Guest Forum

Water Vapor Delivery for Thin Film Vacuum Processes

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Water vapor is known to play a significant role during thin film deposition in ALD, MOCVD, and sputtering processes. Such processes are commonly used to generate transparent conductive layers (TCO) and modify crystal structures via grain size or defect repair. The ability to supply water vapor free from atmospheric contaminants is critical to film integrity. A novel method for control and delivery of water vapor using ionic fluoro-polymer membranes has been tested and results are presented in this paper. One side 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 mass spectrometric 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. Separately on a humidity test stand and under a 20 sccm purge flow of dry nitrogen, 2.8×10^{-3} sccm of water was added, raising the concentration of water to 1400 ppm from less than 1 ppm.

ALD法, MOCVD法, およびスパッタ法による薄膜形成過程において, 水蒸気が重要な役割を果たすことが知られている。これらの薄膜形成法は, 透明導電膜(TCO)の形成や粒度・欠損の修復による結晶構造転位の目的で一般的に使用されている。高品質の薄膜を形成するためには, 大気由来の不純物を含まない水蒸気を供給することが重要である。本稿では, イオン透過性フッ素樹脂膜を用いて, 水蒸気を制御・供給する新しい手法についてその試験結果を報告する。イオン透過性フッ素樹脂膜の一方の側は, 最初は大気に, 続いて脱イオン(DI)水に接触させた。もう一方の側は高真空状態とし, 小型の質量分析法残留ガスアナライザ(RGA)により各ガス種の分圧を測定した。膜が大気に曝されていたときの水蒸気と窒素の体積比は10:1であった。膜の外側表面を水に曝すと, 水蒸気の比率は200:1まで増加した。これとは別に, 湿度試験装置上にて, 流量20 sccmの乾燥窒素によるパージ流に2.8×10^{-3} sccmの水を添加したところ, 水分濃度は1 ppm未満から1400 ppmまで上昇した。

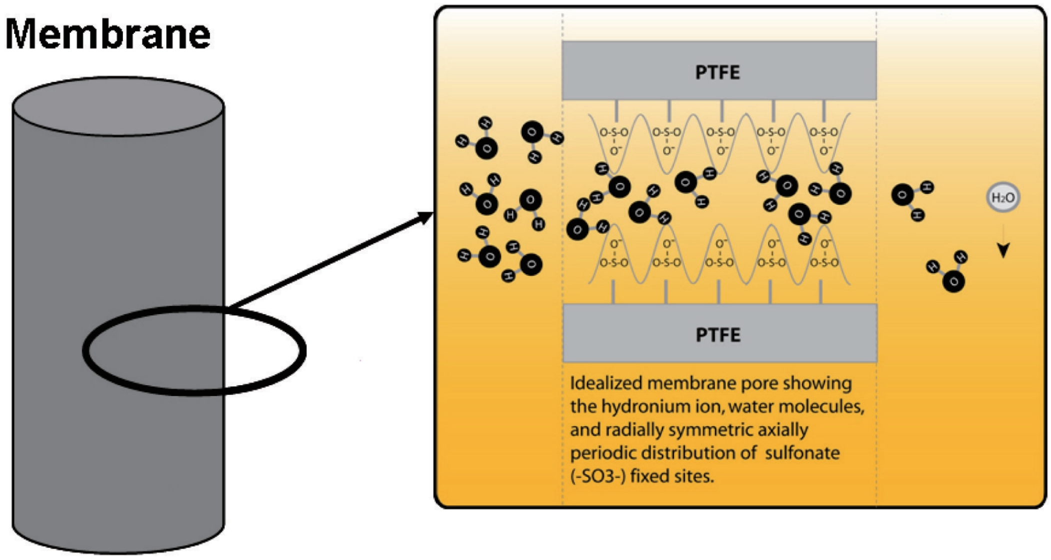
INTRODUCTION

Water vapor is critical to ZnO deposition[1] and insertion of TiO layers under ZnO during sputtering[2]. Water vapor reduces optical losses at the TCO interface in indium-tin-oxide (ITO) devices[3]. CIGSe solar cells grown with water vapor using MBE were found to have efficiencies of 18.1% as water was responsible for the decrease in donor defect density[4]. 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 in order to remove residual oxygen and nitrogen in the water. Most problematic is that the bubbler cannot be directly exposed to the vacuum environment as violent boiling can occur. Furthermore water droplets varying with the vacuum level are carried into the process chamber making the actual volume of water delivered neither controlled nor repeatable.

In this paper we present the performance results of a new technique developed by RASIRC in collaboration with Implant Sciences. The method consists of using a membrane for the control and delivery of water vapor into vacuum processes. Due to differences in permeation rates the membrane process selectively allows water into a gas or a vacuum process at the detriment of other components. 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 membrane is now part of the RainMaker Humidification System (RHS), which adds controlled amounts of water vapor to any carrier gas.

Membrane processes can be thought of as simple separation techniques which employ the membrane as partitioning phase. In the process, a driving force, usually pressure or concentration, is applied to one side of the membrane and the selective component(s) preferentially pass to the other side as the permeate. The permeation can be described by Fick's Law. The non-porous ionic perfluoropolymer membrane (Figure 1) 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



Idealized membrane pore showing the hydronium ion, water molecules, and radially symmetric axially periodic distribution of sulfonate (-SO3-) fixed sites.

Figure 1 Non-porous ionic membrane is selective for water vapor 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 make the transition 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

Four ionic perfluoropolymer membrane assemblies were fabricated (Figure 2); one blank and three devices under test (DUT). Each assembly consists of a 3" long 1/8" O.D. stainless steel (SS) tubing terminated at both ends with 1/4" VCR fittings. The 1/8" O.D. SS tube of the DUT units features two diametrically opposed 0.04" diameter holes drilled through the tube. The entire length of tube was then sleeved with 0.005" I.D. tubular membrane.

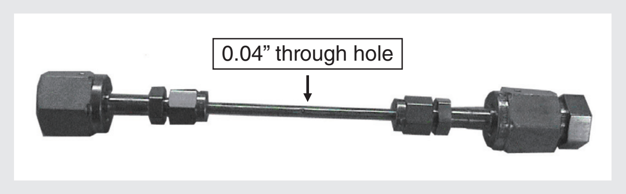


Figure 2 Membrane assembly (DUT)

A Teflon sleeve (not shown on Figure 2) was machined to snap over the hole to allow water drops to be added directly in a controlled manner.

These assemblies were first leak tested using a mass spectrometer leak detector and then mounted onto the vacuum test station. A miniature 100 amu mass spectrometric residual gas analyzer (RGA)[5] manufactured by Horiba, was used to perform permeation analysis (Figure 3). The Horiba device is a high pressure RGA with an dynamic range extending from ultra high vacuum up to 11 mTorr. It is therefore capable of withstanding large pressure excursions anticipated in this project.

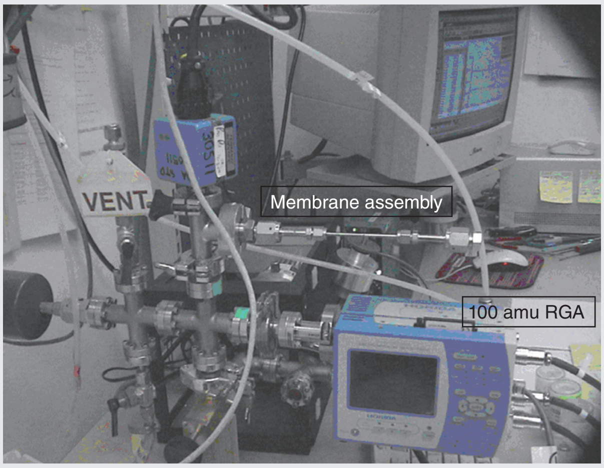


Figure 3 RGA test setup

The testing procedure consists of:
1. Acquiring a baseline spectrum using the blank membrane assembly unit
2. Acquiring a baseline spectra using each of the three DUTs
3. Assembling Teflon sleeves on the three DUTs
4. Acquiring spectra with the three DUTs “immersed” in water
5. Testing for water permeation rate under internal nitrogen purge

RESULTS AND DISCUSSION

The Helium leak test results for all four assemblies are shown on table below:

Table 1 Helium Leak Test results

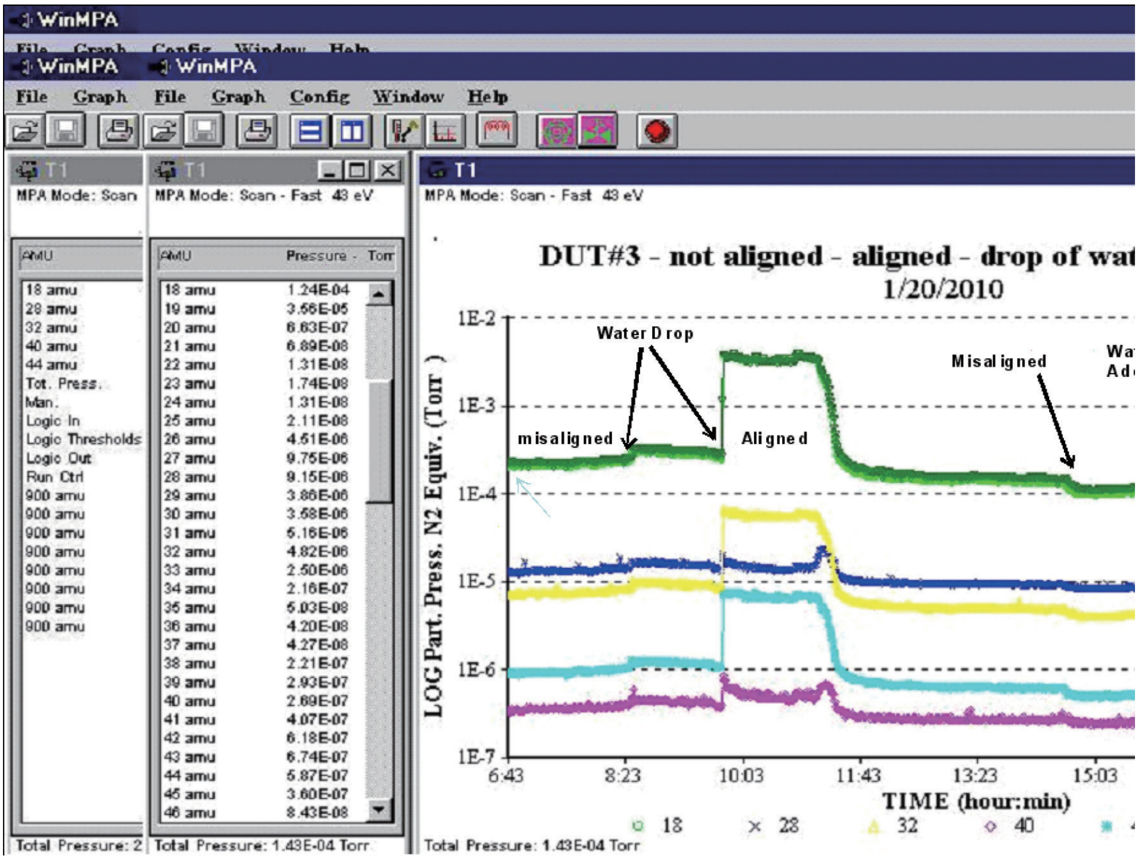
Assembly	Leak Rate (sccs)
Blank Unit	< 10^{-9}
DUT #1	1.2×10^{-8}
DUT #2	2×10^{-8}
DUT #3	5×10^{-9}

These results show negligible leak rates compared to the anticipated permeation under water conditions rates. The assemblies were then mounted on the RGA vacuum test stand one after the other to ensure repeatable performance.

The 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 by 60%. There was a significant swing in oxygen pressure exceeding nitrogen pressure when water was added to the membrane. The results were repeatable (see Figure 4).

Figure 5 show superimposed mass spectra of dry versus wet. Upon submerging the membrane in water the total pressure increased from high 10^{-6} to about 2×10^{-3} Torr. Such a pressure excursion is mostly accounted for by the surge of the partial pressure of water. Given the pumping speed inside the vacuum chamber the water permeation rate through the 0.04" diameter hole at 22 °C is calculated to be 0.29 sccm.

The Nafion membrane permeation rate is therefore calculated to be 142 sccm/in^2. Higher water enrichment factors can be obtained at higher water temperatures as can be seen on Figure 6.



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MPA Mode: Scan

AMU
18 amu
28 amu
32 amu
40 amu
44 amu
Tot. Press.
Man.
Logic In
Logic Thresholds
Logic Out
Run Ctrl
900 amu
900 amu
900 amu
900 amu
900 amu
900 amu
900 amu
900 amu

Total Pressure: 2
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```
MPA Mode: Scan - Fast  43 eV

AMU              Pressure - Torr
18 amu           1.24E-04
19 amu           3.56E-05
20 amu           6.63E-07
21 amu           6.89E-08
22 amu           1.31E-08
23 amu           1.74E-08
24 amu           1.31E-08
25 amu           2.11E-08
26 amu           4.51E-06
27 amu           9.75E-06
28 amu           9.15E-06
29 amu           3.86E-06
30 amu           3.58E-06
31 amu           5.16E-06
32 amu           4.82E-06
33 amu           2.50E-06
34 amu           2.16E-07
35 amu           5.03E-08
36 amu           4.20E-08
37 amu           4.27E-08
38 amu           2.21E-07
39 amu           2.93E-07
40 amu           2.69E-07
41 amu           4.07E-07
42 amu           6.18E-07
43 amu           6.74E-07
44 amu           5.87E-07
45 amu           3.60E-07
46 amu           8.43E-08

Total Pressure: 1.43E-04 Torr
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MPA Mode: Scan - Fast  43 eV

Total Pressure: 1.43E-04 Torr
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Figure 4 Screen shot of RGA of DUT #3 over time sequence. The diffusion through the membrane increased with water. Nitrogen diffusion rate was not significantly influenced while oxygen increased 10 fold.

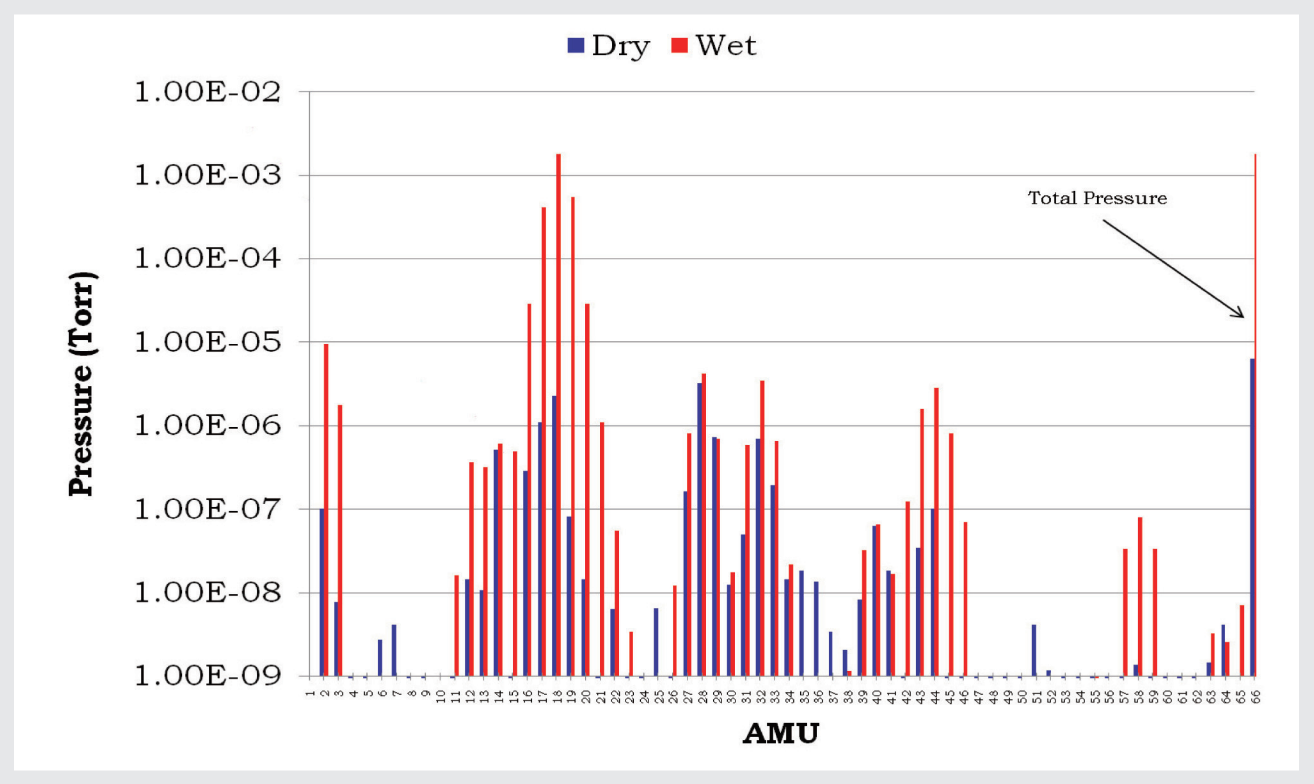

Figure 5 Histogram of mass peaks of dry versus wet performance

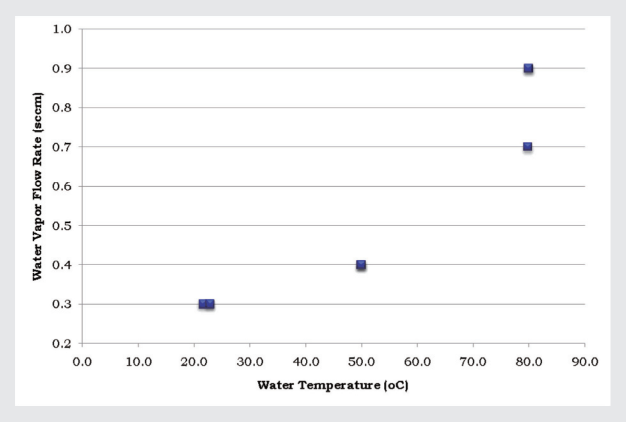

Figure 6 Water permeation rate versus temperature

Following the RGA testing, water permeation was measured using a Vasalia humidity probe. For comparison purposes DUT#3 was used. 20 sccm of dry nitrogen was run through the device as set by a 100 sccm Unit Instruments mass flow controller. The humidity was recorded downstream. The water ppm value was 272 ppm in air at 20 sccm and 2045 ppm in water. Relative permeation rates are shown on table 2 below.

Table 2 Results of relative permeation tests

Relative Permeation		
Species	Dry	Wet
H_2O	24	684
N_2	1.6	1.1
O_2	2.1	4
H_2O/N_2	10	430
H_2O/O_2	34	522

While the permeation ratios are qualitatively similar to the ones obtained with the RGA more accurate control of the surface area of the membrane exposed to water is needed for quantitative comparisons.

SUMMARY AND CONCLUSION

An ionic perfluoropolymer membrane was tested under vacuum conditions to determine if it could selectively allow water vapor to diffuse 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.

References

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