Further Development of Surface Metrology Methods for Predicting the Functional Performance of Flexible PV Barrier Films

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Abstract. Surface topography analysis plays a very significant role in determining the functional performance for many engineering surfaces. In this paper, feature characterisation techniques, based on the 'Wolf pruning' method are implemented to characterise micro and nano-scale features which have a dominant effect on the functional lifespan of flexible Photovoltaic (PV) modules. The densities and dimensions of the potential significant features are calculated by means of the feature "characterisation toolbox". The outcome of this study has shown the potential of areal feature segmentation for detecting functionally significant defects present in Atomic Layer Deposition (ALD) barrier coatings of Al_2O_3 on polymer films. The analysis provides the basis for the development in process metrology for Roll-to-Roll (R2R) production of barrier coatings as applied to flexible PV arrays and is a first step in the demonstration of in-process use of feature parameters.

1. Introduction

The effort of the Photovoltaic (PV) industry to reduce production costs has led to highly efficient Roll-to-Roll (R2R) production processes being adopted. Such flexible and lightweight solar cells are set to open up new markets in sectors like portable electronics, automotive / transportation and architecture. Flexible PV thin-film technologies can offer particular design options for building integrated applications and have the potential to meet Building-Integrated-Photovoltaics (BIPV) product requirements [1]. For conventional rigid thin-film solar modules, glass provides sufficient environmental protection for solar cells. Appropriate materials that can be used as front cover encapsulation in flexible solar modules are still under investigation. Flexible solar cells need to be protected from moisture and oxygen ingress to ensure sustained module performance; unfortunately common transparent plastic barriers do not provide sufficient barrier properties against the environment. However, modifying the plastic barrier with inorganic coatings can significantly improve its barrier properties while maintaining the high transmission of light through to the cells. To achieve this, a multi-layer composition of alternating polymer and very thin (a few nanometres) inorganic layers is required [1]. Studies of gas permeation through polymer films with an inorganic coating have concluded that permeation occurs through defects in the coating [2, 3]. Therefore, a process such as ALD which can produce a defect free conformal coating [4] could provide an excellent barrier to gas permeation. During the processing of such multilayer materials, defects within the inorganic coating such as Al_2O_3 have to be avoided. Characterisation and ultimately minimisation of these defects should lead to lower WVTR and improved PV module efficiency and lifespan. This study seeks to use Areal surface feature parameters to assess and functionally characterise defects in

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PV barrier films that potentially have a negative effect on the water vapour transmission rate (WVTR) through the barrier coatings.

1.1 Encapsulation of Flexible Thin-Film PV modules

Flexible $CuInGaSe_2$ (CIGS) modules with an efficiency of approximately 19% can be manufactured on high temperature polyimide substrates as shown in Fig (1). However, a potential weakness of these cells is their moisture sensitivity [5]. Exposure to damp heat (D-H) at 85°C and 85% relative humidity results in a significant loss in cell performance and lifespan. This is attributed to the existence of micro and nano-scale defects/features over the barrier film coating that are thought to facilitate water vapour ingress. Hence, to ensure long term performance and stability of the solar module, an effective and robust encapsulation is required to prevent penetration of water and oxygen into the device. Without any protection the solar module would degrade rapidly, mostly because of conductivity losses of the front contacts and interconnections, since the electronic properties of ZnO: Al is sensitive to moisture and Mo, like any other metal contact, can suffer from corrosion [6].

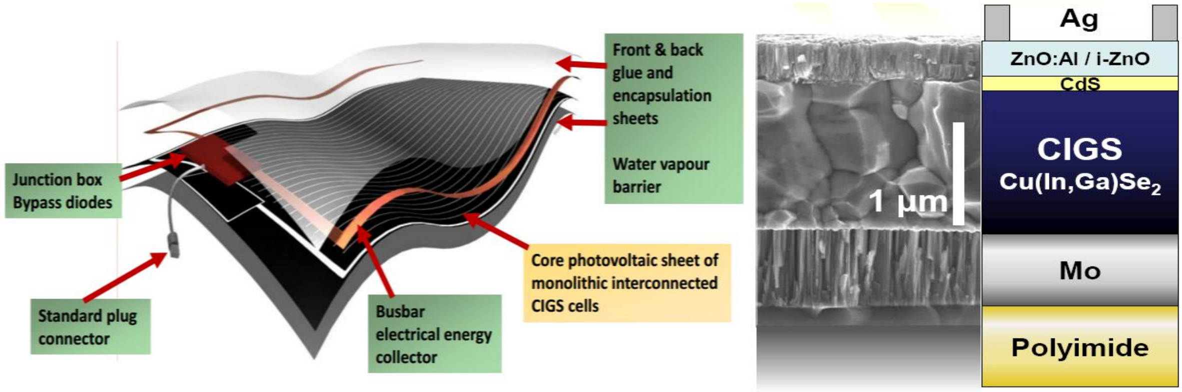

Figure 1. Typical structure of flexible CIGS PV Module
(Courtesy of Flisom, Switzerland)

One of the possible solutions to this critical problem is to encapsulate the PV module by an effective transparent barrier film. The choice of the encapsulation material for a given application depends on a range of factors such as, the type of the encapsulated material, light transmission, chemical composition, size, storage conditions, and expected shelf life. Hence, in order to provide sufficient protection for CIGS PV modules, the encapsulation material must be multifunctional, as it must serve as a barrier against gases, moisture, and must be physically durable.

1.1.1 Selection of PV barrier film materials

Aluminum oxide (Al_2O_3) films deposited through atomic layer deposition (ALD) are known to be effective permeation barriers due to their uniformity and assumed pinhole-free morphology. Studies regarding the selection of the encapsulation materials for PV modules have indicated that Al_2O_3 contains a very high density (up to 10^{13} cm^{-3}) of negative charges (n-type) which makes the material unique for CIGS (p-type) surface passivation [7]. Moreover, several groups have recently reported excellent barrier properties for polymeric substrates coated with a thin layer of Al_2O_3 ALD. For example, Carcia *et al* [8] reported that thin films of Al_2O_3 ALD on polymeric substrates reduce the water vapour transmission rate from ~ 1 to 10^{-5} g/m^2day at room temperature. Hegedus *et al*. [9] studied two configurations; one where the Al_2O_3 was deposited directly on the substrate, and the other where it was deposited onto a flexible Ultraviolet PolyEthylene Terephthalate (UV-PET) and laminated on to the substrate. The authors exposed samples with ALD barrier, and other barriers for comparison, to accelerated degradation including 1000 hr. damp-heat, 1200 hour Ultra Violet (UV), and 10 freeze-thaw cycles. The authors verified that an ALD coating on Polyethylene naphthalate

(PEN) (5 mils thick) polymer can reduce WVTR from ~1 g/m^2-day, for the bare polymer, to ~ 6x10^{-6} g/m^2-day at room temperature. As a result, these ALD diffusion barrier films are very attractive as PV encapsulation layers to meet and satisfy the international standard (IEC 61646), which requires the module efficiency does not degrade below 100% after 1,000 hours in an environment of 85C° and 85% relative humidity (RH) [10]. Therefore, single or double layers of Al_2O_3 deposited by atomic layer deposition (ALD) are excellent transparent front moisture barriers for $CuInGaSe_2$ devices.

2. Barrier Film Fabrication Process

The substrate material used in the present study was Polyethylene naphthalate (PEN), and the thickness of this material is specified to be 125 microns. This material has a good transparency and relatively low cost but it has a high density of "pits" from fillers and belt marks and other defects from dust and surface scratching. These features are believed to be a source of shunt defects in the dielectric [11]. Hence, the surface quality needs to be improved to reduce possible defects to an acceptable level. Therefore, another PEN thin-layer of approximately 3-4 microns thick was applied on top of the PEN substrate to planarise the pits and spikes features. Following planarisation a barrier film of Al_2O_3 was deposited by thermal and plasma-assisted ALD employing Tri-methyl aluminium Al $(CH_3)_3$ precursor dosing together with a H_2O oxidant source. ALD is a unique process that produces dense, nearly pinhole-free thin films that are ideal for gas diffusion barriers. The ALD can also effectively coat the substrate with a highly conformal film, control the film thickness precisely, and tune the film composition flexibly [12]. However, ALD films can suffer from process-induced defects that inhibit their stability [13]. In this study, six representative Al_2O_3 ALD samples processed by the Centre for Process Innovations (CPI), which are coded in pairs as (12k1001, 12k1002), (12k0901, 12k0902), (12K0803 and 12K0804), were assessed. These samples have an 80mm diameter area that has been ALD coated with 40nm Al_2O_3, where each pair of samples was prepared in a clean room under different conditions shown in table 1.

Table 1. Shows the samples condition

Sample No	Practice No	Conditions
12k1001 12k1002	Practice 1	Polymer surface unprotected before loading for ALD
12k0902 12k0901	Practice 2	Polymer surface protected to the last moment before loading into ALD. However, some visible scratches were reported on sample 12k0902
12k0803 12k0804	Practice 3	Contact cleaning of the polymer before ALD

3. Water Vapour Transmission Rate (Permeation Test)

In order for the next generation of CIGS PV modules to survive > 20 years, they require barriers with WVTR < 1×10^{-4} g/m²/day, using materials with low defects density [10]. The permeation rates are often used a key measure of how well the barrier film maintains the module performance. Usually a system to measure WVTR comprises a wet and adjacent dry chamber separated by a sheet of barrier material under test as shown in Fig (2). The water vapour transmission rates (WVTR) of the study were made according to Isostatic Standard test method (MOCON®) at specified conditions of (38C° and 90% RH respectively). This method involves the test specimen being held such that it separates two sides of a test chamber as shown in the Fig (2), where all water vapour which enters is converted to a measurable charge [14]. The method uses the following basic principle: one side of the sample is exposed to the gas or vapour to be studied (feeding side); this can be done statically or with a continuous stream of permeant gas to maintain a constant pressure/concentration. On the detector side the permeating gas or vapour is swept away with a carrier gas (usually nitrogen) and fed into a coulometric phosphorous pentoxide sensor. The permeability of the membrane is determined from the amount or rate of permeation and experimental parameters such as time, sample area, sample thickness, pressure difference, concentrations, etc. In order to investigate which type and size of the micro and nano-scale defects which have a negative effect on the PV barrier performance and lifespan, the WVTR results were initially concealed so all surface topography analysis was conducted blind with no knowledge of the WVTR values.

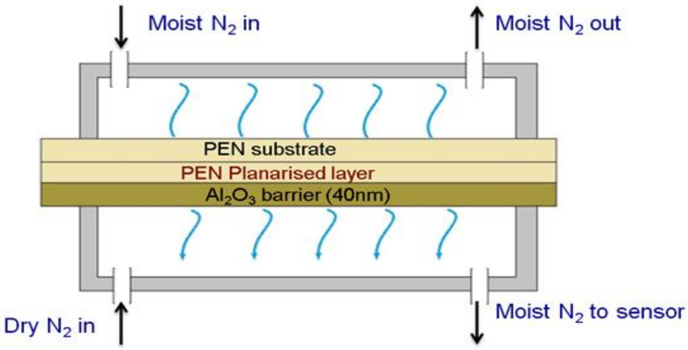

Figure 2. MOCON instrumentation test

Table 2. MOCON Technical Specifications

WVTR Range	5 x 10 $^{-4}$ gm./(m^2 - day) - 5gm/(m^2 - day)
Sensor	AQUATRACE®
Test Temperature Range	(5 - 50 ° C)
RH	Films - 100% RH
Test Sample Sizes	Films - 80 cm^2

4. Surface topography Characterisation

The characterisation of the Al_2O_3 ALD barrier film surface topography has been implemented to aid the interpretation of the functional properties of the micro and nano-scale features, which are postulated as being directly responsible for the degradation of the whole PV module. The main purpose of this study is to assess which type and size of surface topography features have a negative effect on the PV module performance and lifespan. To capture all the potential features which might be classified as "significant defects", three key metrology techniques were employed to characterise the samples' surfaces at different scales of measurements, and acquire both two-dimensional (2D) and full areal surface topography information over varying fields of view. These techniques were Optical Microscopy, Scanning Electron Microscopy, and White Light Scanning Interferometry.

Initially an optical microscope (Keyence VHX-600 digital HD CCD), equipped with 20 to 200× objective lenses was utilised in a clean room environment for initial characterisation of the samples. This technique was employed to give an initial indication of the types of surface features existing on the samples' surfaces before carrying out any further measurements. The investigation showed that, different types of features were noted on each sample; these features are different in terms of their type, width and height. A typical example of these features is shown in Fig (3). The figure shows a pit type feature which has allowed the water vapor to permeate through the barrier causing delamination of the Al_2O_3 layer from the planarised polymer layer around the pit boundary.

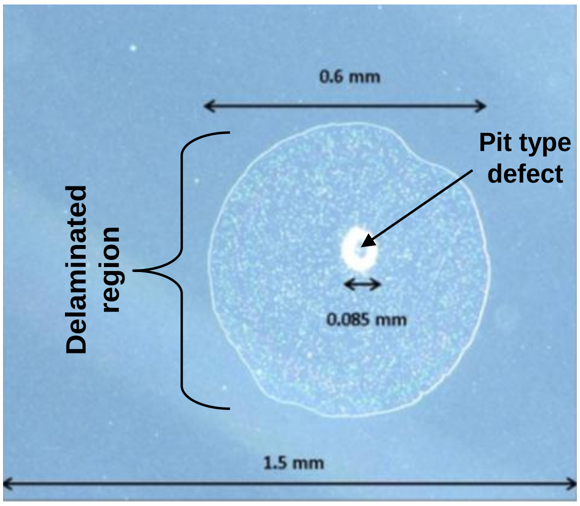

Figure 3. Form and scale of large defect feature

The optical microscopy (Keyence) in fact can show useful magnification only up to 200 times. To go beyond the limitations of this instrument, a FEI Quanta 250 field emission gun environmental scanning electron microscopy (FEG-ESEM) was performed to image the Al_2O_3 barrier layers. The instrument has a higher resolution, higher magnification (up to 2 million times) and greater depth of field compared to the optical microscopy. The instrument allowed for the visualisation of the structures of the Al_2O_3 layer that would normally be not visible by the optical microscopy. A cross-sectional electron micrograph was collected near the edge of the Al_2O_3/polymer structure, see Fig (4a).

To better image the surface of the Al_2O_3 layer a sample tilt of 40° and electron beam energy of 30 keV was employed. Utilizing these imaging conditions in SEM increases the surface sensitivity of the technique and makes it possible to observed small surface features. The investigation of the typical defect which previously detected by the optical microscopy was carried out in the ESEM, see Fig (4b). The image shows a 40nm Al_2O_3 barrier layer which exhibits pit like defects between 100nm to 500nm in diameter on the surface.

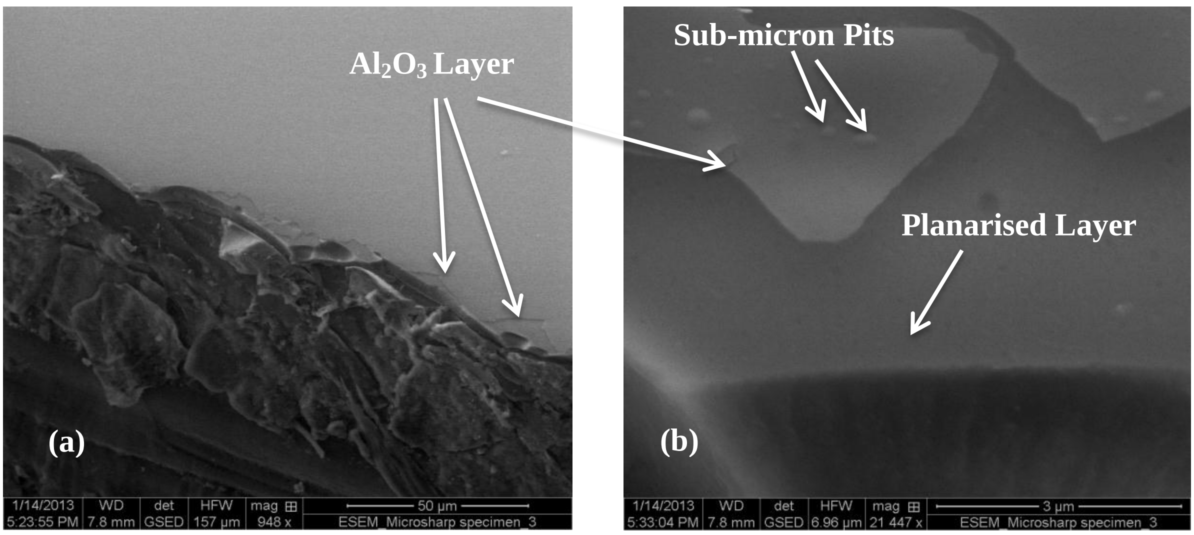

Figure 4. ESEM of defects in Al_2O_3 barrier layer (a) Al_2O_3/polymer cross-section, (b) typical pits type defect

4.1. 3D Surface topography analysis

While the ESEM and the optical technique (Keyence) can only characterise the samples' qualitatively, White light scanning interferometry (Ametek Taylor Hobson) Coherence Correlation Interferometer (CCI) 6000 [6] was used to conduct areal surface analysis over a relatively large field of view without contacting or otherwise damaging the samples. The data taken from the CCI can provides a number of important areal surface texture parameters, with a nanometer-level accuracy and repeatability, making them ideal to predict the functional performance of the samples. The investigation in this study was performed on the previously described samples (see section 2); where100% of the overall area was measured on each sample (≥ 2000 measurements) using X20 objective lens, and this lens allows this instrument to measure a sample area of approximately $1mm^2$ (imaged onto a CCD array of 1024×1024 pixels).

5. Results and Discussion

The WVTR for each sample after stabilisation time of five days is shown in table (3). There were three distinct groups of rates; these were classified as equal, below and above the MOCON detection limit of ($5x10^{-4}$ g/m²/24 hrs.).

Table 3. WVTR values

Sample No	AlO_x thickness	WVTR (g/m²/24 hrs.)
12k1001	40nm	$5x10^{-4}$ (equal to detectable level)
12k1002	40nm	$<5x10^{-5}$ (below detectable level)
12k0902	40nm	$1x10^{-3}$ (above detectable level)
12k0901	40nm	$<5x 10^{-4}$ (below detectable level)
12k0803	40nm	$6x10^{-4}$ (above detectable level)
12k0804	40nm	$<5x10^{-4}$ (below detectable level)

The presence of defects is postulated to be directly responsible for higher WVTR levels. As a result simple counting all the defects (significant or non-significant) as shown in Fig (5) based on the visual assessment if the CCI data was undertaken. In this initial phase no specific criteria is applied as a means of identifying which defects are responsible for the high WVTR value an no correlation was obvious as to which defects were responsible for the WVTR. Thus, to evaluate functionally significant attributes, such as the defects density, size and distribution feature parameters were used to effectively discriminate between the most significant and non-significant defects,

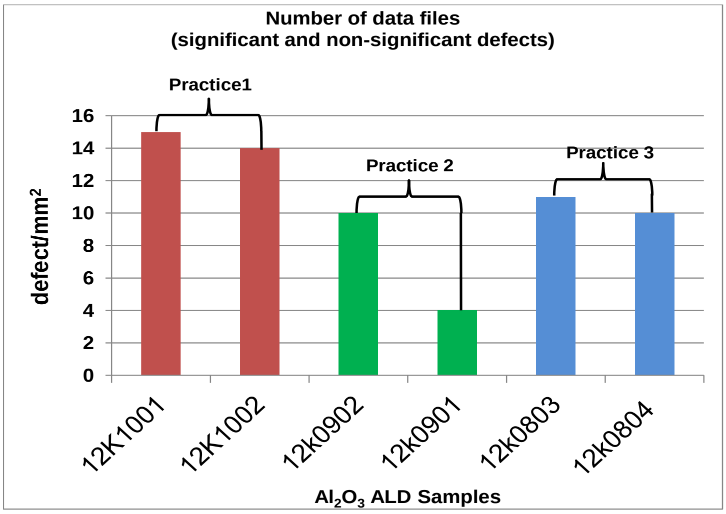

Figure 5. All defects count for Al_2O_3 ALD samples

5.1 Areal feature parameters

Choosing a set of areal parameters which are functionally correlated in such applications is a particularly difficult topic. Noise and measurement errors can also create artificial "small" insignificant features which need to be accounted for. It is therefore essential to distinguish between those features that are functionality significant from those which are non-functionally significant. The solution to this problem in most cases is usually based on analysing large amounts of experimental data [15]. To facilitate the examination of the relevant surface texture, the waviness and form components were removed using a suitable robust Gaussian filter at 0.025 cut-off length [16].

Numerous numerical parameters have been proposed previously [16, 17] and in the present study initially only simple amplitude parameters were investigated. The average roughness parameter Sa results are shown in Fig (6) does not clearly differentiate between the most defective and non-defective samples. However, this parameter has shown that samples coded (12k001, 12k0902 and 12k0803) have a higher average roughness variations than the other samples, and this was be attributed to the existence of larger defect sizes on these samples than others. This conventional analysis method (which use all the data at all scales) has shown to be deficient if functionally significant topographic features need to be characterised. Using this parameter, the results showed no clear correlation with the WVTR results.

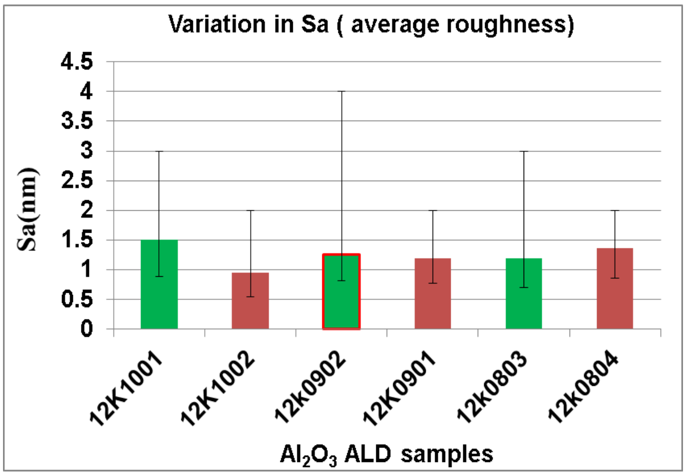

Figure 6. Variations in roughness average

Table 4. Roughness average mean values

Sample No	Sa parameters mean value (nm)
12k1001	1.51
12k1002	0.94
12k0902	1.26
12k0901	1.19
12k0803	1.19
12k0804	1.36

5.2 Feature segmentation analysis

Wolf pruning, as defined in ISO 25178-2, allows the detection of significant features on the barrier surfaces and their characterization in terms of dimension, area, volume, shape or morphology. Wolf pruning at different thresholds, produces different counts of the number of significant features. The present study is based upon the supposition that defects above a certain scale determine the water vapour transmission through the barrier coatings. To this end feature segmentation analysis [17] was implemented in order to separate the significant from non-significant surface topography features. Feature parameters are not specifically defined by an equation, as are field parameters but rather use a toolbox (Surfstand) of pattern recognition techniques. The characterisation consisted of five steps; (1) selection of type of texture feature, (2) segmentation, (3) determine the significant features, (4) selection of feature attributes, and (5) quantification of feature attributes statistics. Therefore, a method of area pruning was performed by trying out various segmentation criteria. The segmentation was applied by means of an "iterative" process. The protocol used for characterising the barrier films was as follows. Firstly, the surface was filtered to eliminate data noise, where the box filtering (Gaussian filtering) uses a cut-off of 2^n points; where n is the smooth level (from 1 to 5), and n was specified to be 5. After the smoothing process, edge processing was performed on the data using a Sobel type operator [19]. The edge data is then "pruned" by means of Wolf pruning [17], where all data elements below 1% of the Sz value are combined, and those elements higher than 1% Sz were retained as significant. Following Wolf pruning an area prune was applied where if an area was found to be less than 2.5% of the total area (this area being defined by optical and SEM analysis) it was deemed insignificant and combined with its neighboring region. Figure 7 (a-b) show defects following the segmentation process for two different samples. The figure shows the power of the procedure for extracting defects from the surface data. Following the extraction the defect density for significant defects can be simply calculated.

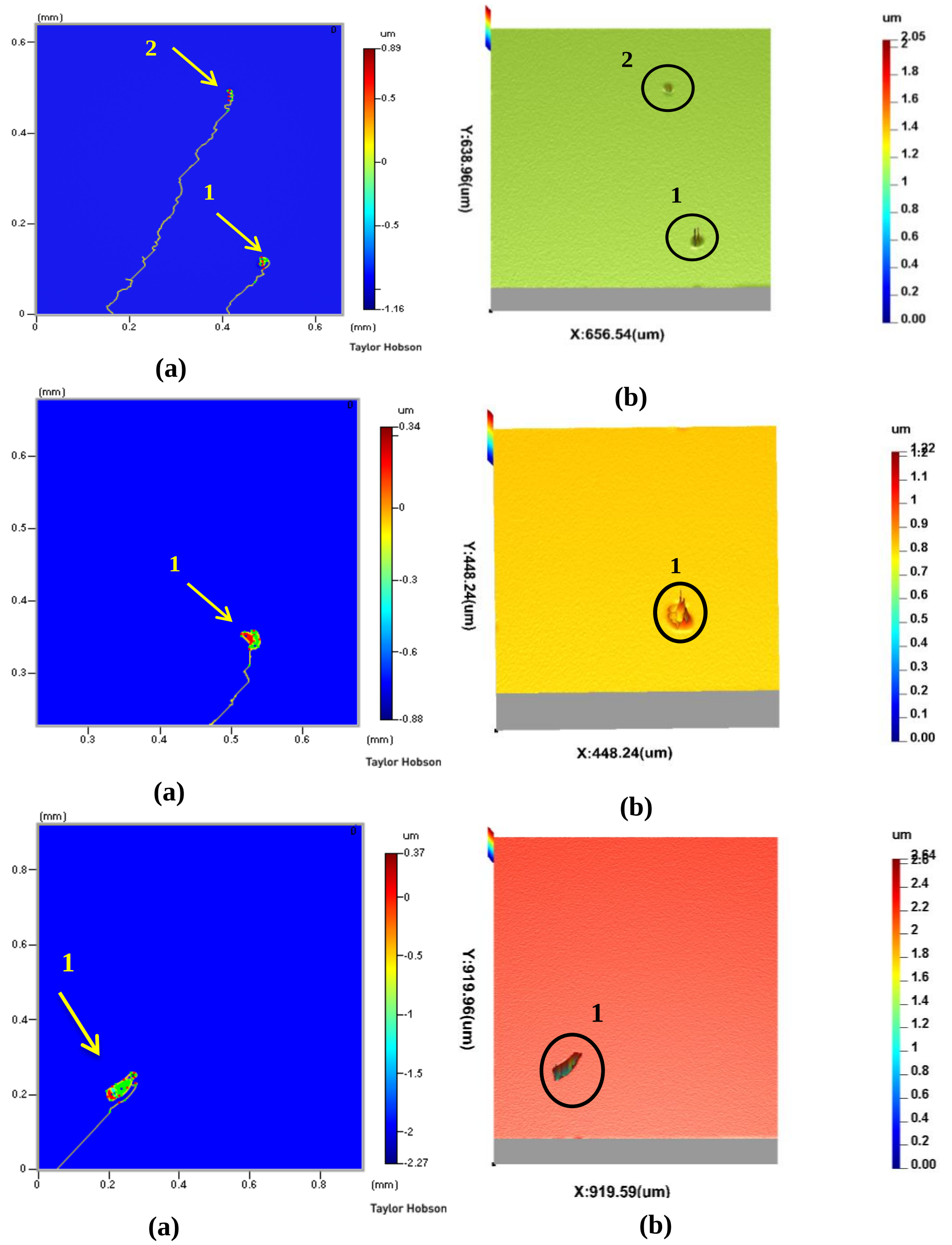

Figure 7(a). Defects count after segmentation

Figure 7(b). Defects before segmentation

5.3 Correlation between defects size-scale and WVTR.

As a result of the lack of correlation between the defects size-scale and the WVTR values using the conventional surface analysis method (S_a-parameter) as mentioned in section (5.1), segmentation analysis [16,17,18,19] was carried out (using the criteria outlined above) on the data measured by the CCI instrument.. The results show that for each pair of surfaces corresponding to a differing pre processing of the polymer prior to coating that, the sample with the highest WVTR value (12k0902) corresponds to the sample with the highest defect density. The sample with the lowest WVTR value (12k0901) shows the lowest defects density. This sample had the least contaminating processing prior to coating. Finally, it is interesting to note that where visible large scratches were reported (sample 12k0902) the highest defect density and WVTR occurred.

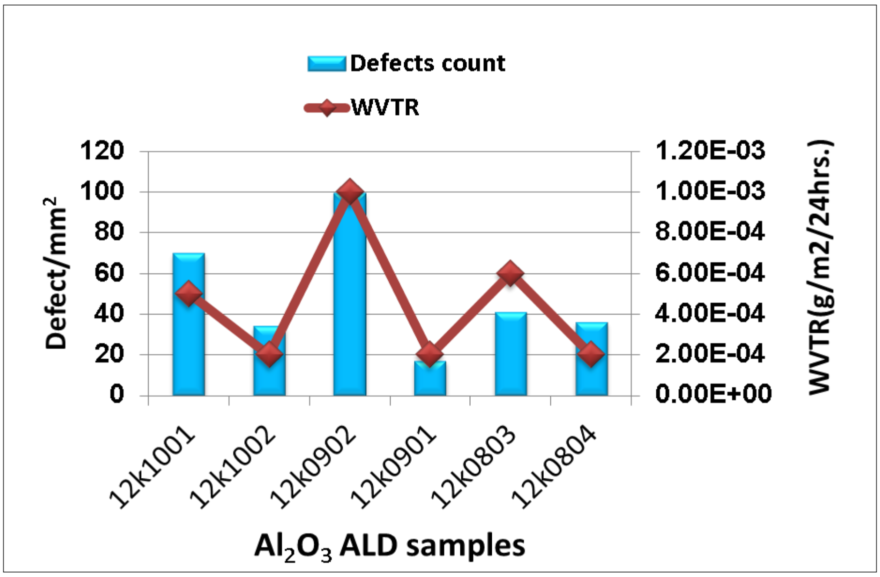

Figure 9. Defects density versus WVTR values

The results seem to show that for the Al_2O_3 ALD barrier coating a small number of large defects dominates the WVTR and thus these defects should be the focus of any detection system.

6. Conclusion

Aluminum oxide (Al_2O_3) films deposited by atomic layer deposition are known to be effective permeation barriers due to their uniformity and pinhole-free morphology. Areal surface texture parameters have been shown to be a potentially effective tool to predict the PV module performance and develop a process quality assessment protocol. The type, shape and the size of the defects which have a negative effect on the WVTR value were determined. Surface segmentation through area pruning method with optimized threshold conditions was shown to have the ability to extract information pertaining to significant defects. The approach has indicated that there is a clear evidence of correlation between defects size-scale and the transmission of water vapor through the barrier coating layer. The total permeation rate appears to be determined by the presence of small numbers of larger defects. These results provide novel information to enable the development of automatic detection measurement system based on in the line measurement. Work is continuing to check repeatabiliy of these tests and produce low defect. density substrates.

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References

[1] Schwager, F. (2012). "Encapsulation of Flexible Thin-Film Photovoltaic Cells." 20th World Petroleum Congress Proceedings (978 0 85293 615 3 F17).

[2] Rossi, G. and M. Nulman (1993). "Effect of local flaws in polymeric permeation reducing barriers." Journal of Applied Physics 74(9), pp. 5471-5475.

[3] Graff, G. L., R. E. Williford and P. E. Burrows (2004). "Mechanisms of vapor permeation through multilayer barrier films: Lag time versus equilibrium permeation." Journal of Applied Physics 96(4): 1840-1849.

[4] Groner M.D.; Elam J.W.; Fabreguette F.H.; George S.M (2002). Electrical characterization of thin Al_2O_3 films grown by atomic layer deposition on silicon and various metal substrates. Thin Solid Films, Vol. 413, No 1, pp. 186-197(12).

[5] J. S. Britt, E. Kanto, S. Lundberg, and M. E. Beck, Proc. (2006) 4th IEEE World Conference Photovoltaic Energy Conversion (Waikoloa 2006),pp. 352-355.

[6] Brémaud, D. (2009). Investigation and Development of CIGS Solar Cells on Flexible Substrates and with Alternative Electrical Back Contacts. Switzerland: A dissertation submitted to ETH ZURICH for the degree of doctor of science.

[7] Matti Putkonen, D. S. T. (2011). "Atomic Layer Deposition Technology from R&D Efforts to Industrial PV Production." (Laboratory of Inorganic Chemistry, University School of Science and Technology , Espoo, Finland), pp. 1-44.

[8] P. F. Carcia, R. S. McLean, M. H. Reilly, M. D. Groner, and S. M. George (2006), Ca test of Al_2O_3 gas diffusion barriers grown by atomic layer deposition on polymersAppl. Phys. Lett. 89, 031915.

[9] Hegedus, S., P. F. Carcia, R. S. McLean and B. Culver (2010). Encapsulation of $Cu(InGa)Se_2$ solar cells with ALD Al_2O_3 flexible thin-film moisture barrier: Stability under 1000 hour damp heat and UV exposure. Photovoltaic Specialists Conference (PVSC), 2010 35th IEEE.

[10] Carcia, P. McLean, R and Hegedus, S. (2010). ALD Moisture Barrier for Cu (InGa) Se_2 Solar Cells. The society for solid-state and electrochemical science and technology. 2 (20), 1435.

[11] Almanza-Workman, M. (2012). "Planarization coating for polyimide substrates used in roll-to-roll fabrication of active matrix backplanes for flexible displays." HP Laboratories: 1-12.

[12] George, S. M. (2010). "Atomic Layer Deposition: An Overview." 110(1): 111–131.

[13] A Bulusu, H. K., D Samet and S Graham Jr (2013). "Improving the stability of atomic layer deposited alumina films in aqueous environments with metal oxide capping layers." Journal of Physics D: Applied Physics 46084014(8).

[14] Wennerberg, J. (2002). Design and Stability of Cu (In, Ga) Se_2-Based Solar Cell Modules. Acta Universitatis Upsaliensis. Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 683.91pp. Uppsala. ISBN 91-554-5214-0.

[15] De Chiffre, L., et al. (2000).Quantitative Characterisation of Surface Texture. CIRP Annals - Manufacturing Technology. 49(2), pp. 635-652.

[16] Stout, K. J., Sullivan, P. J., Dong, W., Mainsah, E., Luo, N., Mathia, T. & Zahouani, H. (1993). The development of methods for the characterisation of roughness in three dimensions. EUR(Luxembourg).

[17] International Standard (2012). ISO 25178-2:2012(E), Terms, definitions and surface texture parameters. Switzerland. 1-47.

[18] Wang, J, Jiang, X, Gurdak, E., Scott, P. J., Leach, R., Tomplins, Blunt, L. (2011) Numerical characterisation of biomedical titanium surface texture using novel feature parameters. Wear, 271 (7-8). pp. 1059-1065. ISSN 0043-1648.

[19] Blunt L, Xiao. S., “The Use of Surface Segmentation Methods to Characterise Laser Zone Surface Structure on Hard Disc Drives” Wear Vol 27 2011 pp. 604-609