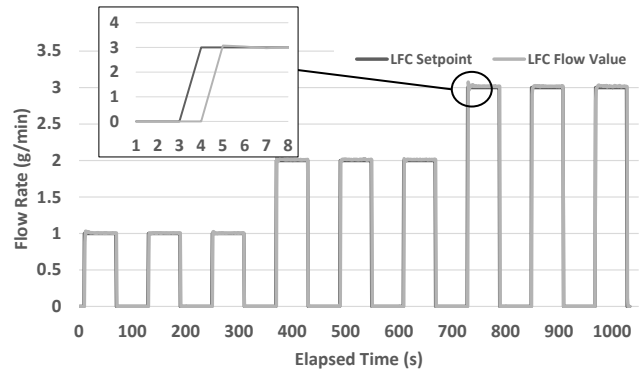


Fig. 3. LFC response time with a Model 2800PE Turbo-Vaporizer.

The vapor response time is a function of dead volume, pressure differential, carrier gas flow rate, vaporizer volume, and operating temperature. The vapor response time of the Model 2800PE Turbo-Vaporizers is shown below.

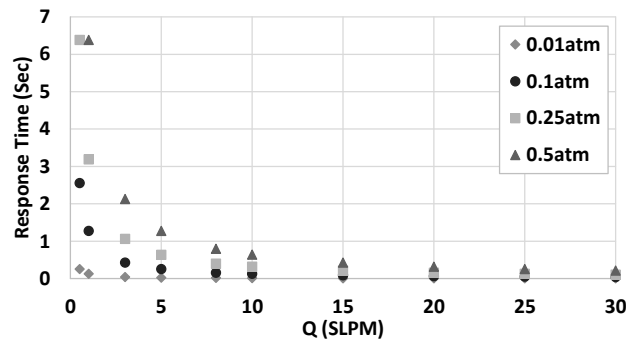


Fig. 4. 2800PE calculated response time vs. carrier gas flow rate at different downstream vacuum levels, N₂, 150°C

V. CONCLUSION

The Performance Enhanced Turbo-Vaporizer utilizes droplet atomization combined with variety of heat exchanger designs to provide complete vaporization for a diverse range of applications. This line of vaporizers can be used to provide lower risk of thermal decomposition, vapor concentrations closer to the theoretical limits, stable vapor concentration output and fast response times.

REFERENCES

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- [4] B. Liu, US Patent US8132793B2, “Method and apparatus for liquid precursor atomization”, March 13, 2013.