

Predicting the Lifetime of Flexible Permeation Barrier Layers for OLED Displays

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Abstract

Water diffusion through a single-layer barrier is measured with Secondary Ion Mass Spectrometry, electrical capacitance, and mechanical film stress. The time taken for one monolayer of water molecules permeate into the OLED is defined as the lifetime. Extrapolated to $T = 38^\circ\text{C}$ and 90% relative humidity, a $3\mu\text{m}$ thick barrier is predicted to seal for 13 years.

Author Keywords

Permeation barrier; intrinsic barrier performance; diffusion coefficient; water solubility; Water Vapor Transmission Rate; lifetime; barrier evaluation; barrier characterization; SIMS; capacitance; stress.

1. Objective and Background

Flexible displays and lighting panels with Organic Light Emitting Diodes (OLEDs) require high quality flexible protection in the form of encapsulation barrier layers. However, the ongoing intensive search for low-cost flexible barrier layer materials is made difficult by the lack of reliable techniques for predicting their operating lifetime. While the decisive inherent barrier material property is its bulk permeability, in laboratory tests barriers often fail by permeation along embedded particles or along their interfaces with the substrate. These failure modes prevent the methodical exploration and selection of barrier materials by the criterion of true bulk permeability. In addition, the long operating life expected from flexible barrier layers demands accelerated testing at elevated temperature (T) and relative humidity (RH). Yet no straightforward procedure has been identified to date for extrapolating high- T high- RH results to real-life operating conditions. Finally, no agreed-on criterion has been defined for barrier failure. Our objectives have been to (i) define such a criterion, (ii) work out a quantitative procedure for relating high- T high- RH results to typical OLED display operating conditions, and (iii) develop and apply fast-turnaround techniques for characterizing the diffusion of water through the bulk of a single-layer barrier. Meeting these three objectives requires the quantitative evaluation of barrier permeability, and the quantitative prediction the operating lifetime of a barrier layer.

We expose barrier layers to water (H_2O or D_2O) vapor at temperatures from 65°C to 200°C . Under these conditions water diffuses into the barrier. We measure the concentration of H or D in the barrier material, and evaluate the water diffusion coefficient from either concentration-depth profiles or the total amount of water dissolved in the film. Concentration and concentration-depth profile of deuterium are measured by secondary ion mass spectrometry (SIMS) coupled with sputter profiling. This measurement is used to calibrate the water concentration in all samples. We introduce two fast-turnaround techniques that can be conducted in most laboratories. In one technique changes in water content are evaluated from changes in electrical capacitance. In the other technique changes in

water content are evaluated from changes in mechanical stress of the barrier layer. The two techniques take advantage of the observation that both, electrical capacitance and film stress, vary linearly with the total number of water molecules dissolved in the layer. All three techniques are immune to point defects and particles, as confirmed by experimental results.

In a single-layer barrier film that protects an OLED, water diffuses from the side of the barrier that is exposed to the humid atmosphere ($x=0$) toward the OLED side ($x=h$). This diffusion results in a concentration profile of water molecules $n(x,t)$ in the barrier, where t is time. For short diffusion times t the number of in-diffused water molecules $n(x,t)$ follows a complementary error function, $n(x,t) = n(x=0) \operatorname{erfc}[x/2\sqrt{(Dt)}]$, with the diffusion coefficient D . SIMS measures this erfc profile. On the other hand, the changes in electrical capacitance C and in mechanical film stress σ are proportional to the total number of water molecules $N(t)$ that have penetrated into the layer. In a diffusion controlled process $N(t)^2$ is linear with time, t , and follows equation (1):

$$N(t) = \frac{4n}{\pi} D \times t \quad (1)$$

Therefore D can be determined from measurements of the changes of electrical capacitance and mechanical film stress with time. The total amount of water molecules $N(t)$ dissolved in an effective barrier layer ranges from a fraction of monolayer of water to at most a few monolayers. Even such small quantities of water can cause marked changes to capacitance and film stress, which allows determination of diffusion coefficient and water concentration. Conventional gravimetric and spectroscopic measurements are not sensitive enough to measure such small quantities of water.

2. Results

The barrier layer under study is deposited by plasma-enhanced chemical vapor deposition (PECVD) on substrates at room temperature¹⁻³.

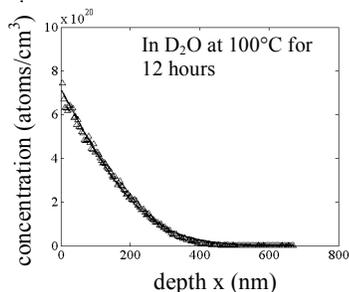


Figure 1. Deuterium profile measured by Secondary Ion Mass Spectrometry (SIMS). The surface concentration $n(x=0)$ and the diffusion coefficient are 1.6×10^{20} molecules/cm³ and 4.2×10^{-15} cm²/s, respectively

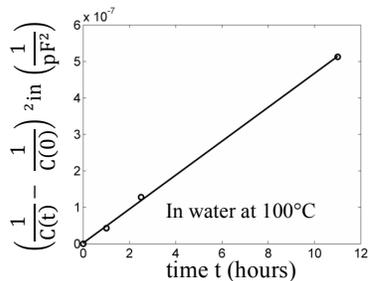


Figure 2. Square of the change in inverse capacitance. From the slope a diffusion coefficient of $5.6 \times 10^{-15} \text{cm}^2/\text{s}$ is extracted

For SIMS measurement, a 660nm thick barrier layer was deposited on a silicon wafer substrate. This sample was held in boiling heavy water (D_2O) for 12 hours. Then the deuterium concentration profile was measured by SIMS. Figure 1 shows the measured concentration profile of deuterium concentration n as a function of depth x . We take $n_{\text{D}2\text{O}} = \frac{1}{2} n_{\text{D}}$. $n_{\text{D}2\text{O}}$ follows a complementary error function with a surface concentration $n(x=0)$ of 1.6×10^{20} molecules/ cm^3 . The diffusion coefficient extracted from the complementary error function profile is $4.2 \times 10^{-15} \text{cm}^2/\text{s}$ (at 100°C in boiling water).

For capacitance measurements samples are prepared by evaporating a 100nm thick chromium blanket bottom electrode onto a glass substrate. Then a 200nm thick blanket barrier layer is deposited by PECVD, followed by evaporation through a shadow mask of 25nm thin chromium top electrodes. Shadow masking is specifically used instead of photolithography to prevent any exposure of the sample to elevated temperatures and solvents. The capacitors were held in boiling water at 100°C . The change in capacitance C is proportional to the change of the dielectric constant ϵ , which in turn is proportional to the change in the amount of dissolved water molecules $N(t)$. For a capacitor of thickness h the capacitance at time t , $C(t)$, is described by the equation:

$$\left(\frac{1}{C(t)} - \frac{1}{C(0)}\right) = \left(\frac{1}{C(\infty)} - \frac{1}{C(0)}\right) \frac{2}{h\sqrt{\pi}} \sqrt{Dt} \quad (2)$$

$C(0)$ is the capacitance before exposure to water and $C(\infty)$ the capacitance of the sample when saturated with water. Figure 2 shows the change of the square of the inverse capacitance (which is the square of the left-hand side of Eq.(2) as a function of time, t . The value of D then is extracted from the slope in Figure 2. The diffusion coefficient extracted from the capacitance measurement, $5.6 \times 10^{-15} \text{cm}^2/\text{s}$, is very close to the SIMS measurement result of $4.2 \times 10^{-15} \text{cm}^2/\text{s}$.

Film stress measurements are the simplest approach to measuring the diffusion coefficient. Barrier layers with thickness ranging from 100nm to $2\mu\text{m}$ were deposited on 4-inch diameter, $\langle 100 \rangle$ oriented, $525\text{-}\mu\text{m}$ thick silicon wafers. When exposed to high temperature and humidity, water diffuses into the barrier layer and makes it expand. The expansion is constrained by the thick silicon substrate. This puts the barrier film under stress and the layer-substrate couple bends. The stress is evaluated from measurements of the curvature of the silicon wafer, using a surface profilometer. Using the Stoney equation, the curvature is translated to physical stress⁴.

The square of the change in stress is found to be perfectly linear with time t as shown in Figure 3. From the slope a diffusion

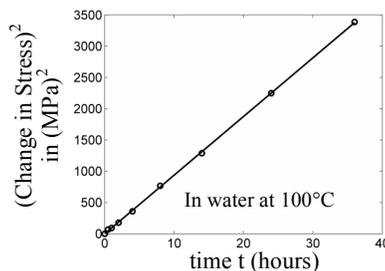


Figure 3. Square of the change in film stress. From the slope a diffusion coefficient of $4.4 \times 10^{-15} \text{cm}^2/\text{s}$ is extracted

coefficient of $4.4 \times 10^{-15} \text{cm}^2/\text{s}$ is extracted. Table 1 summarizes the results from all three techniques. The three techniques sample surface areas that differ by a factor of more than 1,000, and layer thicknesses that differ by a factor of nearly ten. The close results obtained for the value of D suggest that the results are independent of defects and substrate interfaces, and that the barrier layers are homogeneous.

Table 1. Summary of results from SIMS, electrical capacitance and film stress measurements

	SIMS	Electrical Capacitance	Mechanical Film Stress
Thickness (nm)	660	200	1500
Area	0.5mmx0.5mm sputter target	1mmx1mm capacitor size	4 inch silicon wafer
Solubility at P=1atm and T=100°C	1.6×10^{20} molecules/ cm^3	-	-
Diffusion Coefficient at T=100°C	$4.2 \times 10^{-15} \text{cm}^2/\text{s}$	$5.6 \times 10^{-15} \text{cm}^2/\text{s}$	$4.4 \times 10^{-15} \text{cm}^2/\text{s}$
Solubility Activation energy E_s	0.71eV	-	-
Diffusion coefficient activation energy E_d	-0.20eV	-	-

The film stress measurements were calibrated against SIMS to determine the conversion factor from film stress to water concentration. Because the film stress measurements are simple to conduct we performed them over ranges of temperature and humidity. Figures 4 and 5 describe the temperature dependences of the saturated concentration of water $n(t=\infty)$ and the diffusion coefficient D . To obtain the thermal activation energy of the solubility of water in the barrier layer, the stress of films saturated with water at 100°C and 100% humidity was calibrated previously against SIMS solubility. The saturated concentration of water in the barrier layer has an activation energies of -0.20eV, negative because the solubility drops with rising temperature when the partial pressure of water in the environment is held constant at $p = 1 \text{ atm}$. For the diffusion coefficient the activation energy is 0.71eV.

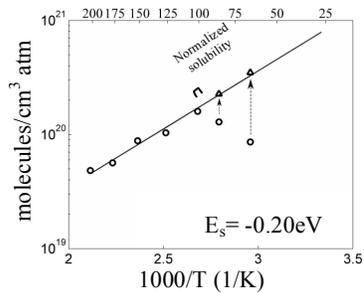


Figure 4. The activation energy of water solubility n is -0.20eV (normalized to 1 atmosphere water vapor pressure)

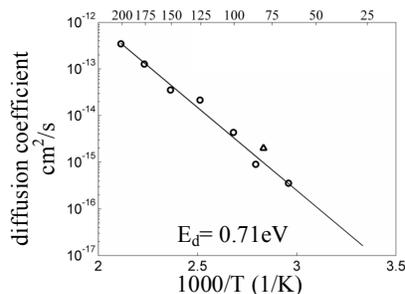


Figure 5. The activation energy of the diffusion coefficient is 0.71eV . Silica glass^Δ has a diffusion coefficient of $2 \times 10^{-15}\text{cm}^2/\text{s}$ at 80°C

Our criterion for barrier failure is the permeation of one monolayer of water molecules to the OLED. We use the activation energies of Table 1 to extrapolate from our measurements at high temperature to typical OLED operation conditions. For a typical operating environment of 38°C and 90% relative humidity, the surface concentration $n(x=0)$ is extrapolated to be 0.96×10^{20} molecules/ cm^3 and the diffusion coefficient D is $5.4 \times 10^{-17}\text{cm}^2/\text{s}$. The corresponding steady state water vapor transmission rate for a $3\mu\text{m}$ barrier is $1.5 \times 10^{-7}\text{g}/\text{m}^2/\text{day}$. The one-monolayer lifetime under these conditions is calculated to be 13 years.

3. Discussion and conclusion

We take the operating lifetime of permeation barriers as the time until one monolayer of water has permeated. Using our results this time can be calculated for the accelerated T and RH test conditions, and at typical OLED display operating conditions. For example, at $T=38^\circ\text{C}$ and 90% RH a $3\text{-}\mu\text{m}$ thick barrier layer will pass one monolayer of water in 13 years. The acceleration

factor for 1 monolayer of water for the same $3\text{-}\mu\text{m}$ thick barrier layer to permeate from this condition to 85°C and 85% RH calculated from the activation energies is 52. The intrinsic performance of a barrier layer material so far has never been demonstrated in such detail because diffusion along particles and interfaces have dominated conventional permeation tests.

4. Impact

After calibration with one SIMS sputter profile, electrical capacitance and film stress measurements provide information on the intrinsic performance that can be used to:

1. Compare the intrinsic permeability of different barrier materials.
2. Design new single or multilayer barrier films to achieve a target OLED display or lighting lifetime.
3. Extrapolate and predict room temperature performance from high temperature accelerated tests.

This information would set a framework for designing a barrier film for encapsulation of OLED displays and lighting panels.

5. Acknowledgements

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6. References

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