



# RainMaker Humidification System for Precise Delivery of Water Vapor into Atmospheric and Vacuum Applications

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Water vapor has multiple applications across industries including semiconductor, photovoltaic, fuel cells, carbon nanotubes, glass coating, and pharmaceuticals. Precise control of this water vapor is necessary to ensure that product yield and performance are consistent. In many of these applications, the process is performed in a vacuum. For a proper reaction to occur the water level needs to be kept low relative to the other gas species, with values below 500 ppm requested. This can require delivery at 1 sccm or less. This paper will briefly review applications and competitive technologies for water vapor and then present information on a new technology for delivery of water vapor into a vacuum.

## Water Vapor Applications

**Semiconductor** applications for water vapor include rapid thermal processing (RTP), atomic layer deposition (ALD), plasma stripping, and selective oxidation. RTP needs high flow rates of water vapor for short periods of time. ALD needs very small amounts of water vapor for High K film formation where the purity of water vapor is critical for good film formation. Plasma stripping is more effective when water vapor helps lift the film off the wafer surface. Next generation DRAMS need small amounts of water vapor to grow very thin metallic gates.

For fabrication of **photovoltaics**, water vapor is needed to grow transparent conductive oxides, backside insulating layers and for annealing of both thick and thin films. Transparent conductive oxides or TCOs are a necessary part of the PV cells. They enable the cell to collect solar energy efficiently by reducing backscatter as well as allowing for conduction through the film to the front electrode. TCO can be composed of ZnO, SnO, SiO, or TiO. These films need to be applied at low temperatures due to glass substrates. While commonly reacted with oxygen and plasma, the



deposition rate can be increased two to five times by adding small amounts of water, which speeds the decomposition of the organometallic precursor.

Photovoltaic efficiencies can be gained through both water vapor annealing and adding additional passivated barrier layers. Annealing improves the cell efficiency by removing stresses and healing the as-deposited silicon layers.

Water vapor also plays an important role in **Carbon NanoTube** (CNT) fabrication. The technology required to improve CNT growth rate and uniformity faces major hurdles in its transfer from research to production. For repeatable and reliable CNT fabrication, tools are needed to control whether CNTs are single or multi-wall, straight or bent, long or short, and clean or dirty. Water vapor is pivotal to the process. Precise delivery of water vapor will determine what the CNT looks like, what its yield is, and how contamination free the structure is.

### **Technologies for Water Vapor Delivery**

Up to now the delivery of water to a process has been difficult to control consistently. Choices have been limited. The simple boiling of high purity de-ionized water to yield water vapor can avoid the problems and dangers inherent in the direct reaction of hydrogen and oxygen to yield steam. However, removing dissolved gases can be difficult and often requires multiple boiling/condensation cycles in a hermetically sealed environment, which can be expensive. Moreover, aerosols containing materials that are not normally volatile, such as salts or metals, can be produced during the boiling process and can add unwanted impurities.

Current technologies include:

- **Bubblers.** These are low cost, but have inaccuracies due to the temperature of the gas and liquid, operating pressure, liquid level, and thermal droop. They leave behind some contamination during vaporization and cannot prevent entrainment of dissolved gas, volatile molecular contaminants, and micro-droplets that can carry particulate and ionic molecular contaminants. Bubblers have very limited gas flow rates. If the flow rate exceeds limited velocities, explosive bubbles blast the source liquid out of the vessel and into the downstream piping, forcing the use of phase separators that lead to increased



particulates, condensation, and flow instability. Another issue is entrainment of dissolved gas, volatile molecular contaminants, and micro-droplets that can carry particulate and ionic molecular contaminants.

- **DLI.** This technology is costly and problematic with different flow rates. At low flow rates control has limited accuracy and at high flow rates is susceptible to bubbles in the liquid, generating erratic values. DLI needs a metallic vaporizer or an additional metal hot plate to convert the liquid to gas, can vaporize only limited quantities due to thermal transfer rates, and there is a potential for chemical decomposition. Most critically, it cannot provide any purification of the liquid being vaporized; everything in the liquid is vaporized into the process.
- **Vaporizers.** These atomize the water and then try to combust the small droplets into molecular water. The heat of vaporization is very high and the ability to get the energy to the water molecule is limited by the heater transfer rate through the vaporizer plate and the carrier gas that is mixed in with the carrier gas. In addition, the water is aggressive and can corrode the vaporizer internal components, leading to long term stability and reliability issues.
- **Membrane contactors.** These can be used to allow gas transfer between a liquid and gas, but are not specific to which gases can permeate so they have no purification capability. They are made with hollow fiber membranes that are porous, allowing simultaneous transfer of the gas into the liquid and the liquid into the gas, so the carrier gas can permeate the liquid source. This can be problematic if the carrier gas is pyrophoric or toxic. The porous membranes cannot prevent the penetration of microdroplets across the hollow fiber into the carrier gas. Microdroplets are known to carry particulate and ionic impurities that cannot be carried by pure vapor alone. In addition the porous nature requires that operating pressures be carefully managed. This generally requires gas pressure be lower than the water source pressure. This can lead to severe process limits in design of humidification systems. Most hollow fibers are hydrophobic and must be modified to work with hydrophilic molecules. Some hollow fibers can be chemically modified, but it is a surface treatment that is only partially effective.



None of these technologies can deliver precise control of water vapor and at the same time remove particles, dissolved gases, and ionic impurities. For applications requiring high purity, safety, and ROI, a new solution is required.

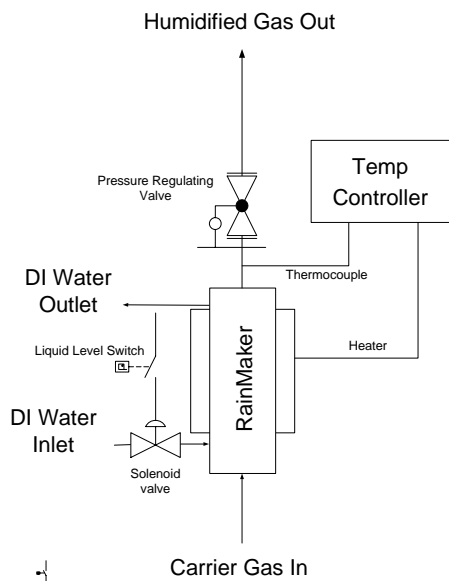
### **Introducing the RainMaker Humidification System**

The RainMaker Humidification System (RHS) adds controlled amounts of water vapor to any carrier gas. Needing only house de-ionized (DI) water and power, it can humidify inert gases, as well as oxygen, hydrogen, and corrosive gases. The system is capable of delivery into atmosphere as well as vacuum process pressures.

The RHS works as follows:

1. Carrier Gas to be humidified flows into the RHS
2. Water diffuses across the humidification membrane into the Carrier Gas
3. Temperature of the humidified gas is measured and fed back to a temperature controller to adjust the humidification level
4. Internal pressure control maintains independence from variations in downstream process pressures which allows operation into atmospheric and vacuum pressure environments.

The RHS consists of a non-porous membrane that excludes particles, micro-droplets, volatile gases, and other opposite charged species from being transferred to the carrier gas and ensures only water vapor is added. The membrane is highly selective, preventing most carrier gases from crossing over into the source. This allows the safe use of gases that should be constrained from mixing with liquid water. Other contaminants in the liquid source cannot permeate across the membrane or enter the carrier gas stream, resulting in a saturated product that is consistent and pure. The membrane allows the rapid transfer water vapor into carrier gas such as nitrogen, compressed clean dry air, forced ventilation air, helium, oxygen or hydrogen.



Temperature (°C)	Water Vapor delivered with 100 sccm Carrier Gas (sccm)
21	2.5
33	5
44	10
57	20
63	30
68	40
72	50
75	60
77	70
82	100

The RHS fully saturates the carrier gas based on the temperature at the gas/water interface, providing accurate delivery of water vapor. With the addition of a back pressure regulation device, low vapor pressure gases can be delivered into sub-atmospheric processes. The temperature range is from the freezing point to the boiling point for the liquid with a maximum operating temperature of 95°C. Because the RHS works on 100% saturation of the carrier gas, the system can be cycled on and off without significant effect on accuracy as long as the diffusion rate through the membrane is not exceeded.

In addition, when working with flammable chemicals such as hydrogen or isopropyl alcohol, local codes may require metallic containment. With the use of the RHS, metallic impurities are prevented from contacting the carrier gas, so safety and purity are both improved. The unique ultrapure design is either all Fluoropolymer or Fluoropolymer and 316L Stainless steel depending on the application.

Figure 1 shows selectivity of up to a million to one water molecules over nitrogen. In addition, the glass transition temperature is above 180°C, well above the boiling point of water.

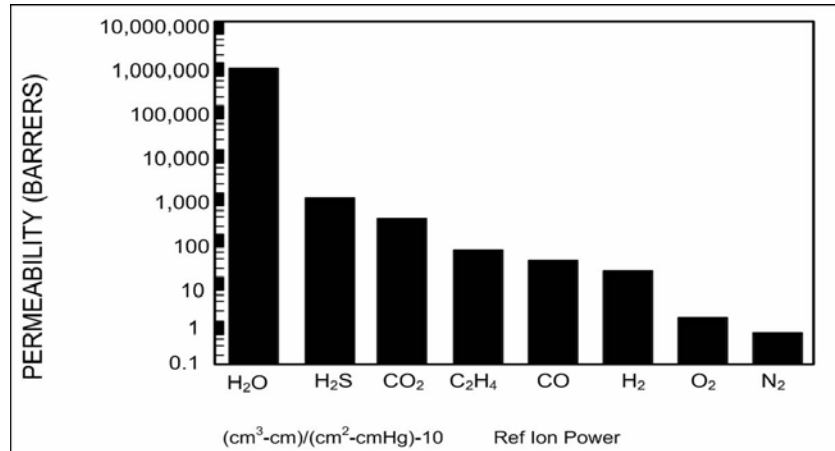


Figure 1: Selectivity of Water Molecules over Nitrogen

Purification tests run on the RHS showed a significant reduction in metallic contamination. On testing for 67 different metals, the number of metallic contaminant species was reduced from 31 to 18 specific contaminants (Figure 2). Total quantity of metallic impurities was reduced from 19.8 ppb in the source de-ionized water to 4.9 ppb.

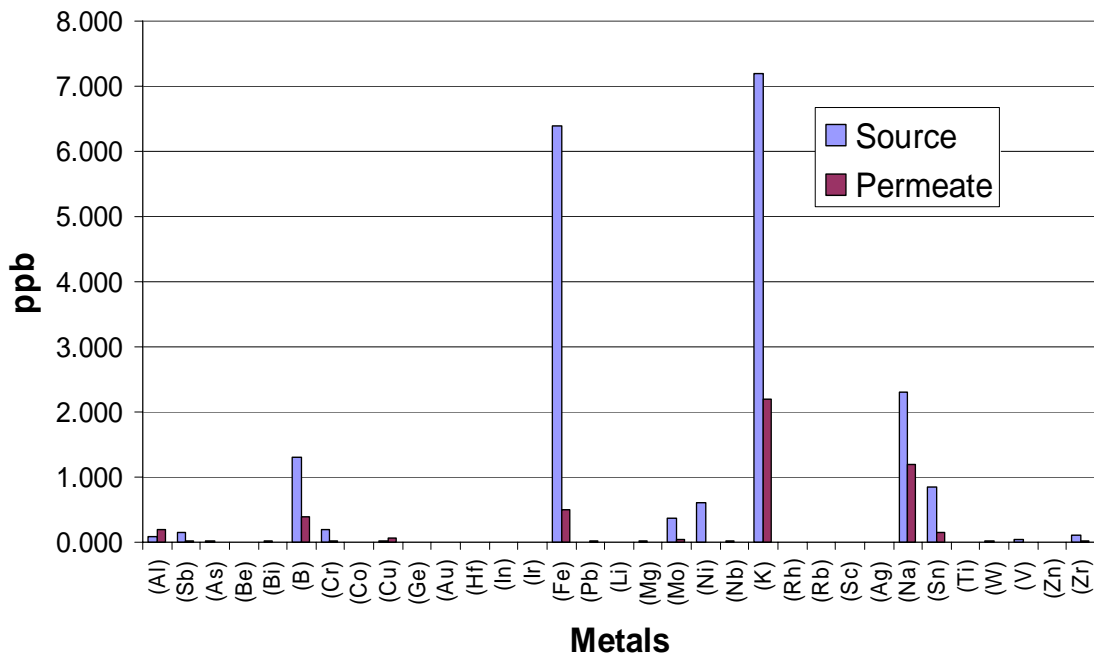


Figure 2: Metals Test Results

### Microdroplet Control

Microdroplets lead to entrainment of ion contamination and particulates. In addition where microdroplets land, cold spots occur leading to nonuniformity and warpage. For oxide films to work properly, the film thickness and uniformity are critical.

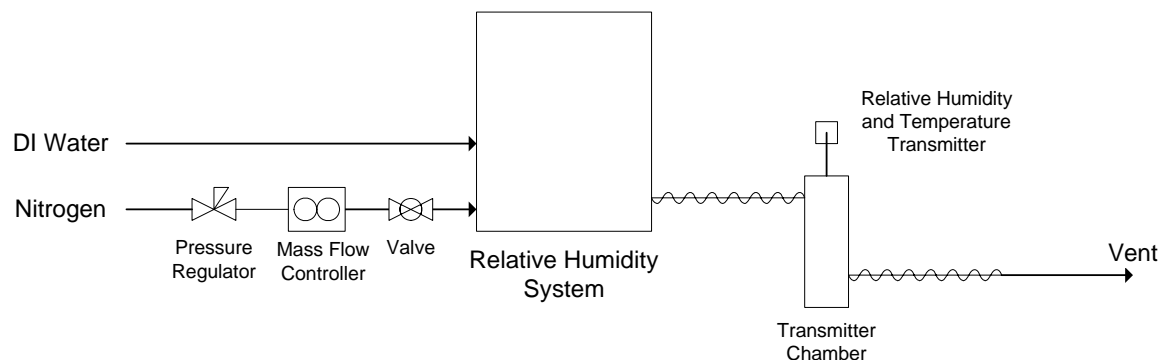
The RHS solves many of the challenges for direct delivery of water vapor by completely changing the way water molecules are converted from liquid to gas phase. Where bubblers and vaporizers depend on water molecules overcoming the surface tension and water molecule binding energies, the RASIRC products are based on a hydrophilic membrane that use the ion charge of

the membrane to separate each water droplet into its molecular components. The energy required to enter the membrane is equal to the heat of vaporization. Transfer across the membrane is restricted to single and small channel transfer rates.

Once molecules cross the wall of the membrane, they are energized and ready to enter the gas phase based solely on the vapor pressure curve that relates to the temperature of the water. Using the membrane as the phase separator prevents water droplets from permeating the membrane and ensures very smooth consistent flow.

### Performance

To measure the performance of the RHS a new test method was developed that uses a humidity probe downstream. The Vaisala probe is able to read dewpoint and temperature. Along with the process pressure, the ratio of water vapor-to-carrier gas can be determined within 2% of reading. An accurate and fast response value can be generated based on the water vapor pressure and the mass flow rate of the carrier.



*Figure 3: Test Set Up for RHS Performance Testing*

A series of tests were run to determine RHS performance at different temperatures, carrier gas flow rates, and process pressures. Long term values were plotted as well as turn-on times.

The first two charts below show the wide range of water vapor that can be controlled by only changing the temperature of the RHS. Water vapor was controlled from 4 sccm up to 85 sccm with a carrier gas flow rate of 40 sccm nitrogen. This translates to a water-to-carrier gas ratio from 1:10 to 2.1:1.

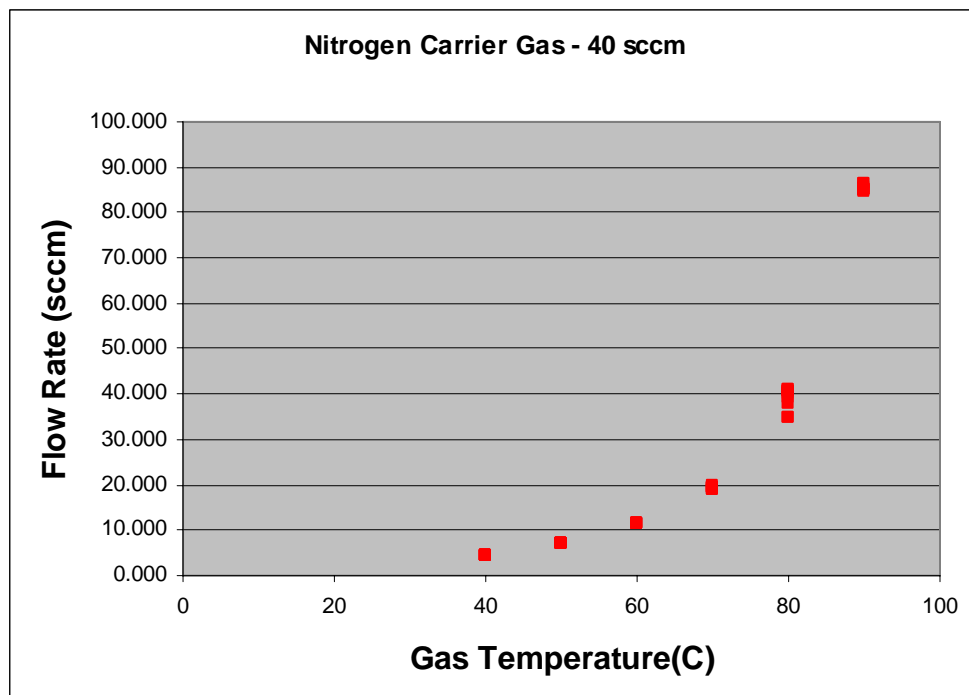
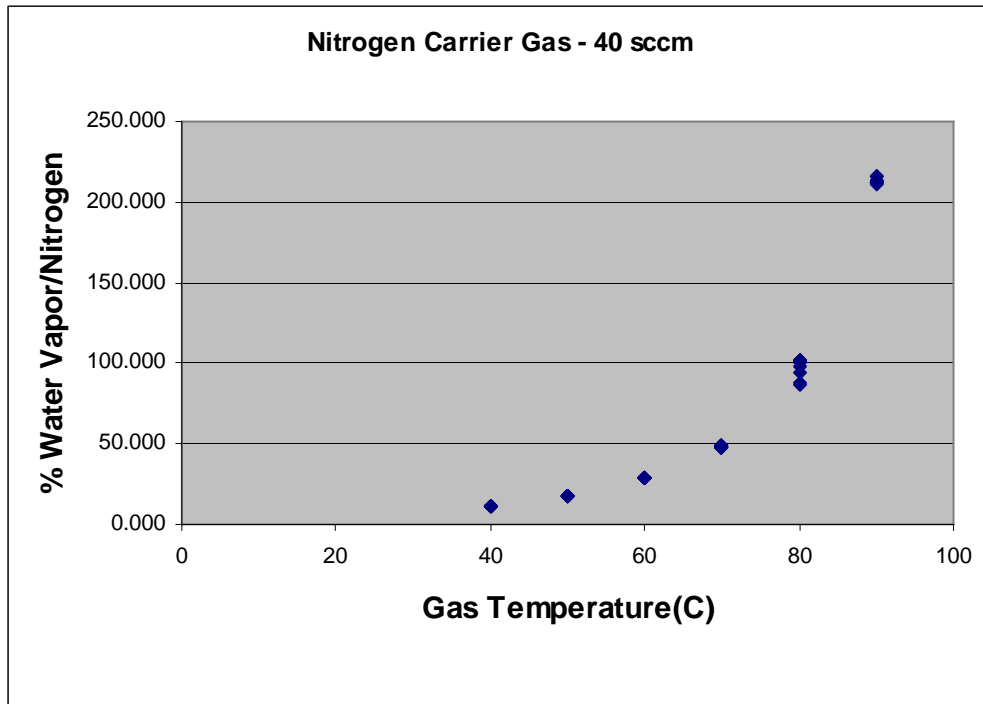


Figure 4: Temperature was varied from 40°C to 95°C with a carrier gas flow rate of 40 sccm.



*Figure 5: Temperature was varied from 40°C to 95°C with a carrier gas flow rate of 40 sccm replotted as normalized by the carrier gas flow rate.*

It is also important to be able to vary the carrier gas flow rate. At a steady temperature of 90°C, the water vapor delivered was varied from a low of 50 sccm to a high of 208 sccm.

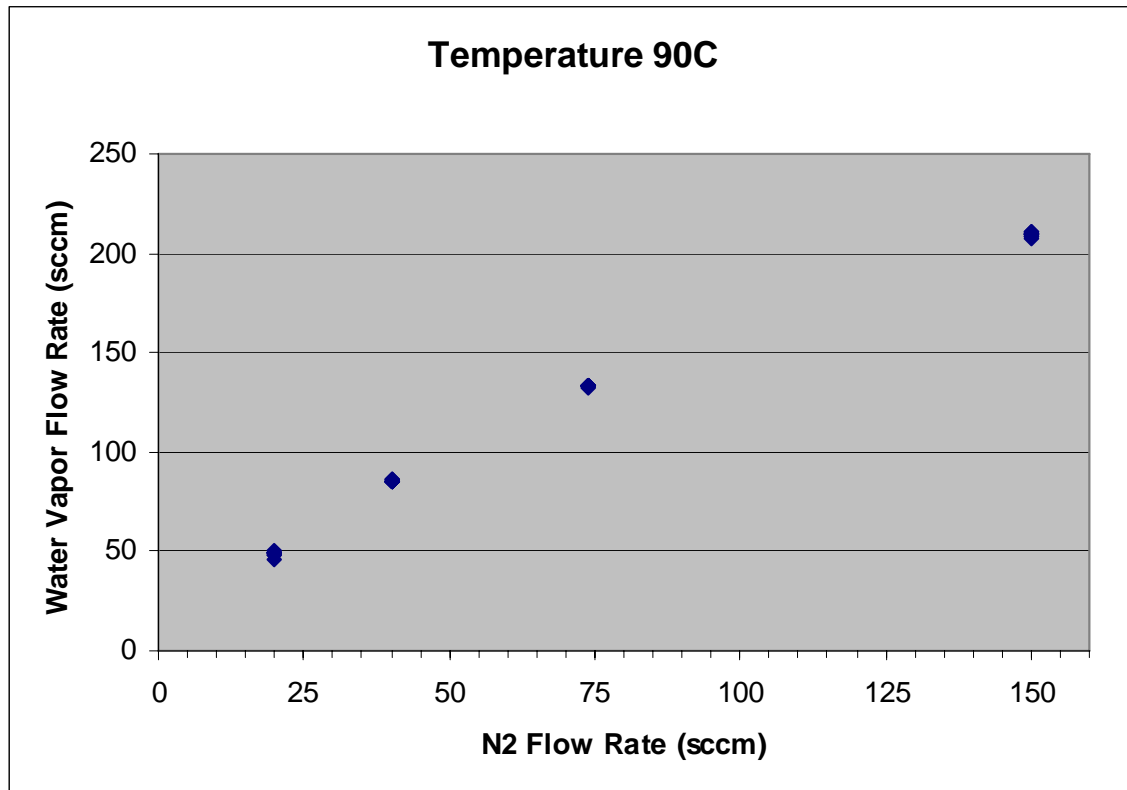


Figure 6: Carrier gas flow rate was varied from 20 to 150 sccm while the temperature was held steady at 90°C.

The ability to deliver water vapor at very low concentrations is critical for many vacuum applications. The graph below shows both stability and lower level delivery. For a 5 sccm carrier gas 1 sccm was delivered. At 10 sccm of carrier gas 2 sccm was delivered. The lower level range could be extended down to 0.1 sccm by adjusting either the operating pressure or the MFC full scale range.

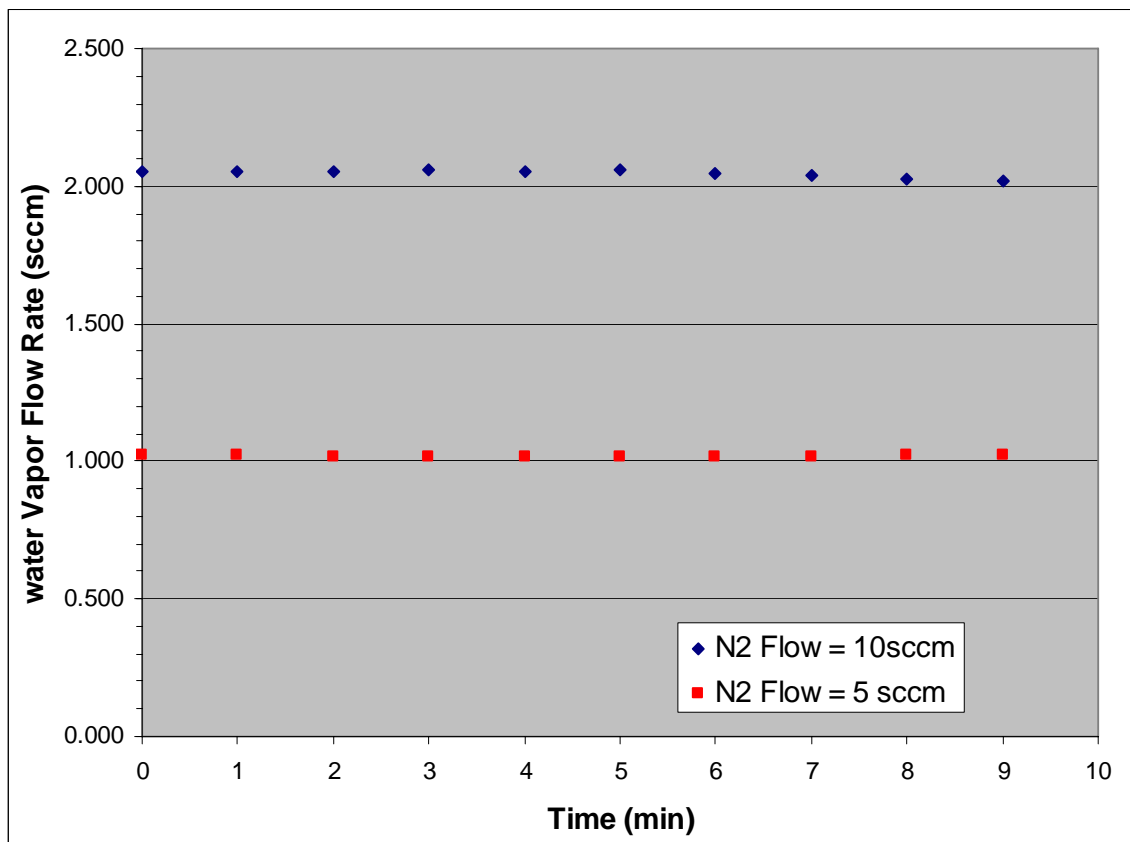


Figure 7: The flow data for 1 and 2 sccm of water vapor.

Because most low end processes occur in vacuum it is important to look for any differences in performance when delivering to vacuum or atmospheric pressure. In the data collected the values differed less than the accuracy of the instrumentation except at 80°C.

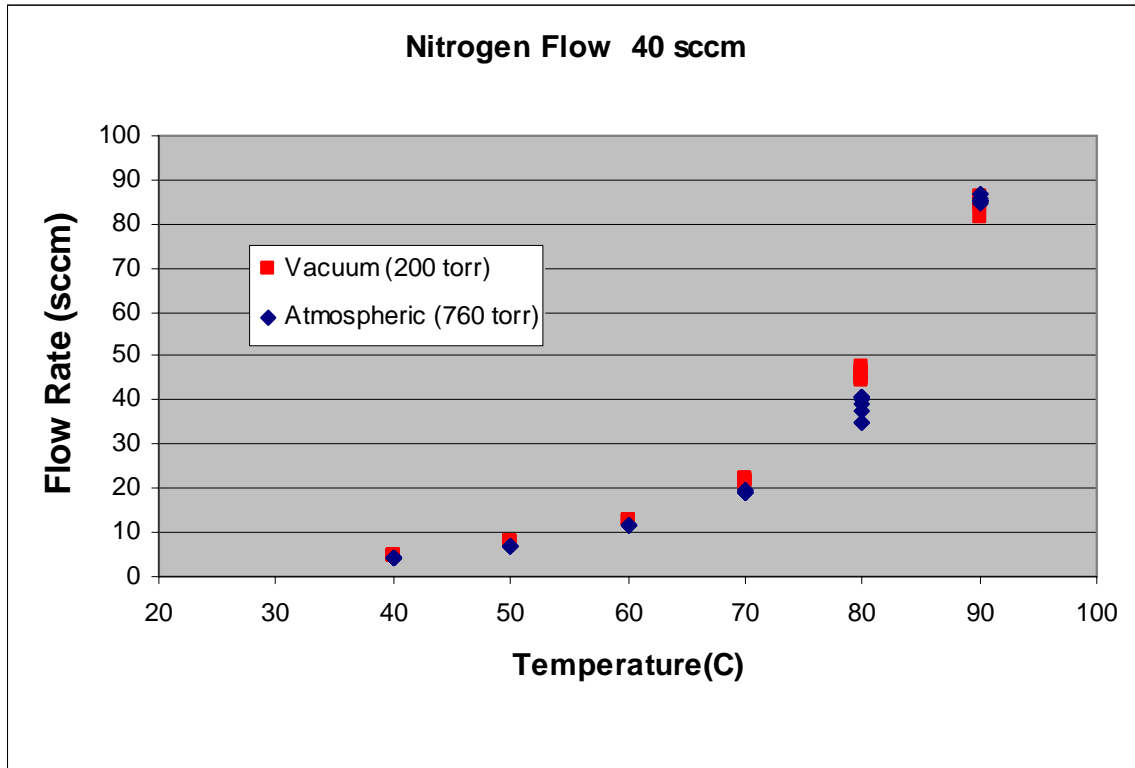


Figure 8: Temperature was varied from 40°C to 95°C with a carrier gas flow rate of 40 sccm. The only difference was that delivery pressure was changed from atmosphere to 200 Torr.

Response time can be critical for semiconductor applications where cycle times are in minutes not hours. The results from the response test for the three different flow rates are represented in the figure below. As shown, an increase in nitrogen flow resulted in a decrease in response time. The response time for 20, 40, and 80 sccm was measured at 41.0, 35.2, and 13.2 seconds respectively. In trying to find the exact response time of the RHS, a couple of aspects of the test setup need to be addressed. Part of the decreased response time based upon an increase in nitrogen flow can be correlated to the time required for the transmitter chamber to fill with the humidified gas. The approximate volume of tubing downstream of the RHS and the transmitter chamber, minus the transmitter volume, was calculated to be 11.24 cm<sup>3</sup>. With the assumption that the water vapor leaving the RHS was equal to the final stabilized flow rate for each nitrogen flow, the time required to for the downstream tubing and chamber to fill with humidified gas would be

33.7, 16.9, and 8.4 seconds for 20, 40, and 80 sccm respectively. If these times are subtracted from the experimental response times, the response times would be 7.3, 18.3, and 4.8 seconds for 20, 40 and 80 sccm respectively. However, this result indicates that the longest response time is at 40 sccm.

When considering the response time of the RHS, the humidity transmitter's response time needs to be considered. The response time of this probe with the grid filter is 8 seconds to fully saturate. This represents the time required to reach a stable reading. If this value and the time required to fill the chamber are subtracted from the measured response times, the response times vary significantly from -3.6 second to 10 seconds. Response time is a factor of MFC response, data collection response, humidity transmitter response, volume of the data collection system, and response of the RHS.

These results show that the exact response time for the RHS is difficult to determine and further experimentation is required to reach a more consistent result. However, we do believe at this time response to setpoint from turn on to be less than 10 seconds and possibly close to 1 second.

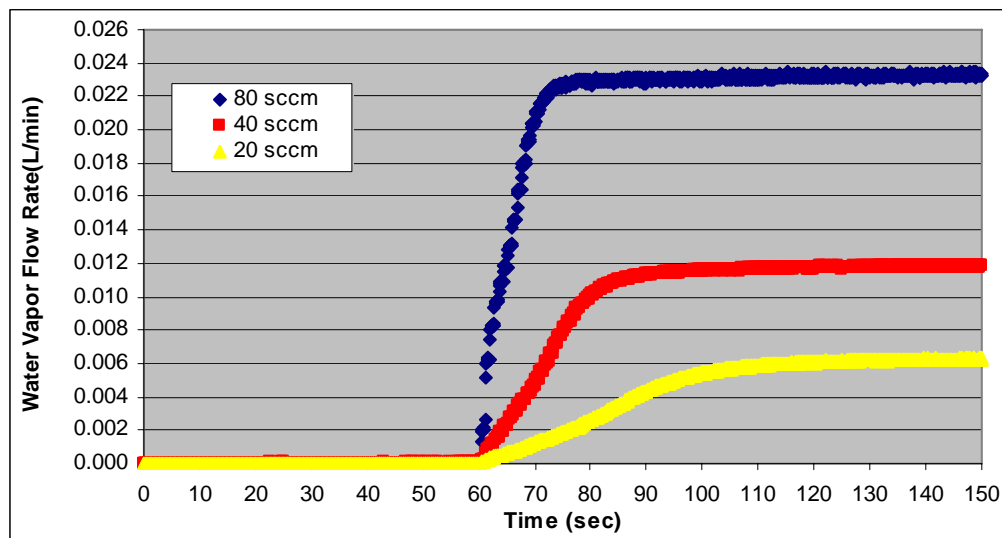


Figure 9: Results from Response Time Test

The thermal load on the system to saturate 40 sccm of nitrogen is low enough to provide stable instantaneous supply of water vapor that now becomes mass flow controller response driven.



## Summary

The RainMaker Humidification System is capable of controlling water vapor from 1 sccm to over 200 sccm into both vacuum and atmospheric process pressures. The unique membrane vaporizer allows independent addition of water vapor without directly mixing liquid water and the carrier gas. The membrane also provides a contamination barrier that prevents particles, dissolved gases, and metallic ions from transferring into the carrier gas. These capabilities make the RHS an attractive alternative for generation and delivery of ultra pure water vapor used in the fabrication of semiconductors, nanotechnology, photovoltaics, fuel cells and other applications.