Roll-to-roll Processing of Transparent and Robust Permeation Barrier Films for Flexible Electronics

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ABSTRACT

Water vapor permeability of permeation barrier films and thin film encapsulation coatings is determined both by intrinsic factors: material and technology selection and extrinsic factors: particle contamination, defect formation during processing and robustness in subsequent device integration processes. This paper discusses influence factors and optimization strategies to achieve low permeability gas barrier films that are robust in roll-to-roll processing and integration steps to devices. Water vapor transmission rates of < $5 \cdot 10^{-4}$ g/(m²d) at 38°C / 90 % r.h. are demonstrated reproducibly in a full roll-to-roll process using a sputtered zinc tin oxide (ZTO) layer on an ultra-clean polyethylene terephthalate (PET) substrate film.

1 INTRODUCTION

Permeation barrier films and coatings are widely used to encapsulate flexible electronic components such as thin film solar cells, organic light emitting diodes or flexible sensors [1]. The purpose of the films is to protect the devices against corrosive gases such as water vapor and oxygen, against mechanical impacts such as scratches and against radiation such as ultraviolet (UV) light.

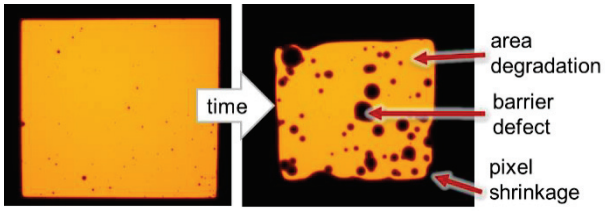

Figure 1: water induced degradation of flexible opto-electronic devices

Water vapor induced degradation of such devices is driven by three mechanisms as shown in Figure 1: (1) local defect formation and growth at particles and defects in the gas barrier system; (2) area degradation through homogeneous water ingress through the barrier film; (3) active area shrinkage through side-leakage caused by interface diffusion or diffusion through adhesive materials. Multiple studies demonstrates that side leakage might account for a considerable high amount of water vapor ingress in a typical device layout [2].

To quantify water permeation through the barrier film itself, two major performance indicators are used [2]:

(1) the water vapor transmission rate (WVTR) that describes – depending on the used measurement method – either an intrinsic water permeability through (a defect free area of) the film or an average permeability on a large sample area including the influence of all surface defects.
(2) the density of local defects on the surface that leads to local damage in devices

It is commonly agreed that OLED devices are very sensitive to such local defects while flexible solar cells suffer mainly from the total amount of water that reaches the device area during the device lifetime [4][5].

The performances of permeation barriers (both WVTR and defect density) are determined by not only the coating technology and material selection but as well by extrinsic factors such as material storage conditions, particle contamination in the machine and cutting and material handling procedures. Application integration processes such as roll-to-roll lamination – in particular at higher temperatures – may further reduce the performance of the coatings [6][7].

In an earlier publication, machine cleanliness and the avoidance of mechanical contact of the coated film were identified as key factors for high quality permeation barrier layers [7]. Based on these results, this paper compares the performances of sputtered metal oxide gas barrier layers on different plastic substrates and evaluates two different possible solutions to achieve a robustness of the surface of these gas barrier coatings in subsequent roll-to-roll processes. The two solutions are (1) lamination of a permanent protective liner film and (2) combination of the sputtered barrier layer with a SiO_xC_y/ polydimethylsiloxane (PDMSO) layer deposited by a hollow cathode assisted plasma enhanced chemical vapor deposition (arcPECVD) process.

2 EXPERIMENT

2.1 Substrate Film Selection

Commonly used plastic substrates for flexible electronics comprise polyethylene terephthalate (PET)

with and without thermal stabilization or polyethylene naphthalate (PEN) films. Recently, ultra-clean PET webs have been developed that exhibit a significantly lower surface defect density compared to standard grade films. The PET webs are co-extruded with a sacrificial protective polymer layer on the surface. This protective polymer will be un-peeled directly before thin film deposition to ensure a particle free surface in the process [8].

This paper compares the performances of sputtered oxide gas barrier layer on:

(1) Standard grade PET Melinex 401 CW (DuPontTeijin Films), 75 µm thickness.
(2) Planarized PEN TEONEX PQA-1 without protective film with 125 µm thickness (DuPont Teijin Films)
(3) Ultra-Clean PET "Peelable-Clean-Surface – Melinex PCS" 125 µm thick (DuPont Teijin Films)

The films distinguish through the intrinsic surface roughness, the density of surfaces defects and particles (measured using optical microscopy) and the use of a coextruded sacrificial protective interleave (PCS).

2.2 Reactive sputter deposition of ZTO

All permeation barrier layers discussed in this study were deposited in the 650 mm wide pilot-scale vacuum roll coaters *coFlex® 600* and *novoFlex® 600*. The coFlex® 600 is shown in Figure 2. The novoFlex® 600 was described elsewhere [9].

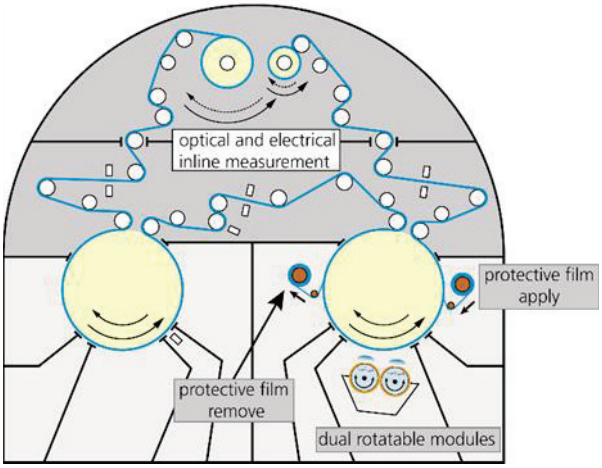

Figure 2: vacuum roll coater *coFlex® 600* with 650 mm coating width and 6 different deposition stations arranged around 2 process drums.

Figure 2 illustrates the machine configuration that was used to process the Melinex PCS PET web. The protective film was removed from the surface after reaching the process drum on which the ZTO layer was deposited. Immediately after ZTO deposition, a new protective film was applied to the surface. This procedure protects the web surface from mechanical contact with any rollers in the machine. All other substrates were wound through the machine without any surface protection.

A reactive dual magnetron sputtering process with zinc tin mixed (52 wt.% zinc) planar (900 x 183 cm² target area) or cylinder (1000 mm long) targets was used for Zn_2SnO_4 (ZTO) gas barrier layer deposition. ZTO has proven to provide the best balance between a dense amorphous layer structure, low water vapor permeability, and deposition rate [10]. The reactive gas (oxygen) flow was adjusted in a closed control loop with the optical emission of zinc vapor in the plasma zone as control variable. Plasma power density was 3.6 W/cm² in a bi-polar pulsed sputtering configuration. The substrate passed the deposition station on a cooled process drum (20°C) with a web speed between 0.2 and 5 m/min.

2.3 Hollow-cathode assisted PECVD of mechanical protection layers

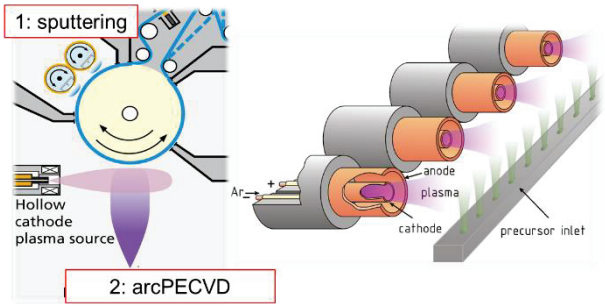

Figure 3: left: arrangement of sputtering and PECVD source in the *novoFlex® 600* machine; right: array of hollow cathode plasma sources

Mechanical protection layers have been deposited in a hollow-cathode plasma assisted chemical vapor deposition process (arcPECVD) in a roll-to-roll configuration as described elsewhere [10]. The hollow cathode is thereby located in deposition chamber directly next to the ZTO sputtering process (Figure 3). A pressure separation chamber between the two processes eliminates the process gas transport between the stations. PDMSO like SiO_xC_y layers were deposited in a reactive gas mixture of argon, oxygen and hexamethyldisiloxane (HMDSO) at a DC discharge current of 100 A at each hollow cathode.

2.4 Barrier layer characterization

Water vapor transmission rates were measured as large-area average on 78 cm² using a Brugger WDDG permeameter at 38°C and 90% relative humidity. The WDDG exhibits a lower limit of detection of $1 \cdot 10^{-3}$ g/(m²d). Samples that reach this lower limit of detection were further measured using tunable diode laser absorption spectroscopy (TDLAS: HiBarSens, SEMPA Systems, Germany) on 134 cm² sample area with a lower limit of detection $<10^{-5}$ g/(m²d). The HiBarSens system was used to confirm the WVTR at elevated temperatures: 60°C/ 90% r.h. and 85°C/ 85% r.h.

Mechanical robustness of the surfacess was evaluated in a combined bending/rolling tester (LSA, Germany) that allows the evaluation of samples with a size of 20 x 20 cm² with a variety of bending radii and

roller surfaces. A roller with 19 mm radius, 3 kg weight (on 25 cm length) and with a metal surface was used to evaluate the robustness of the barrier-films in 1000 bending/rolling cycles at 0.1 m/s rolling speed. The barrier layer was in direct contact with the roller surface.

The surface particle density of the substrates was evaluated using a camera based inspection unit (IsraVision, Germany) with an attached optical microscope (limit of detection: > 1.1 µm particle size).

3 RESULTS AND DISCUSSION

3.1 Permeation Barrier Layer on Clean PET Substrates

Figure 4 illustrates the water vapor transmission rate of zinc tin oxide (ZTO) layers that were deposited on different substrate surfaces. Although using the same sputtering process parameter a variety in the WVTR of up to two orders of magnitude was observed. This difference is cause by two major effects:

(1) different levels of surface contamination which vary from > 1000 particles/cm² (Melinex 401 CW) to < 6 particles/cm² (planarized PEN/ Melinex PCS)

(2) mechanical contact and damage of the surface with rollers and particle contamination during processing.

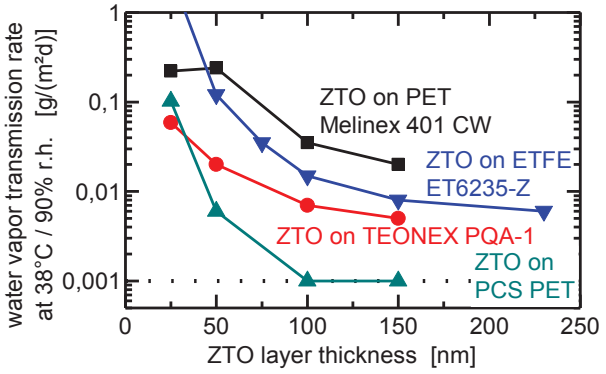

Figure 4. WVTR of ZTO layers on different substrates

The effect of the cleanliness of the machine during processing is well visible when comparing the WVTR of ZTO on the PEN web with the results achieved for the Melinex PCS substrate. The PEN exhibits a clean surface and a planarization coating on the surface. However, it was wound through the machine without a protective polymer film. Therefore, the surface had to pass a set of rollers in the machines both before and after ZTO deposition (see Figure 2). As already described in [7], the surface defect density increases from 6 to 650 defects/cm² during winding through the *coFlex® 600* machine. For the Melinex PCS instead, the protective interleave was removed from the surface after passing the last roller before reaching the ZTO deposition station. Furthermore, a new protective interleave was laminated to the surface immediately after ZTO deposition. The new protective interleave forms a permanent bond with the ZTO surface acting as protective layer in any subsequent process [12].

The ZTO layer on the PCS surface achieved a WVTR below the limit of detection of the BRUGGER WDDG permeameter. Thus the WVTR was measured again with a HiBarSens TDLAS system. Table 1 shows the WVTR of the ZTO layers on PCS for different measurement conditions.

Table 1: WVTR of ZTO on PCS PET measured using different characterization methods and conditions

Layer stack	Method	Conditions [°C/ % r.h.]	WVTR [g/(m²d)]
protective film 25 µm ZTO 0,075 µm Mel.PCS 100 µm	WDDG	38 / 90	$< 1 \cdot 10^{-3}$
	TDLAS	38 / 90	$3.2 \cdot 10^{-4}$
	TDLAS	60 / 90	$1.8 \cdot 10^{-3}$
	TDLAS	85 / 85	$1.5 \cdot 10^{-2}$

3.2 PECVD mechanical protection layers

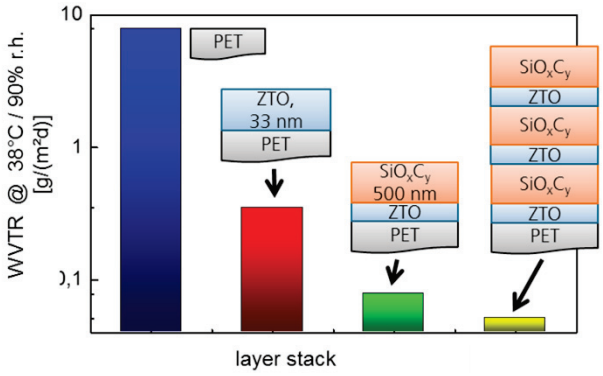

Figure 5: effect of $SiO_xC_yH_z$ coating on ZTO barrier layers

Adding a 25 µm protective polymer layer to the barrier layer surface is, however, not suitable for all specific application cases and not possible in some machine configurations. In particular, side-leakage through the protective polymer or the requirement for subsequent high temperature processes may require alternative solutions to the laminated polymer layer. Such a solution could be the in-line/simultaneous deposition of a SiO_xC_y plasma-polymer layer immediately after the ZTO deposition on the same process drum. Figure 5 compares the WVTR of thin (33 nm) ZTO layers on a standard grade PET (Melinex 401 CW) deposited in a roll-to-roll configuration with and without a 500 nm thick protective SiO_xC_y top coat. All samples were wound through the machine at 2 m/min without using protective interleaves. Although the SiO_xC_y layer does not exhibit an own barrier performance, it results in an improvement of the WVTR of the ZTO layer by a factor 3. Stacking multiple ZTO / SiO_xC_y dyads (dual layers) results in a reduction of the WVTR to ≈ $2 \cdot 10^{-2}$ g/(m²d).

The mechanical protection performance thereby depends on the thickness of the PECVD layer. Figure 6 depicts the WVTR of a dual stack of ZTO and arcPECVD SiO_xC_y on a PET Melinex 401 CW before and after the

bending/rolling test described above with 200 rolling cycles. After the test, the WVTR of an unprotected ZTO single layer is increased by an order of magnitude while the SiO_xC_y layer may effectively protect the ZTO surface if its thickness is 1 µm and higher. As the ratio between the deposition rates of ZTO and the PECVD process can be adjusted between 1:5 and 1:20, an 1 µm thick SiO_xC_y layer can be deposited on a 50 nm ZTO layer simultaneously in one deposition run (at 1 m/min). This provides protection of the ZTO surface before contact with other rollers.

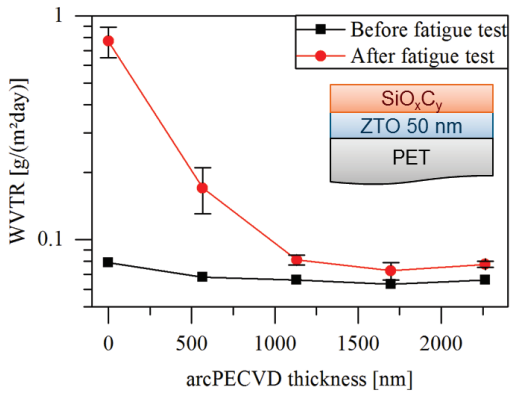

Figure 6: WVTR of a dual stack ZTO + SiO_xC_y on PET Melinex 401 CW before and after a bending test

Using the PCS PET web with ZTO and lamination of a permanent protective polymer layer, WVTR of $<10^{-3}$ g/(m²d) at 38°C / 90% r.h. were maintained even after 1000 bending/rolling cycles. Further, the system has proven to be robust in subsequent roll-to-roll processes such as lamination onto flexible electronic devices. Manufacturing of 13 different rolls (200 m length each) under similar process conditions has revealed a reproducible WVTR of $(3.2 \pm 1.8)\cdot10^{-4}$ g/(m²d) both across width and length of one roll and between the 13 rolls.

4 CONCLUSIONS

Performance of permeation barrier coatings and encapsulation films not only depend on the used materials and deposition technology but also on extrinsic factors such surface particle contamination and process damage in roll-to-roll processes. This study demonstrated reproducible, cost-effective deposition of mechanically robust gas permeation barrier films that can be used for flexible electronics encapsulation with a WVTR $< 5\cdot10^{-4}$ g/(m²d) at 38°C / 90%. The films are based on an ultra-clean surface PET that is provided with a sacrificial protective polymer layer.

Two strategies for mechanical protection of the coated barrier layer surface were discussed: (1) the lamination of a protective polymer layer / interleave and (2) the in-line deposition of a SiO_xC_y protective layer using a high-rate hollow-cathode activated PECVD process. Both increase robustness to roller contact and mechanical damage significantly. Further, the PECVD process has the potential to be used for the direct thin film encapsulation of devices as it does expose the surface to high temperature or radiation.

5 ACKNOWLEDGEMENTS

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