The use of water as a precursor has economic and safety benefits compared to other oxide sources. However the controlled delivery of pure water vapor is challenging.

By Jeffrey Spiegelman
Introduction

Water vapor has been shown to have significant effect on thin film layers in ALD, MOCVD, and sputtering processes. Such processes are commonly used to generate TCO layers and modify crystal structures via grain size or defect repair. The ability to deliver water vapor free from atmospheric contaminants is critical to film integrity. A novel method for control and delivery of water vapor using ionic Fluoropolymer membranes has been tested. One side of the vacuum of the membrane was exposed to ambient air and then de-ionized (DI) water. The other side of the membrane was exposed to high vacuum where a miniature Residual Gas Analyzer (RGA) was used to monitor pressures of individual gas species. When the membrane was exposed to air the water-to-nitrogen ratio was 10:1 by volume. When the outer surface of membrane was submerged in water the ratio increased to 200:1. The partial pressure of water increased from 1.4e-4 Torr to 3.9e-3 Torr. Nitrogen increased from 1.4e-5 Torr to 2.0e-5 Torr while oxygen was found to increase from 6.5e-6 Torr to 6.6e-5 Torr. Separately on a humidity test stand and under a 20 sccm purge flow of dry nitrogen, 2.8e-3 sccm of water was added, raising the concentration of water to 1400 ppm from less than 1 ppm.

Water vapor is critical to ZnO deposition and insertion of TiO layers under ZnO during sputtering. Water vapor reduces optical losses at the TCO interface in ITO devices. CIGSe solar cells grown with water vapor using MBE were found to have efficiencies of 18.1% where the water was attributed to a decrease in donor defect density. Many ALD films use water as the oxygen source. The use of water as a precursor has economic and safety benefits compared to other oxide sources. However the controlled delivery of pure water vapor is challenging. Direct flow control of the water needed in such applications is difficult due to the expansion of 1 gram of water to 1,244 cc of gas at room temperature and atmospheric pressure. Volume flows needed in sputtering applications are often less than 0.1 sccm. In its vapor phase water typically condenses unless it is added to a carrier gas stream. This requires the use of water bubblers, which add water vapor based on the partial pressure of the water relative to that of the carrier gas. Bubblers have problems with contamination and bacterial growth, as well as variability with
temperature, pressure and fill level. Microdroplet entrainment can also increase variability in the delivered water. The DI water in the bubbler must be degassed before use, to remove residual oxygen and nitrogen in the water. Most problematic is that the bubbler cannot be directly exposed to the vacuum environment. When exposed to vacuum violent boiling can occur, water droplets varying with the vacuum level are carried into the process chamber and therefore the actual volume of water delivered is not controlled or repeatable.

Using a new technique developed by RASIRC for the control and delivery of water vapor into vacuum processes, tests were conducted to determine actual selectivity under vacuum for atmospheric species. The new membrane process selectively allows water into a gas or a vacuum process. The membrane is part of the RainMaker Humidification System (RHS), which adds controlled amounts of water vapor to any carrier gas. Needing only house DI water and power, it can humidify inert gases, as well as oxygen, hydrogen, and corrosive gases at atmospheric or vacuum process pressures.

The non-porous ionic perfluoropolymer membrane 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 of water vapor into carrier gas such as nitrogen, compressed clean dry air, forced ventilation air, helium, oxygen or hydrogen.

**Microdroplet Control**

Microdroplets lead to entrainment of ion contamination and particulates. Furthermore cold spots occur where microdroplets land leading to non-uniformity and warpage. In order for oxide films to work properly, the film thickness and uniformity are critical. The membrane process 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 uses 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 and consistent flow.

**Experimental**

**Parts on-hand:**
- Three ionic perfluoropolymer (Naflon®) membrane assemblies or devices under test (DUT) and one blank assembly all using 3” long 1/8” SS tubing terminated at both ends with 1/4” VCR fittings. Each DUT consisted of 1/8” O.D. stainless steel tube with two diametrically opposed 0.04” diameter holes drilled through the tube. The entire length of tube was then sleeved with 0.005” of membrane.
- Three Teflon sleeves were machined to snap over one of the holes to allow water to be added directly over one hole.

**Process flow:**
- Perform leak test on all four assemblies with supplied caps mounted
- Mount assemblies onto the mass spectrometer test station.
- Here a Residual Gas Analyzer (RGA) manufactured by Horiba was used.
- Acquire baseline spectrum using blank assembly unit
- Acquire baseline spectra using the three DUTs
- Assemble Teflon sleeves on the three DUTs
- Acquire spectra with the three DUTs immersed in water
- Test for water permeation rate under internal nitrogen purge
After helium leak testing and RGA testing, water permeation was measured using a Vasalia humidity probe and 100 sccm unit instruments mass flow controller at 20 sccm flow rate.

Results and Discussion
One blank and three separate membrane assemblies were first helium leak tested and then moved to the RGA for permeation analysis.

<table>
<thead>
<tr>
<th>Blank Unit:</th>
<th>&lt; 10-9 sccs</th>
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<tbody>
<tr>
<td>DUT #1:</td>
<td>1.2x10-8 sccs</td>
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<tr>
<td>DUT #2:</td>
<td>2x10-8 sccs</td>
</tr>
<tr>
<td>DUT #3:</td>
<td>5x10-9 sccs</td>
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The results indicated that while air did leak across the membrane, the leak rate was low enough to enable direct connection to the RGA. The blank without membrane or 0.04” diameter hole was leak tight to the resolution of the detector.

After helium leak testing each DUT was mounted on the vacuum chamber of the RGA. Results showed stable background with a 10:1 water to nitrogen rate and 25:1 water to oxygen rate when exposed to air with 50% relative humidity. The Teflon water trap was added to allow for local application of water. When the droplet was added away from the orifice in the tube, the diffusion increase was slight. However, when directly aligned with the orifice, the gas diffusion rates increased significantly. The water vapor pressure increased 20 times while oxygen increased 10 times and nitrogen pressure increased 60%. There was a significant swing in oxygen pressure exceeding nitrogen pressure when water was added to the membrane. The results were repeatable.

The water permeation rate through DUTs with 0.040” diameter holes at 22°C was:

- 0.29 sccm
- 115 sccm/inch²
- 1.29E-5 moles/min (7.5E-8 std. dev.)

After RGA testing, DUT 3 was tested on a humidity test stand. 20 sccm of dry nitrogen was run through the device. The humidity was recorded downstream. The water ppm value was 272ppm in air at 20 sccm and 2045 ppm in water.

Conclusion
An ionic perfluoropolymer membrane was tested under vacuum conditions to determine if it could selectively allow water vapor to pass into the vacuum process. The results indicated that in ambient air, water could be added in a 10:1 ratio relative to nitrogen and 200:1 when immersed in water. The ability to add ppm levels of water make the membrane ideal as a water source for MBE processing of CIGSe films and for sputtering applications including ITO, TiO, and ZnO.

About the Author
Jeffrey Spiegelman has worked in the microelectronics industry since 1986. In 1990 he founded AeroneX, which was named one of Inc. Magazine’s Top 500 Fastest Growing Private Companies and was awarded the prestigious University of California’s Connect award for Most Innovative New Product in 2002. After selling the company to Entegris, he founded Rasirc to address generation and delivery of low vapor pressure chemistries, with an initial focus on steam and pure condensate for use in next-generation photovoltaic devices. Spiegelman has a B.S. in bioengineering, an MS in applied mechanics from the University of California at San Diego and holds over 50 international patents and publications. The article was presented at the 35th IEEE Photovoltaic Specialists Conference in Honolulu, Hawaii June 20-25, 2010.

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