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Functional Modelling of Water Vapour Transmission through Surface Defects Using Surface Segmentation Analysis

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Abstract. Flexible photovoltaic films have been recently shown to have efficiencies comparable to those of solid Si based photovoltaics. Flexible PV films have significant advantages in terms of ease of manufacture by roll-to-roll (R2R) techniques and in easy building integration. A significant challenge is the protection of the flexible solar cells from water vapour ingress, which seriously reduces cell life and efficiency. Transparent barrier films are a possible solution to addressing the water vapour transmission rate (WVTR) challenge. Consequently thin barrier films such as those made from Al₂O₃ are the subject of increasing research interest when used for the encapsulation of flexible PV modules. The film can be produced by several thin film deposition processes such as atomic layer deposition (ALD). However, micro-scale defects in the barrier film such as pinholes and particulate debris have been shown to have serious consequences in terms of WVTR. Our previous research has empirically shown that small defects ($\leq 3\mu\text{m}$ lateral dimension) were less significant in determining water vapour ingress. In contrast, larger defects ($\geq 3\mu\text{m}$ lateral dimension) have been shown to have a greater effect on the barrier functionality. The present paper illustrates the use of surface segmentation techniques to efficiently extract defect data from measured surface topography of barrier film sheets. Experimental results are presented where the defect information is correlated with the WVTR tests. A model is then presented to test the hypothesis that the major contributing defects to water vapour transmission rate (WVTR) are small numbers of large defects. The model presented in the paper shows excellent correlation with experimental results and provides a theoretical basis for the development of in process surface measurement for thin film R2R manufacture.

1. Introduction

Aluminum-oxide (Al₂O₃) coatings are widely used as oxygen and water vapour barriers in flexible photovoltaic (PV) industry. In this study, a thin layer (approx. 40 nm) of Al₂O₃ deposited via atomic layer deposition (ALD) method, have been used on PEN polymer films to allow PV module transparency, flexibility and to provide an effective barrier layer to prevent the possibility of water vapour ingress into the final PV unit. This barrier material ideally has a water vapor transmission rate (WVTR) of less than 10^{-4} g/m²/day[1]. Nevertheless, the barrier film properties are often affected by the chemical and physical structures of the barrier, concentration of the permeant, temperature and humidity as well as surface defects in the surface layer induced during the ALD deposition processes. In this paper, a theoretical model is developed to predict the quantity of water vapor permeation through the Al₂O₃ ALD barrier films defects. The results of the model are then compared to experimental results where defects densities and size measured using lab based surface metrology techniques and analysed by means of “segmentation”, the results are then correlated with measured barrier functionality.

1.1 Theoretical background

Ashley [2] developed an equation to calculate the permeability coefficient of the water vapor through a polymer barrier film, and indicated that the permeability coefficient P_r depends on the solubility coefficient S and the diffusion coefficient D ($P_r=DS$). This equation is mathematically represented as;

$$P_r = \frac{(\text{quantity of permeant}) \times (\text{film thickness})}{(\text{area}) \times (\text{time}) \times (\text{pressure drop across the film})}$$

$$P_r = DS = \frac{qL}{At\Delta P} \left(\frac{\text{cm}^3 \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} \right) \quad (1)$$

Where q/t represents the quantity of permeant per unit of time (t), L refers to the film thickness, A is the area of the film and ΔP is the partial pressure difference of permeant across the film. However, in a typical water vapour permeation measurement such as the “MOCON[®]” test which has been used in this study, ΔP in equation (1) relates to the partial pressure difference between nitrogen containing water at 90% RH on one side, and ultra-pure nitrogen on the other side, and in a such type of permeation test there is no pressure gradient across the sample so it is then reasonable to use the absolute value of the permeant’s partial pressure P , instead of ΔP [3]. Thus, equation (1) can be presented as the following;

$$P_r = DS = \frac{qL}{AtP} \left(\frac{\text{cm}^3 \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} \right) \quad (2)$$

Da Silva Sobrinho *et al* [3] developed an equation to determine the quantity of permeant per unit of time through a polymer layer; this equation was based on Henry’s law of solubility [4], and expressed as;

$$Q = \frac{q_H}{t} = \frac{ADSP}{L} = \frac{AD\emptyset}{L} \quad (3)$$

Where; the validity of Henry’s law is assumed, and \emptyset represents the water vapor concentration in the film surface = SP , and it has been estimated to be 1 g/cm^3 , D is the diffusion coefficient of the barrier film (m^2/s)[3].

In this present paper a model of water vapor permeation through the barrier film defects is presented, where the vapour transmission is assumed to be completely governed by defects geometries and densities.

2. Theoretical model

The basic assumption of the model presented in this paper is that, the combined film of thickness L has a transparent flexible barrier coating of (Al_2O_3) with a single circular hole (defect) as shown in figure (1), and that it is exposed to permeant water vapour from the lower side as shown in figure (2). This orientation is consistent with that used in a MOCON[®] test.

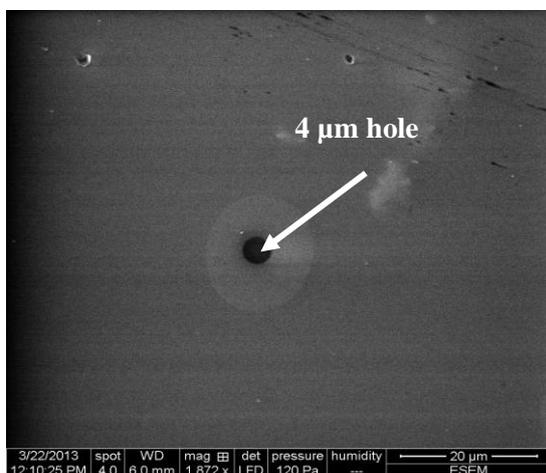


Figure 1. SEM image of hole type defect in the Al_2O_3 ALD barrier film

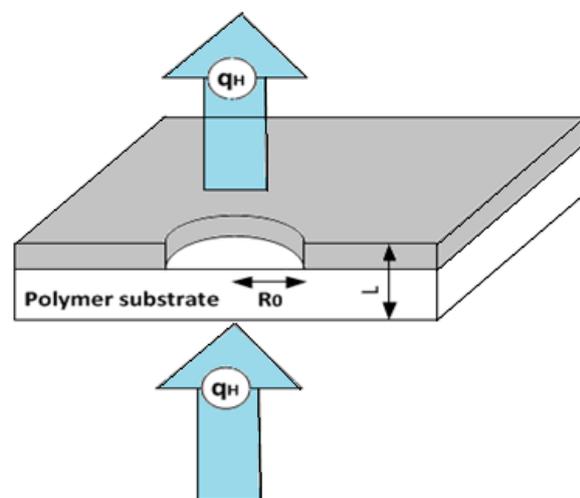


Figure 2. A schematic representation of a hole defect

To determine the quantity of the water vapour q_H , leaving the barrier film in the case of the hole present as shown in figure (2), the quantity of permeant traversing the polymer and through the hole per unit time can be provided by modifying equation (3) and introducing the barrier film as having a circular hole area (πR^2);

$$Q = \frac{q_H}{t} = \frac{\pi R_0^2 D \Delta C}{L} \quad (4)$$

Where R_0 is the hole radius, D is the diffusion coefficient of the barrier film (m^2/s), ΔC is the water vapor concentration (g/cm^3) and L is the combined film thickness. However, to determine the rate of the water vapour that penetrates the hole over the whole substrate area ($g/m^2/day$), Eq. (4) can be expressed as the following [5];

$$WVTR = \frac{Q}{A} \quad (g / m^2 / day) \quad (5)$$

Where; Q is the amount of the water vapor passing through a film of thickness L and total area A during time t driven by a partial pressure differential P across the film.

Moreover, in order to discuss water vapor permeation through a barrier coating containing several defects (holes), equation (5) can be modified for (N) pinholes as follows:

$$WVTR = \sum_0^N \left(\frac{Q}{A} \right) N \quad (6)$$

N , is the number of defects (pinholes) in the sample area.

3. Experimental work

The study was based on a set of two 80 mm diameter film samples coated with 40nm of Al_2O_3 using ALD method. The base film substrate used was Polyethylene Naphthalate (PEN); where the thickness of this substrate was specified to be 125 μm . According to the manufacturer's data, this material (PEN) has a water vapor diffusion coefficient of $4 \times 10^{-12} cm^2/s$ at 38 C°. Prior to the surface measurements, the Al_2O_3 ALD samples were measured for water vapor transmission rate (WVTR) using Isostatic standard test (MOCON®) instrumentation [6] at 38°C and 90% RH.

Table 1. WVTR at 38C° and 90% RH

Sample No	Water vapor transmission rate (g/m ² /24 hrs.)	Stabilisation time (day)
1	4.1×10^{-3}	5
2	2.0×10^{-3}	5

The MOCON® test results in table (1) show that sample 1 had the highest WVTR after a stabilization time of 5 days. In this study, quantitative surface measurement was carried out using optical interferometry (CCI-3000 Taylor Hobson Ltd.) and the topography was characterized using areal parameters (ISO25178-2, 2012). The proportion of the surface area characterised was 14% of the total area of each sample equating to 703 mm², this comprised 700 measurements per sample.

3.1 Surface topography analysis

Segmentation analysis was carried out on the data (700 data files) in order to extract and count the number of significant defects present on the substrates, using a series of mathematical and thresholding techniques [7, 8] as shown in figure (3) and figure (4).

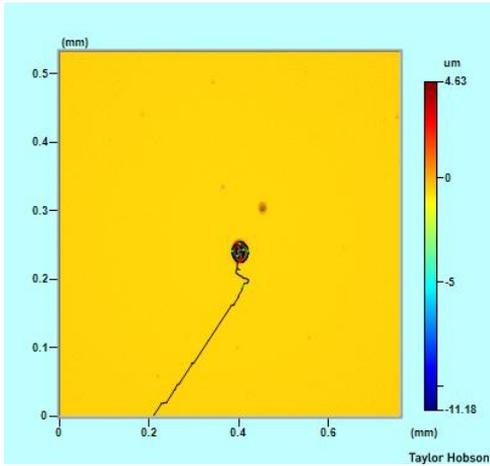


Figure 3. Segmentation analysis for single defect

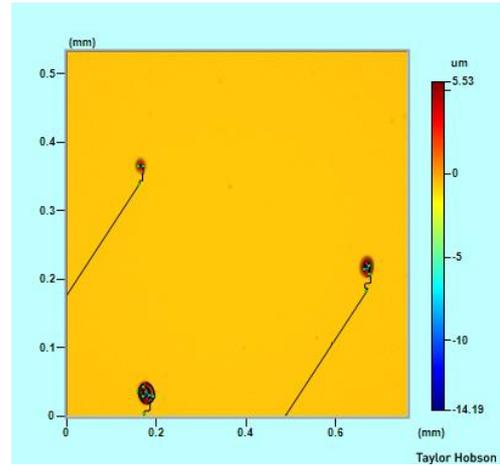


Figure 4. Segmentation analysis for multiple defects

In this case a significance value of $3 \times S_q$ vertical (where, S_q for non-defective area = 0.8 nm per field of view, see figure 5) and $\geq 15 \mu\text{m}$ (based on optical microscopy analysis) lateral was applied to compare defects on the two samples. Using these criteria it was possible to segment the surface data and record the defect density/count across the surface data sets collected from the ALD coated barrier layers. Figure (6) shows significant defects count at $3 \times S_q$ vertical and $15 \mu\text{m}$ lateral pruning conditions.

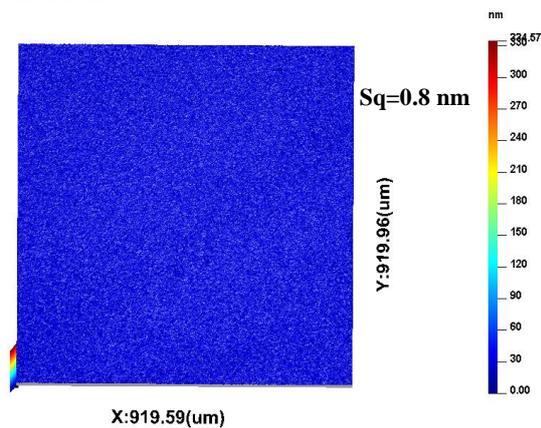


Figure 5. S_q for non-defective area

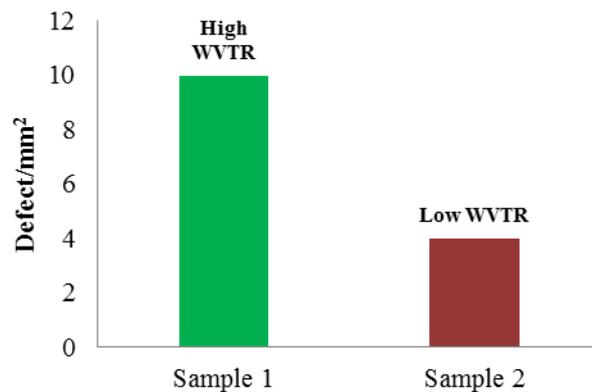


Figure 6. WVTR versus defects density

The analysis of the results in figure (6) indicated that there was evidence of correlation between the number of large defects and the WVTR value. The high WVTR specimen had a larger density of significant defects as compared to the better performing substrate. However, even for sample (2) there are still approximately four significant defects affecting the barrier performance by allowing water vapor ingress. The question that remains is, what is the cut-off level between large significant defects and small insignificant defects?

Therefore, different area pruning conditions were applied whilst the height prune condition of $3 \times S_q$ remained the same. Using these criteria the defect density count appeared to converge around $2.5 \mu\text{m}$ (lateral dimension) see figure (7). Above this lateral cut off value the significant defect density level was consistently higher for the sample with the higher WVTR (sample 1) and from approximately $3 \mu\text{m}$ the defect density count remained stable. These results appear to indicate that defects of less than $3 \mu\text{m}$ in lateral size have less significant impact on the barrier film functionality. Further evidence of this is provided by the fact that the sample with the lower WVTR has a higher defect density when smaller defect sizes are considered as shown in figure (7).

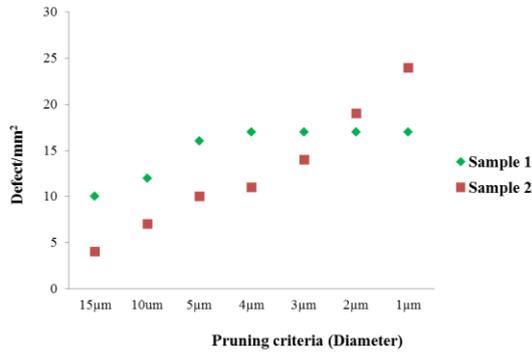


Figure 7. Defects count at different lateral pruning conditions

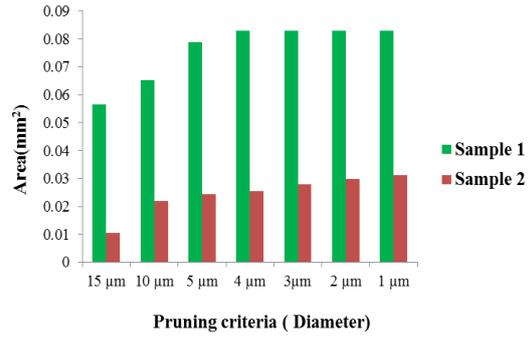


Figure 8. Cumulative defect surface area at different lateral pruning conditions

Also, figure (8) shows a plot of the accumulated surface area of the defects measured on the two samples. The results show that when all defects with a lateral widths down to 1 μm are used in the analysis, sample 1 (higher WVTR) consistently has a higher cumulative surface area value. Therefore, it is possible now to classify the defects in terms of their significance in accordance to the lateral and vertical scale as shown in table 2.

Table 2. Shows the Al₂O₃ barrier film defects size

Type of defect	Feature Size	
	Sq (vertical)	Width
Significant	≥ 2.4 nm/ field of view	≥ 3 μm lateral dimension
Non -significant	≤ 2.4nm/ field of view	≤ 3 μm lateral dimension

3.2 WVTR results analysis

The WVTR tests (MOCON®) were conducted on an area of 80 mm diameter as mentioned previously. Hence in order to compare the experimental and the theoretical model results, the surface topography analysis data needs to be scaled up for an area of 80 mm diameter. Thus assuming that all the defects over the samples are essentially circular and have a homogeneous distribution, based on these two suppositions figure (7) and (8) can be scaled up to 80mm² as shown in the following figures.

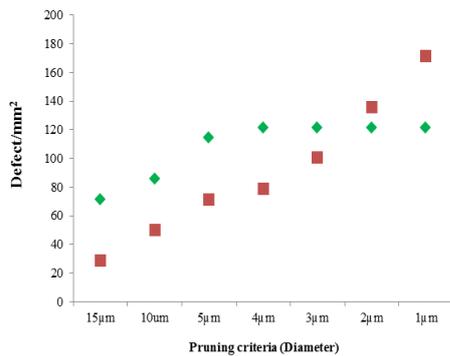


Figure 9. Defects count at different lateral pruning conditions for an area of 80 mm²

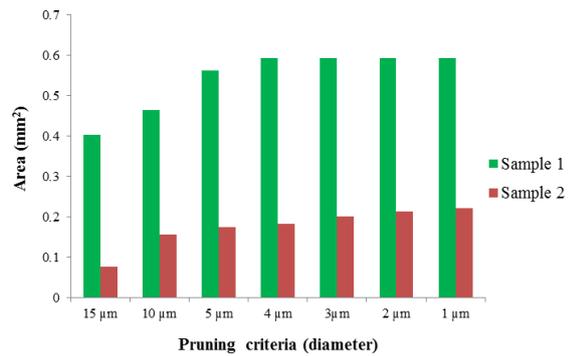


Figure 10. Cumulative defect surface area at different lateral pruning conditions for an area of 80 mm²

Referring back to the theoretical model presented earlier in this paper and using Eq. (5) and Eq. (6) for the given sets of parameters and variables for each sample, as shown in appendix (1), and substituting all the known data in equation (6), the theoretical model based on the approach of Da

Silve Sobrino *et al* [3] led to results which are similar to those obtained by surface topography analysis and experimental WVTR test results. Calculations are shown in appendix (1).

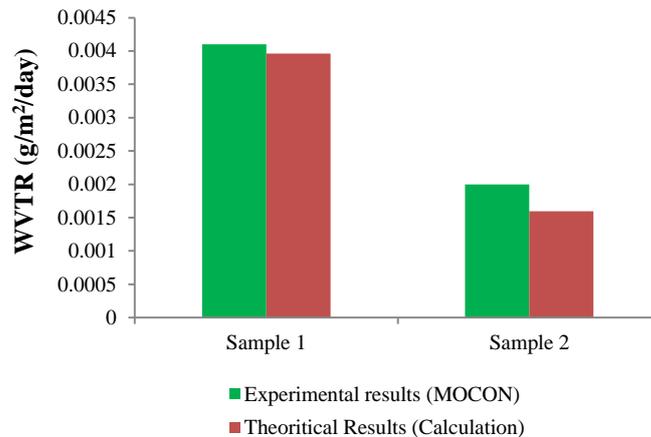


Figure 11. Comparison between the theoretical at ($3\mu\text{m}$ lateral cut-off) and experimental (MOCON®) results

The results in figure (11) indicate that sample (1) has a higher WVTR value than sample (2). This result is similar to that obtained experimentally using MOCON® test. This would seem to confirm that the theoretical model presented in this paper after Da Silva Sobrino *et al* [3] has the potential to be used for understanding the mechanism of water vapor permeation through flexible PV barrier films defects.

4. Conclusion

The present findings from the segmentation analysis and the theoretical model developed in this paper both seem to suggest that the total permeation rate through small numbers of larger defects ($\geq 3\mu\text{m}$) is much more significant for barrier functionality than the total permeation rate through large numbers of small pinhole-type defects ($\leq 3\mu\text{m}$) over the same area of substrate. The model presented in this paper could therefore also be used for the understanding of the overall PV module performance and lifespan and provides a theoretical basis for the development of in process surface measurement for thin film R2R manufacture.

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Appendix (1)

Sample (1) data		
<i>Parameter</i>	<i>Given unit</i>	<i>Metric unit (m)</i>
L (film thickness)	125.04 μm	0.000125 m
D (Diffusion coefficient)	$4 \times 10^{-12} \text{ cm}^2/\text{s}$	$4 \times 10^{-16} \text{ m}^2/\text{s}$
\emptyset (Water vapor concentration)	1 g/cm^3	1000000 g/m^3
Accumulated defects area (A)	0.592558 mm^2	$5.93 \times 10^{-7} \text{ m}^2$
Sample area (A)	5024 mm^2	0.00524 m^2
N (total number of defects at $3 \mu\text{m}$)	121	121

$$Q(\text{one hole}) = \frac{q_H}{t} = \frac{\pi R_0^2 D \emptyset}{L}$$

$$Q(\text{many holes}) = \frac{q_H}{t} = \frac{A_{\text{cumulative}} D \emptyset}{L}$$

$$Q = \frac{5.93 \times 10^{-7} \times 4 \times 10^{-16} \times 1 \times 10^6}{0.000125} = 1.90 \times 10^{-12} \text{ g/s}$$

$$\text{WVTR} = \frac{Q}{A} \times N \times 86400 \text{ (day)}$$

$$\text{WVTR} = \frac{1.90 \times 10^{-12}}{0.00524} \times 121 \times 86400 = 3.96 \times 10^{-3}$$

$$\text{WVTR} = 3.96 \times 10^{-3} \text{ g/m}^2/\text{day}$$

Sample (2) data		
<i>Parameter</i>	<i>Given unit</i>	<i>Metric unit (m)</i>
L (film thickness)	125.04 μm	0.000125 m
D (Diffusion coefficient)	$4 \times 10^{-12} \text{ cm}^2/\text{s}$	$4 \times 10^{-16} \text{ m}^2/\text{s}$
\emptyset (Water vapor concentration)	1 g/cm^3	1000000 g/m^3
Accumulated defects area (A)	0.2003 mm^2	$2.003 \times 10^{-7} \text{ m}^2$
Sample area (A)	5024 mm^2	0.00524 m^2
N (total number of defects at $3 \mu\text{m}$)	136	136

$$Q(\text{one hole}) = \frac{q_H}{t} = \frac{\pi R_0^2 D \emptyset}{L}$$

$$Q(\text{many holes}) = \frac{q_H}{t} = \frac{A_{\text{cumulative}} D \emptyset}{L}$$

$$Q = \frac{2.003 \times 10^{-7} \times 4 \times 10^{-16} \times 1 \times 10^6}{0.000125} = 6.82 \times 10^{-13} \text{ g/s}$$

$$\text{WVTR} = \frac{Q}{A} \times N \times 86400 \text{ (day)}$$

$$\text{WVTR} = \frac{6.41 \times 10^{-13}}{0.00524} \times 136 \times 86400 = 1.53 \times 10^{-3}$$

$$\text{WVTR} = 1.53 \times 10^{-3} \text{ g/m}^2/\text{day}$$