Technical Report~~~

Measurement of Water Vapor Transmission Rate (WVTR) for High Moisture Barrier Films by Using Atmospheric Pressure Ionization Mass Spectrometry

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Recently the demand for evaluating high moisture barrier materials is increasing in the field of electronic industry. In this paper, a rapid and high sensitive measurement method of water vapor transmission rate using atmospheric pressure ionization mass spectrometry (APIMS) was investigated. WVTR measurement using APIMS provides simpler and more rapid evaluation for high moisture materials compared to the conventional methods. The results suggested that APIMS has potential to determine WVTR of films down to 0.002 g/(m² · d).

Keywords : WVTR, high barrier film, atmospheric pressure mass ionization

1. Introduction

In recent years the gas barrier properties of plastic films used for food and pharmaceutical packaging have been highly improved, consequently a super high gas barrier film having an oxygen transmission rate of less than 0.1 cm⁻³/(m²·d·atm) was developed¹). To measure the oxygen barrier property for such films, a method based on the ASTM Standard D3985-81, which corresponds to the JIS Standard K7126-2, using a high sensitive coulometric detector is widely used in industry²).

Regarding the water vapor barrier property, water vapor transmission rates (WVTR) have been currently required in the level of 1 g/(m² · d) for the application of food and pharmaceutical packaging. However, for flexible encapsulation of electronic devices, a few digits higher level of water vapor barrier is demanded. For example, WVTR of 10^{-6} g/(m² · d) for cover films of organic light emitting diode displays(OLED) and less than 10^{-2} g/(m² · d) for backsheets of solar cells are present targets for material development³).

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To measure such low amount of water permeation, the infrared ray method based on JIS K7129, having a detection limit of $5 \times 10^{-3} \text{ g/(m^2 \cdot d)}$, has been used recently⁴). A calcium corrosion method was reported to measure WVTR as low as the level required for OLED⁵). However, this method requires complex procedures and long time for measurement in the order of 500 to 1000 hours.

For evaluation of gas supply systems of semiconductor production, conventional GC or GC-MS is used and its detection limits for water vapor concentration are in the range of 0.1 to 0.01 ppm based on S/N ratio of detectors, which correspond to WVTR of approximately 10^{-2} to $10 \text{ g/(m^2 \cdot d)}$. Recently, atmospheric pressure ionization mass spectrometry (APIMS) has utilized as a water vapor detector due to its higher sensitivity to water molecular⁶.

There are several models of APIMS system available with a range of 1 ppb to 1 ppt of water vapor detection limits based on S/N ratio. Their actual water vapor detection limits are estimated to be 10 to 1ppb due to desorption of residual water adsorbed to piping and parts⁷). More recently, it has been reported that oxygen transmission rates of super high barrier films were rapidly measured using APIMS⁸).

The objective of this paper is to report a rapid and high sensitive measurement method of WVTR using APIMS, by which a low level of WVTR of high water vapor barrier silica coated composite film was determined. Furthermore, behavior of water adsorbed in the measurement instrument was investigated by using heavy water (D_2O) as permeant vapor.

2. Experimental

2.1 Apparatus

A schematic diagram of the apparatus (APIMS permeation tester, Model: Bottle/Film Permeation Tester, APET-100, Youtec Inc. Japan) used in this study is shown in Fig.1 WVTR measurement was carried out by using this apparatus, which consists of a cell for permeation testing based on the isostatic pressure method using argon gas as a carrier gas, and APIMS (High sensitive gas monitor, AP-100, detectable mass-to-charge ratio $m/z = 3 \sim 100$, Nippon API Inc. and Hitachi Inc.) for quantifying permeated gas or vapor.

As shown in Fig.1, argon as a carrier gas was purified by Pd catalytic purifier, and its moisture was removed by molecular sieve. Then, the carrier gas was introduced to one surface of the isostatic pressure cell and mixed with water vapor containing gas permeating through a sample film placed between the two halves of the cell. After that the moisture containing carrier gas was introduced into APIMS. Air with specific humidity or moisturized nitrogen using a bubbling bottle was introduced in the opposite surface of the cell. In APIMS, the gas was densely ionized at atmospheric pressure. Then through the differential pumping region, the pressure of the gas was changed to the high vacuum condition, the ions are separated by their mass-to-charge ratios in Q-pole MS and quantified. The flow rate of argon carrier gas was 1 L/min, and the water vapor content in the argon carrier gas was indicated as a volume ratio (v/v, ppb) under standard condition (STP: 0° C, 1 atm). The measurable concentration of water vapor based on a



Fig. 1 Schematic diagram of APIMS Transmission Tester

correct calibration curve is in the range of 0.1 to 400 ppb. However, high concentration of water vapor gives an adverse effect on the sensitivity of APIMS, therefore, the carrier gas was usually passed through the molecular sieve right before introduction of APIMS, and a measurement of water vapor concentration was carried out by bypassing the molecular sieve for 5 minutes. The calibration curve data between water vapor concentration and ion intensity at a mass-to-charge ratio of 18 was previously obtained.

2.2 Materials

Samples used in this study were cut from a specially prepared high barrier composite film, which is silica (SiOx) coated 12 μ m thick polyethylene terephtalate (PET) film laminated with 50 μ m thick oriented polypropylene (OPP) film. The silica coating was carried out using a physical vapor deposition (PVD) process and the thickness of the coating was in the range of 30 to 40 nm.

2.3 Method of measurement

2.3.1 Measurement of baseline

A 200 μ m thick aluminum sheet was placed between the two halves of the cell. Argon was introduced to one surface at pressure of 1 atm, and was carried to the APIMS for measuring the baseline of water vapor concentration at the condition of no permeation of water vapor.

Since water has high adsorption properties, water adsorbed strongly to the piping of the apparatus and continuously desorbed. This phenomenon affects greatly to the baseline (apparent water content at no water vapor permeation) being unstable even though the moisture of the argon carrier gas was removed by molecular sieve. Therefore, a baking was carried out at the following condition. The piping where the carrier gas flows, and the molecular sieve were maintained at 150°C and 300°C, respectively, for 5 days with argon carrier gas circulation at a rate of 0.2 L/min,

Following the baking, water vapor concentration of argon carrier gas at 1 L/min was measured by APIMS, and the average value taken by triplicate runs was determined to be the baseline of water vapor concentration for the measurements of WVTR of the sample film.

2.3.2 WVTR measurement of the sample film with the permeation area of 5 cm²

To reduce the amount of water vapor permeated through the sample film, the permeation area of the film was reduced to 5 cm² by a use of aluminum masking while the original permeation area of the cell was 50 cm². Air at 28°C and 30 \pm 2%RH was passed over one side of the sample at the flow rate of 0.1 L/min. The argon carrier gas was passed over the other side of the sample at the flow rate of 1 L/min, and baking of the carrier gas line was carried out for 5 days to remove moisture at the same condition of the baseline measurement. Duration of WVTR measurement was 7 days (168 hours).

2.3.3 WVTR measurement of the sample film with the permeation area of 50 cm²

With the permeation area of 50 cm², WVTR were measured by passing air at 28° C and $30\pm2^{\circ}$ RH and moisturized nitrogen at 28° C and $90\pm2^{\circ}$ RH. The baking condition, duration of measurement and the flow rates of air and nitrogen are the same as the conditions of the measurements with the permeation area of 5 cm².

2.3.4 WVTR measurement of the sample film using water vapor consists of various ratios of water (H₂O) and heavy water (D₂O)

Nitrogen at 28°C and 90±2%RH containing various ratios of water (H_2O) vapor and heavy water (D_2O) vapor was generated using bubbling water and was passed over one side of the sample at the flow rate of 0.1 L/min. The first run of measurement was using bubbling water of 100% H_2O (containing ca.0.2% natural D_2O), and the second run was using bubbling water of 90% H_2O and 10% D_2O , then the third run was using 100% D_2O , finally the fourth run was using 100% H_2O . Through all runs, the measurements were carried out using the same sample film without baking except the first run. Heavy water (D_2O) vapor was quantified by APIMS using a mass-to-charge ratio of 20. The retention time for measurement of each run was determined to be the time at the concentration of water reached stable.

3. Results and Discussion

3.1 Measurement of baseline

After triplicate runs, the average value of water vapor concentration in the baseline measurement

was 4.1 ppb, with standard deviation (SD) of 0.53 ppb. Therefore, the values of water vapor concentration obtained by film samples at argon carrier gas rate of 1 L/min were adjusted by subtracting 4.1 ppb.

3.2 WVTR measurement with the permeation area of 5 cm²

The output image of APIMS in WVTR measurements of the film samples is shown in Fig.2 As shown in Fig.2, the ion intensity of the mass-to-charge ratio 18 corresponding to the concentration of water vapor in the permeating gas from the cell was increased during bypassing the molecular sieve. Concentrations of water vapor in argon carrier gas were determined from ion intensity obtained using the calibration curve. Results of WVTR measurements of the sample film with transmission area of 5 cm² are shown in Table 1. The water vapor concentration of carrier gas was 9.7 ppb (SD=0.4 ppb). WVTR of the film sample was obtained using equation (1).



Fig. 2 Output of APIMS measurement

Table 1 Results of WVTR measurements of SiOx laminated film with transmission area of 5 cm²

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No.	Temperature [°C]	Relative humidity [%RH]	Concentration of water vapor in carrier gas [v/v, ppb]	WVTR at 28°C, 32%RH [g/(m ² •d)]
1	28	30	9.6	0.0224
2	28	30	9.4	0.0217
3	28	30	10.1	0.0233
Average			9.7	0.0225
S.D			0.4	0.0008

 $9.7 \times 10^{-9} \times 1 \text{ L/min} \times 1440 \text{ min/d} \times 10000 (\text{cm}^2/\text{m}^2)/5 \text{ cm}^2 \times 18 \text{ g}/22.4 \text{ L} = 0.0225 \text{ g}/(\text{m}^2 \cdot \text{d}) \cdot \cdot \cdot (1)$

WVTR of the film sample at 28°C and $30\pm2\%$ RH was 0.0225 g /(m² · d), (SD=0.0008 g /(m² · d)). Fig.3 shows the relationship between WVTR at 28°C and $30\pm2\%$ RH and elapsed time. WVTR reached stable at the time of 100 hours passed from the initiation of measurement. WVTR at 40°C and 90%RH is estimated to be approximately 0.1 g /(m² · d) by conversion from this data based on the assumption of a linear relationship between water vapor pressure and WVTR, and no temperature dependence from 26°C to 40°C.



(Measurement condition: 28°C, 30±2%RH)

The total time required for WVTR measurement was 12 days, consists of 5 days for baking and 7 days for transmission measurement. The result indicates that WVTR measurement using APIMS requires less complex procedures and less than half of time compared to a calcium corrosion method for evaluation of high moisture barrier materials. With regard to the baseline measurement, the baking temperature is probably not high enough to remove adsorbed moisture, and yielded the relatively high value of baseline. This suggests that the baking temperature is needed to be more than 300°C for higher sensitive level of WVTR measurement.

3.3 WVTR measurement of the sample film with the permeation area of 50 cm².

Table 2 showed the results of WVTR measurements of sample film with transmission area of 50 cm² at two kinds of temperatures and humidity conditions. The average of two WVTR data obtained at 28°C and $30\pm2\%$ RH with the permeation area of 50 cm² exhibits slightly higher than WVTR at the same condition with the permeation area of 5 cm². WVTR at 28°C and 90\pm2\%RH was determined to be 0.099 g/(m² · d) and this indicates that WVTR is in proportion to an increase of water vapor pressure in the range of high humidity.

Table 2 Results of WVTR measurements of SiOx laminated film with transmission area of 50 ci	R measurements of SiOx laminated film with transmission area	of 50 cm ²
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No.	Temperature [°C]	Relative humidity [%RH]	Concentrati on of water vapor in carrier	WVTR [g/(m ² •d)]
1	28	30	127.1	0.0294
2	28	30	101.9	0.0235
Aveage of 1 and 2			114.5	0.0265
3	28	90	427.9	0.0990

The reason of slight difference of WVTR measured with the area between 50 cm² and 5 cm² may be that the concentration of parent ions generated from water molecules became unstable due to an ionization process of excess concentration of water vapor, and surpassed the range of the calibration curve. Therefore, it is expected that more sensitive and reliable measurement can be done in the range of ion intensity for a precise calibration curve. For example, to measure WVTR of super high moisture barrier films with the level of 0.002 g/(m² · d) at 90%RH, the permeation area of 50 cm² is applied for measurement, and to measure WVTR of high moisture barrier films with the level between 0.020 g/(m² · d) d) and 0.2 g/(m² · d), the permeation area of 5 cm².

3.4 WVTR measurement of the sample film using water vapor consists of various ratios of water (H₂O) and heavy water(D₂O)

Table 3 shows the results of WVTR measurements using the permeants with various ratios of H_2O and D_2O . It is found that the concentration of H_2O and D_2O measured in each run did not reflect the ratio of H_2O and D_2O in the bubbling solution. The reasons seem to be a gradual release of strongly adsorbed molecules in piping and the difference of vapor pressure of H_2O and D_2O . However, the WVTR value of each run, calculated from the sum of the concentrations of H_2O and D_2O using the calibration curve of H_2O , indicates roughly constant. Even though the results indicated that the further investigation with the condition of thorough baking and the precise calibration curve of D_2O is needed, much higher sensitive measurement of WVTR is expected using D_2O as permeant replacing H_2O , since the natural exiting ratio of D_2O in water is ca. 0.02%.

Table 3 Results of WVTR measurements at various ratios of H₂O and D₂O

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Run	Retention time for measurement	Contents of bubling solution (%)		Concentration of water vapor in carrier gas [v/v, ppb]			WVTR at 28°C90% RH (for total of
[hrs]	H ₂ O	D ₂ O	H ₂ O	D ₂ O	Total (H ₂ O and D ₂ O)	H_2O and D_2O) [g/(m2/d)]	
1	120	100	0	431	1	432	0.0990
2	312	90	10	383	16	399	0.0917
3	240	0	100	234	262	496	0.1139
4	120	100	0	445	85	530	0.1217

%)Measurement condition: 28°C, 90%RH(bubling with N₂)

※) Retention time for measurment was the time of the concentaration of water vapor reached stable,.

4. Conclusion

WVTR measurement using APIMS provides simpler and more rapid evaluation for high moisture materials compared to the conventional methods. APIMS has proven to be able to measure the minimum level of 10 ppb of water vapor concentration in carrier gas with high accuracy. That means that APIMS is able to determine down to 0.002 g/(m² · d) as WVTR of films with the permeation area of 50 cm². Though this level of WVTR is double-digit higher than the level needed for cover films of OLED, it is sensitive enough to evaluate the high moisture barrier materials needed for backsheets of solar cells.

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大気圧イオン化質量分析器によるハイガスバリアフィルムの

水蒸気透過度の迅速測定法の研究

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近年、電子工業分野では高水蒸気バリア材料の評価のニーズが高まっている。本研究では大気 圧イオン化質量分析器(APIMS)を使用した迅速かつ高精度に水蒸気透過率(WVTR)を計測す る方法を検討した。APIMS は従来の計測方法に比べ、より容易な操作でより短時間に高水蒸気 バリア材料の測定が可能であり、評価結果から、フィルムの WVTR としては、0.002 g/(m²・d). まで測定できる可能性が示された。 Multi-criteria Evaluation Techniques for Sustainable Packaging Systems