Vacuum plasma treatment and coating of fluoropolymer webs – challenges and applications

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1 Introduction

The copolymer ethylene tetrafluoroethylene (ETFE) combines the favorable properties of both ethylene: good processing behavior like hydrocarbon polymers and tetrafluoroethylene: superior weathering stability, chemical resistance and thermal stability [1], [2]. It has a high optical transmittance from ultra violet to near infrared wavelength range. ETFE is used in architecture, e.g. membrane roofs or facades in stadiums, shopping malls and airports, and photovoltaic modules as front-side encapsulation [3]. However, thin film deposition on fluoropolymer webs faces several critical challenges because of poor mechanical and thermo-mechanical properties, inferior surface quality with respect to roughness, surface energy, and low adhesion of coated layers.

This paper discusses solutions for vacuum coating and plasma surface treatment of ETFE webs to enhance layer adhesion properties, reduce residual reflection and to deposit low water vapor permeation barrier layers. Based on these results, the application example of a front side encapsulation film for solar modules according to Figure 1 will be evaluated with respect to permeation barrier and optical performance as well as long term stability in an outdoor environment.

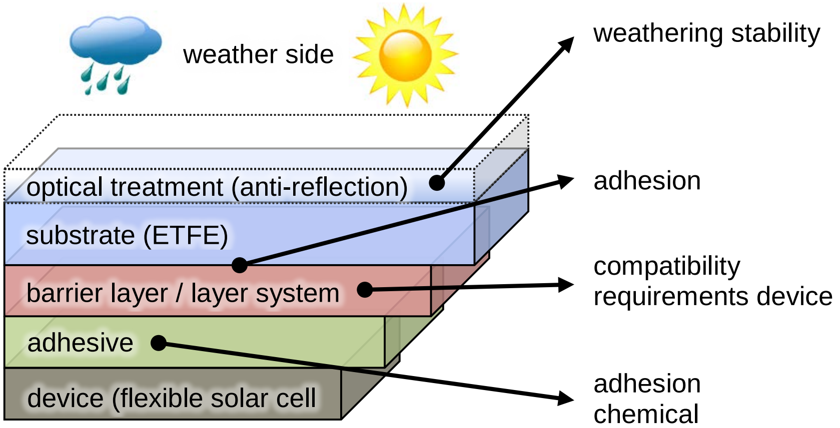


Figure 1. Structure of functionalization of ETFE for connection to a device as well as main challenges for the optical treatment and barrier layer.

2 Experimental

2.1 substrate

The substrate was ethylene tetrafluoroethylene ET6235-Z from nowofol® Kunstoffprodukte GmbH, Germany with a film thickness of 50 µm for experiments of optical treatment. A 100 µm thick ETFE film from the same supplier was used for coating of barrier layers and layer systems as well as adhesion promotion pretreatment. Polyethyleneterephthalat (PET) Melinex 401 (DuPont Teijin Films) with a film thickness of 75 µm was used as reference material.

2.2 vacuum processes

All experiment shown in this paper were done in a roll-to-roll-coater as shown in Figure 2 using dual magnetron systems (DMS).

Permeation barrier coatings were applied using a reactive sputtering process with zinc-tin targets (52 wt-% zinc and 48 wt-% tin) and an oxygen flow that was set in a closed loop control with the optical emission of excited Zn atoms as control variable. Zinc-tin-oxide (ZTO) shows lowest water vapor transmission rate (WVTR) compared to other reactively sputtered barrier materials and was therefore used for the experiments [4]. The backside of the polymer was cooled to 20°C by contact the water-cooled process drum. Web speed was adjusted between 0.2 m/min and 1.2 m/min and the web tension was kept at 100 N for a web width of 400 mm.

Additionally, barrier layer systems were prepared using a combination of inorganic zinc-tin-oxide layers and organic-inorganic hybrid-polymer (ORMOCER®). ORMOCER®-layers deposition was performed at Fraunhofer IVV, Freising, Germany in an atmospheric roll-to-roll-coater using reverse gravure coating and thermal drying at 120°C as described in [5]. More details on the ORMOCER® material itself are given in [6].

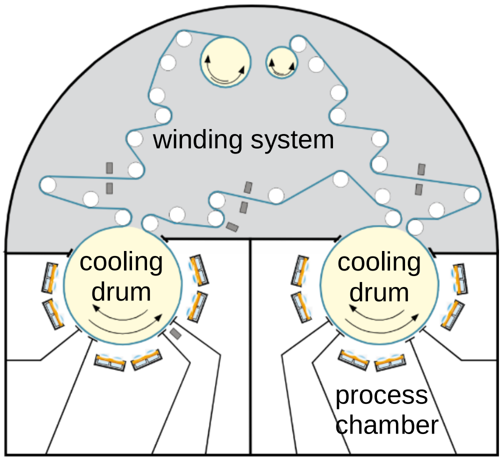


Figure 2. *coFlex® 600* roll-to-roll coater with dual magnetron systems.

Surface nanostructuring was done using a reactive plasma etching process with a dual magnetron as plasma source equipped with aluminum targets. The reactive gas was pure oxygen. The process itself based on the generation of negative oxygen ions which were accelerated to the substrate resulting in a partial etching of the ETFE surface as described in [7]. The web speed was varied in a range between 0.1 m/min and 2 m/min. The process pressure was 0.3 Pa.

2.3 Characterization

Water vapor transmission rate was measured with the coulometric permeameter WDDG (BRUGGER Feinmechanik GmbH, Germany). The sample size was 78 cm² measuring the average (effective) WVTR including all pinhole defects in the sample. The lower measurement limit of the sensor is $1 \cdot 10^{-3}$ g/m²d with an uncertainty of ± 2%. The measurement conditions was 38°C at 90% relative humidity (r.h.) for all samples.

Optical transmission and reflection were measured with a spectral photometer (Lambda 900; PerkinElmer) in a wavelength range from 250 nm to 2500 nm and with an integrating sphere. The transmittance value T_{CIGS} was determined by weighting the measured transmission spectra with the emission spectra of the sun at AM1.5g and the spectral sensitivity of a copper-indium-selenide (CIGS) solar cell [8]. CIGS thin film solar cells have been chosen with respect to their application relevance and high efficiency for large scale energy conversion.

Adhesion measurements were performed according to IPC-TM-650 standard using a 90° peel test. The adhesive tape was TESA 7475.

The surface of cast film and nanostructured ETFE was analyzed by scanning electron microscopy (SEM) (SU8000; Hitachi) with an acceleration voltage of 2 kV measuring the secondary electron (SE) image. The low acceleration voltage allowed scanning the surface without prior deposition of a conductive gold layer.

Weathering stability of the cast film and nanostructured ETFE was examined on top of the roof of the technical building of the Fraunhofer FEP in Dresden, Germany. The samples were adjusted southwards with nearly 45° tilt. The transmission and reflection spectra were measured monthly without any cleaning process.

3 Results

3.1 Adhesion

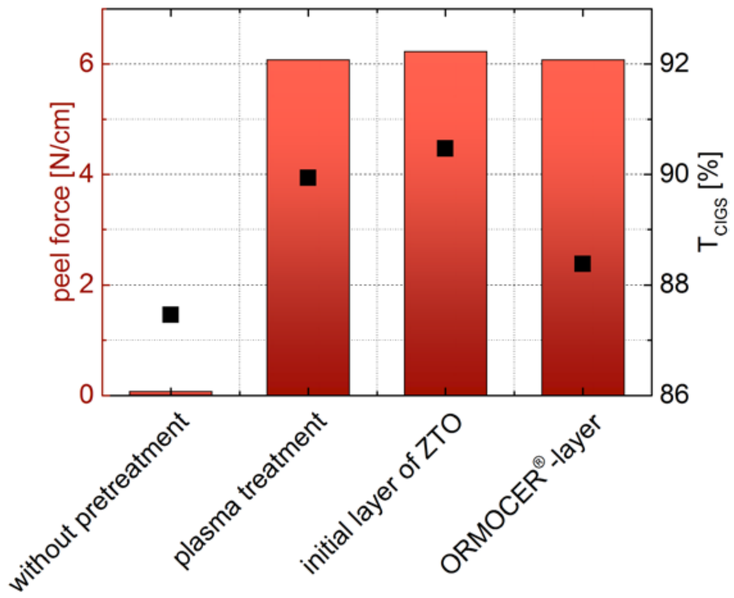


Figure 3. Possibilities of pretreatments to improve the adhesion of aluminum oxide.

The low surface energy of most fluoropolymers results in less adhesion of organic and inorganic coatings. Reactively sputtered inorganic zinc-tin oxide (ZTO) layers and inorganic-organic hybrid polymers (ORMOCER®) show surprisingly good adhesion on ETFE surfaces [9]. But aluminum oxide, a low refractive index material with low water vapor transmission rate shows no adhesion on ETFE. It is know from literature, that plasma treatment changes the surface chemistry of most polymers [10]. The deposition of aluminum oxide after a plasma treatment using an oxygen plasma with a linear ion source (Advanced Energy) results in peel forces stronger than 6 N/cm (Figure 3). Peel forces of aluminum oxide measured after pretreatment do not represent the forces between the layer and the substrate/pretreatment because the interface to the adhesive failed at first. Other possibilities to enhance the adhesion of aluminum oxide are the deposition of thin initial layers of ZTO or wet coating of ORMOCER®-layers.

3.2 Transparent Permeation Barrier

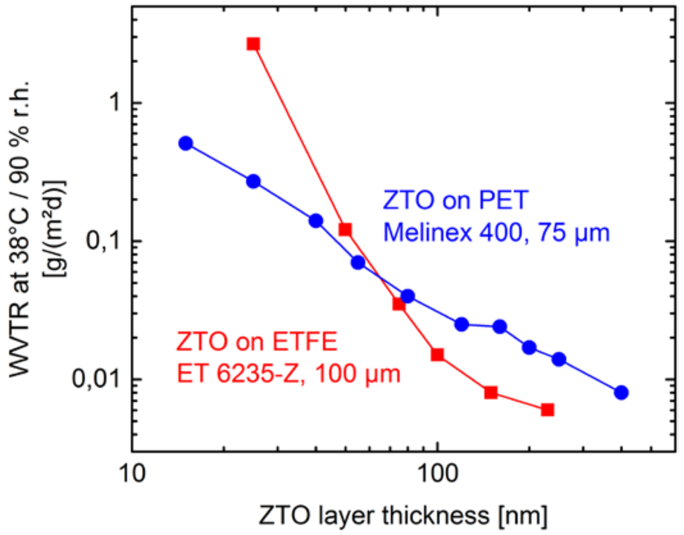
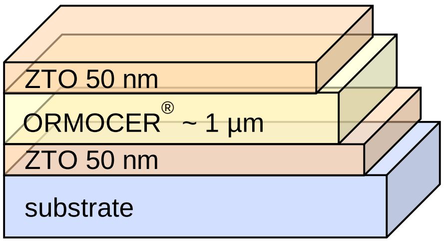
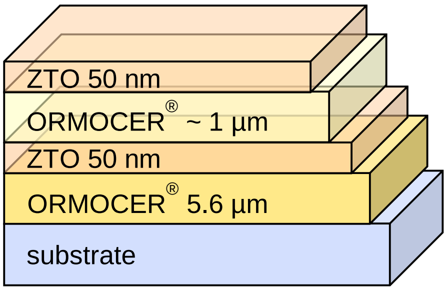


Figure 4. Comparison of permeation barriers on PET and ETFE for different ZTO layer thicknesses.

The water vapor transmission rate of oxide single layers depends on the layer thickness as shown in Figure 4. Although ETFE exhibits a higher surface roughness both on nano-scale (see left SEM surface image in Figure 6) and on larger scale. Both substrates yield roughly the same low water vapor transmission rates when coated with ZTO single layers with a thickness of 50 nm and more. In the range between 100 nm and 250 nm, apparently lower WVTR is achieved with ZTO on ETFE compared to PET. However, this effect is related to a lower particle contamination and defect density on the ETFE surface compared to the specific PET sample used for the measurements. The role of surface contamination for permeation barrier coatings is described in an earlier publication [11]. One possibility to deal with such defect related effects is to apply a multi-layer stack onto the substrate instead of a single layer.

Table 1. Comparison of a state of the art barrier layer system on PET [12] with layer systems on ETFE

Parameter			
Barrier layer system	1		2
Substrate	PET	ETFE	ETFE
WVTR [g/m^{2}d]	0.002	0.035	0.002
OTR [cm^3/m^{2}dbar]	< 0.1	-	< 0.1
T_{CIGS} [%]	76.5	78.3	74.4

The tasks of the polymer layer are interruption of the growth of defects, surface planarization and defect coverage as well as the reduction of mechanical stress to improve the flexibility. A comparison of such a system produced on PET and ETFE shows a difference in WVTR (Table 1). On PET WVTR was measured nearly $1 \cdot 10^{-3}$ g/m^{2}d whereas on ETFE a higher value was determined. Possible explanations for such a high water permeability of the layer system on ETFE are:

1. higher surface roughness on ETFE results in a poor barrier performance of the first ZTO layer
2. thermo-mechanical stress during ORMOCER® printing damages the ZTO layer
3. process tension during ZTO deposition is too high and results in cracking of the ZTO-layer

Starting the barrier stack by depositing an ORMOCER® layer as shown for system 2 in Table 1 results in a planarization of the substrate as shown in [9]. That effect yields a lower water vapor transmission rate of 0.002 g/m^{2}d on ETFE and shows similar WVTR like the state of the art barrier system on PET. A possible explanation for the improved permeation barrier is the planarization effect of ORMOCER®. Another explanation could be the change of the thermo-mechanical properties of ETFE during this first ORMOCER® coating which a known phenomenon also for polyester films and is explained further in [13].

3.3 Optical Treatment

ETFE has a high optical transmittance of around 93.7% at a wavelength of 600 nm. Optical applications such as encapsulation of OLEDs or solar cells benefit from a high transmittance. To increase the transmittance further and thereby enhance the efficiency of such photonic devices, an anti-reflection (AR) treatment is desired. Nanostructuring of the polymer surface results in a gradual change of the refractive index from ETFE (n = 1.39 [14]) to air (n=1). Therefore an anti-reflection (AR) of the surface is achieved [15]. Nanostructured ETFE webs show an improved transmittance of up to 98.7% at a wavelength of 600 nm with using double side plasma surface treatment (Figure 5). This results in a residual reflection of less than 1% per side. However, only a single side treatment is necessary, for the production of a front side encapsulation as shown in Figure 1. A comparison of the surface topography of ETFE cast film and nanostructured ETFE is given in Figure 6.

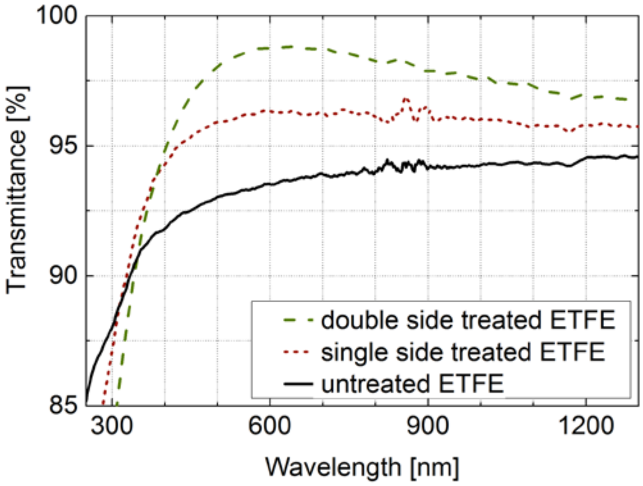


Figure 5. Transmittance of ETFE cast film, single side and double side treated ETFE with thin sputtered SiO_2 top coat [16].

To optimize the AR-effect the etching process itself and the resulting transmittance and surface morphology were investigated in more detail in [17]. In result a maximum transmission increase of around 1.5% per treated side was examined at 0.3 m/min and 1.77 W/cm². The theoretical maximum of transmission increase is 3.1% (absolute) per side in case absorption is negligible. A further improve of the AR-effect results in a $\Delta T_{CIGS} \approx 2.5\%$ with an optimized process as described in [16]. Results have shown a maximum AR-effect of including a thin sputtered silicon oxide top coat and such samples were tested against environmental stability as explained below.

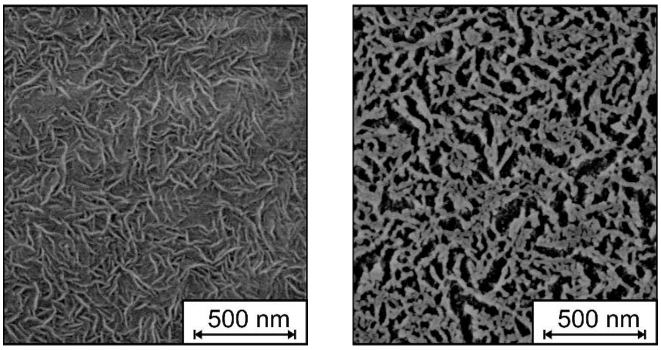


Figure 6. Surface image of ETFE cast film (left) and treated ETFE (right) (according to [17])

3.4 Outdoor weathering test

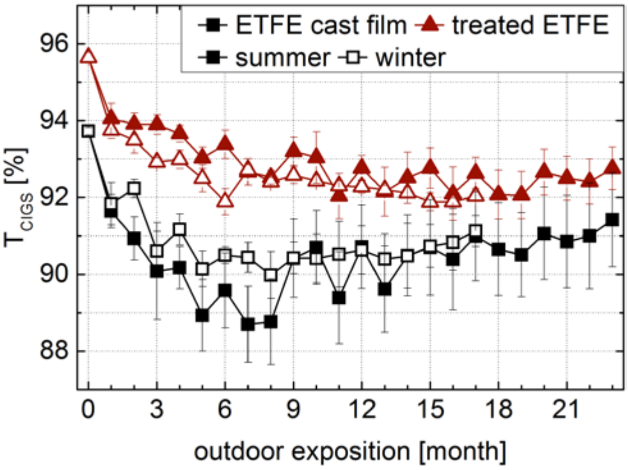


Figure 7. Optical stability of cast film and nanostructured ETFE over 23 month of outdoor exposure

Nanostructured ETFE surfaces need to be stable against environmental effects such as UV irradiation, rain and hail and others to be suitable for encapsulation of photovoltaic cells or other optical devices. Figure 7 illustrates the long time investigation of the optical stability of ETFE cast film and nanostructured samples in an outdoor test. The nanostructured samples were coated with thin silicon oxide top-coat. Nanostructured ETFE maintains a higher optical transmission over the full exposure time of 23 months compared to bare cast film samples. This indicates that the effect of the nanostructures remains active and the structures are not destroyed in outdoor environment. During the first nine months, the transmittance of the cast film decrease and increases slightly afterward but doesn't achieve the initial value of transmittance. Possibly a thin layer of dust / pollution is deposited on the ETFE surface, whereas the nanostructured surface is more resistant against pollution and shows a slight self-cleaning effect.

An influence of the seasons was not observed. The curve progression is similar regardless whether the test is started summer period and winter period. None the less a decrease of the transmittance of the nanostructured ETFE over time is apparent. Further investigations are required to understand whether (cleanable) surface pollution or ageing of the samples causes the transmittance decay over time.

4 Conclusion

This paper demonstrates feasibility of handling and processing of ETFE with vacuum coating and plasma treatment techniques. Possibilities to improve layer adhesion were demonstrated and single layers of inorganic zinc-tin oxide were deposited. The barrier properties are comparable to ZTO layers on PET. Also barrier stacks including a wet coated ORMOCER® layer that was dried at at 120°C were deposited on ETFE with a water vapor transmission rate of 0.002 g/cm². Finally, a plasma etching process was described to achieve anti-reflective surfaces with nanostructures. This nanostructured ETFE shows higher transmittance in the weathering test compared to ETFE cast film over a period of almost 2 years up to now – the outdoor aging test is thereby still running.

However, further research need to be done to get a deeper understanding about the interaction of process parameters in a roll-to-roll process with ETFE films. Especially the structure formation and influence of uniaxial and biaxial stretching need to be examined.

5 Acknowledgment

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6 References

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