

Multilayer barrier structures on ETFE substrate films

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1. Introduction

Thin film photovoltaics based on copper indium gallium diselenide (CIGS) or organic semiconductors has a large potential for the large area production of electrical energy on facades and roofs of buildings [1, 2]. These devices can be produced in cost efficient roll-to-roll coating and printing processes.

A serious disadvantage of CIGS and organic photovoltaics is their sensitivity to oxygen and water vapor from the environment [3, 4]. Photoactive materials and electrodes are degraded in contact with these substances resulting in a decreased efficiency.

Therefore a flexible encapsulation is required to reach an intended device lifetime of up to 25 years. Estimations show that water vapor transmission rates of encapsulation materials for CIGS and organic photovoltaic devices have to be lower than $10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$ [4, 5].

Such high barrier requirements are fulfilled by multilayer barrier structures on top of polymeric films. These structures contain inorganic barrier layers and polymeric intermediate layers deposited as an alternating sequence [6, 7].

The excellent barrier performance of structures of alternating barrier layers is commonly explained by decoupled defects of the inorganic layers resulting in extended diffusion paths within the polymeric intermediate layers [7, 8, 9]. Other explanations refer to the reduction of mechanical stress due to polymeric layers [6] or an increased lag time of permeation; the latter can be caused by extended diffusion paths [10] or by largely differing solubilities of the permeating substance within inorganic and polymeric materials [11].

The high barrier films developed by Fraunhofer POLO[®] alliance utilize the concept of alternating barrier layers in roll-to-roll coating processes [12]. Reactively sputtered Zn_2SnO_4 (ZTO) layers are combined with hybrid polymers (ORMOCER[®] [13]) being applied from the liquid phase on top of polyester substrate films. For the multilayer barrier structure PET Melinex[®] 400 CW / ZTO / ORMOCER[®] / ZTO / ORMOCER[®] a water vapor transmission rate (WVTR) of $(2.0 \pm 1.2) \cdot 10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$ was measured with calcium test at 38°C, 90% r.h. [12].

Consequently the Fraunhofer POLO[®] film exhibits barrier properties in the range that is required for flexible photovoltaics. However, it is not suitable as encapsulation material for long term outdoor applications since polyester films like PET are degraded by UV radiation and humidity in combination with high temperature [14, 15].

Several strategies exist to equip barrier films with UV stable substrate films:

- Protection of substrate films by a UV blocking coating;
- Improvement of the UV stability of polyester films by integration of additives [14];
- Substitution of polyester films by intrinsically UV stable films.

Fluoropolymers, e.g. ethylene tetrafluoroethylene (ETFE), show excellent resistance against UV radiation and also against weathering [16] and therefore qualify well as flexible substrates for encapsulation of photovoltaic devices.

In the joint project *flex25* [17] the Fraunhofer Institutes for Process Engineering and Packaging (IVV), for Organic Electronics, Electron Beam and Plasma Technology (FEP) and for Silicate Research (ISC) currently work on the transfer of the Fraunhofer POLO[®] barrier structure to ETFE substrate films (Nowoflon ET 6235 Z).

2. Dimensional stability of ETFE films

A critical issue of fluoropolymer films regarding their utilization as substrate films for encapsulation materials is their low dimensional stability: Young's moduli of ETFE are about $5 \cdot 10^8 \text{ Nm}^{-2}$ at 23°C and $1 \cdot 10^8 \text{ Nm}^{-2}$ at 120°C [18] and are therefore one order of magnitude lower than the corresponding values $4 \cdot 10^9 \text{ Nm}^{-2}$ and $2 \cdot 10^9 \text{ Nm}^{-2}$ of PET [14].

Used as intermediate layers, ORMOCER[®] coatings are a substantial component of the Fraunhofer POLO[®] barrier structure and have to be dried at a temperature of 120°C . As a consequence of their low Young's modulus at 120°C , ETFE films are significantly strained due to web tension during the roll-to-roll coating process. Since the ETFE film already carries a ZTO layer when the ORMOCER[®] is applied, the strain is transferred to the ZTO layer where it can result in crack formation and therefore degrade the barrier performance [6, 19, 20].

The behavior of ETFE films (Nowoflon ET 6235 Z, thickness $100 \mu\text{m}$) during ORMOCER[®] application at the roll-to-roll lacquering machine of the Fraunhofer IVV was studied systematically; the machine is described elsewhere [12, 21]. In order to understand the combined influence of high temperature and web tension the dimensional change of the films in machine and transverse direction was measured after winding them through the machine at different conditions.

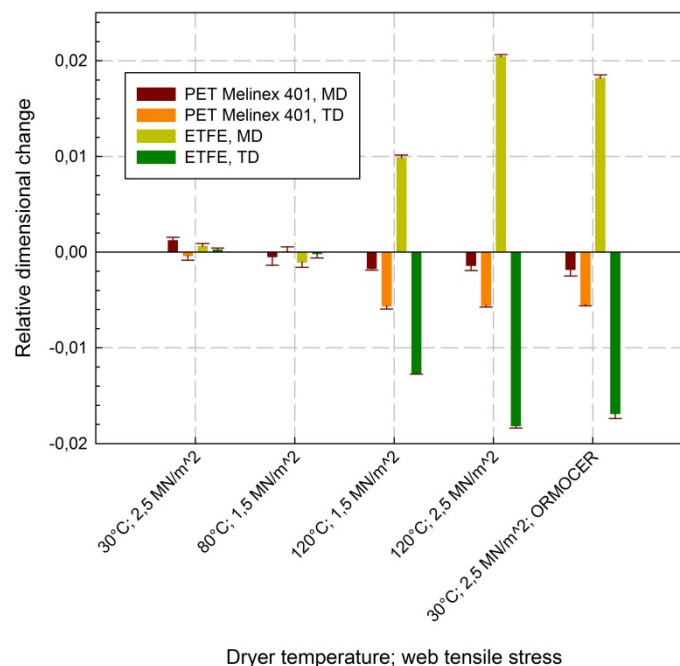


Fig. 1: Dimensional change of ETFE and PET films in the roll-to-roll lacquering machine dependent on temperature and web tensile stress

Fig. 1 shows that the dimensional change of the ETFE film is negligible up to a temperature of 80°C . Significantly different results, however, were observed at 120°C , probably due to the decrease of Young's modulus with increasing temperature and the glass transition of ETFE at 90°C [22]: the film shows a significant elongation in machine direction and a similar shrinkage in transverse direction at 120°C . The values range from 1% to 2%, depending on the web tensile stress. Similar values were obtained when applying ORMOCER[®] during the winding process. These values are in the range of the

crack onset strain of ZTO layers [20] which is defined as the minimum strain at which crack formation can be observed.

The dimensional change of ETFE in machine direction is about ten times higher than the corresponding value for the PET Melinex[®] 401 film; this film shows shrinkage instead of strain in machine direction. These results make clear that the transfer of the Fraunhofer POLO[®] barrier structure from PET Melinex[®] to ETFE is challenging.

The ETFE films which were stressed at different conditions were afterwards coated with ZTO and wound for a second time through the coating machine with temperature set to 120°C. Fig. 2 shows that the dimensional change of ETFE during the second winding is significantly reduced if the film was stressed under the same condition during the first winding.

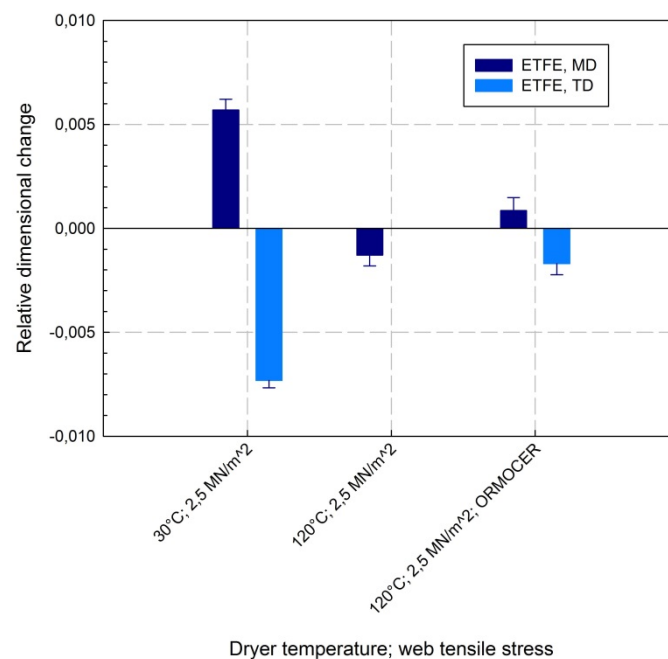


Fig. 2: Dimensional change of the ETFE film in the roll-to-roll lacquering machine at 120°C and a tensile stress of $2.5 \cdot 10^6 \text{ Nm}^{-2}$ after pre-stressing the film at the given conditions

One can conclude that a thermal treatment in the coating machine allows a limited heat stabilization of ETFE films at least eliminating the irreversible contribution to the dimensional change during further processing. Such a thermal treatment is reached by application of an ORMOCER[®] layer on ETFE before ZTO deposition; this ORMOCER[®] primer layer is necessary to obtain high quality inorganic layers on top of the rough surface of fluoropolymer films [23].

3. Permeation through mechanically stressed ZTO coated ETFE films

In order to understand the influence of thermomechanical stress on the barrier properties of ZTO layers on ETFE films the oxygen permeabilities of ETFE / ORMOCER[®] / ZTO (thickness 150 nm) were measured before and after winding them through the lacquering machine at 120°C and a tensile stress of $2.5 \cdot 10^6 \text{ Nm}^{-2}$. Corresponding trials were performed with two other fluoropolymer substrate films: polyvinylidene fluoride (PVDF) and ethylene chlorotrifluoroethylene (ECTFE).

Fig. 3 shows an increase of the oxygen permeability (Q_{O_2}) of two orders of magnitude when the fluoropolymer films are wound through the machine. It can be concluded that the ZTO layers lose their

barrier properties due to thermomechanical stress in the roll-to-roll processes. This barrier loss is probably caused by a reversible dimensional change of the ETFE film during the process since the irreversible contribution described above was eliminated by thermal treatment during the application of the ORMOCER® primer layer before.

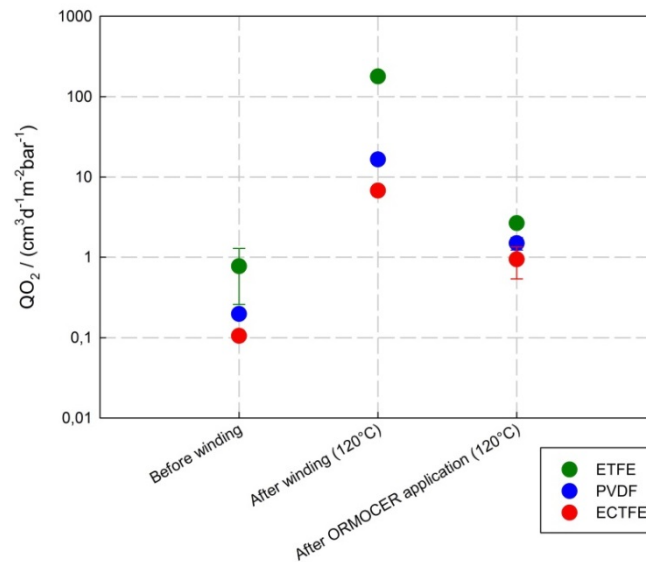


Fig. 3: Oxygen permeability of different fluoropolymer substrate films coated with ORMOCER® / ZTO before and after winding and after ORMOCER® application on top

When an ORMOCER® layer is applied on top of ETFE / ORMOCER® / ZTO lower oxygen permeabilities compared to the pure winding process are obtained due to the synergistic barrier effect between an oxide layer and an ORMOCER® on top of it [13]. However, these permeabilities are in the same range of $1 \text{ cm}^3 \text{ m}^{-2} \text{ d}^{-1} \text{ bar}^{-1}$ as the values before ORMOCER® coating. In contrast, the values measured for PET Melinex® 401 / ZTO / ORMOCER® being a step in the production of the POLO® barrier structure are up to two orders of magnitude lower.

In the view of the intention to transfer the Fraunhofer POLO® barrier structure from PET Melinex® to ETFE the damage of ZTO layers on top of ETFE during ORMOCER® application has to be avoided. The following possibilities seem to be promising:

- Reduction of drying temperature or web tension during ORMOCER® application;
- Reduction of ZTO thickness to increase crack onset strain [19, 20];
- Improvement of the dimensional stability of ETFE films.

The only reduction of the web tension to values still resulting in a good winding quality was found not to be sufficient. Therefore, the influence of the drying temperature and the ZTO thickness on the oxygen and water vapor permeation through ETFE / ORMOCER® / ZTO after winding through the lacquering machine was studied.

Fig. 4 shows that the barrier properties of a 160 nm thick ZTO layer on ETFE / ORMOCER® are lost if this film is stressed at 120°C or 80°C. For a ZTO layer with reduced thickness of 50 nm the loss of barrier properties is also observed at 120°C. In contrast, after treatment at 80°C, significantly lower permeation rates are obtained.

According to these results the drying temperature should be reduced to 80°C during the production of the barrier structure. However, a temperature of 120°C is suggested to guarantee the complete crosslinking of the ORMOCER® lacquer.

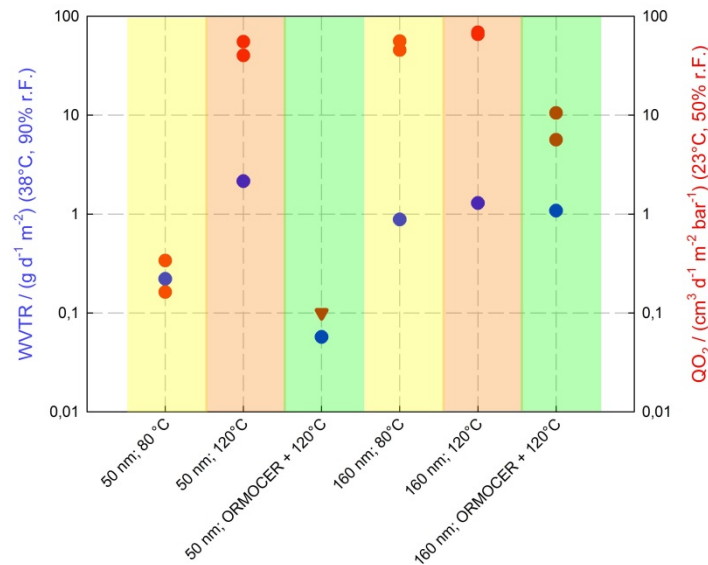


Fig. 4: Oxygen permeability and water vapor transmission rate of ETFE / ORMOCER® / ZTO with ZTO thicknesses of 50 nm or 160 nm after winding at different temperatures and after ORMOCER® application

When, in contrast to the pure winding process, the application of the ORMOCER® layer is considered the loss of the barrier performance of a 50 nm thick ZTO layer is avoided even at a temperature of 120°C. For the ETFE / ORMOCER® / ZTO (thickness 50 nm) / ORMOCER® structure a QO_2 of $< 0.1 \text{ cm}^3 \text{ m}^{-2} \text{ d}^{-1} \text{ bar}^{-1}$ (23°C, 50% r.h.) and a WVTR of $0.06 \text{ g m}^{-2} \text{ d}^{-1}$ (38°C, 90% r.h.) were measured. The ORMOCER® layer therefore seems to protect the ZTO layer against crack formation.

Finally, the barrier structure ORMOCER® / ZTO / ORMOCER® / ZTO with 50 nm thick ZTO layers was deposited on ETFE. The measured WVTR values of about $0.002 \text{ g m}^{-2} \text{ d}^{-1}$ (38°C, 90% r.h.) are in the range of the barrier requirements of flexible photovoltaic modules with intended lifetimes of several years. These results show that the transfer of the POLO® barrier structure to ETFE is possible if the ZTO thickness is reduced to 50 nm. Promising results were also obtained when PVDF or ECTFE were considered as substrate films.

4. ETFE films with improved dimensional stability

Although positive results were obtained by the deposition of multilayer barrier structures with 50 nm thick ZTO layers on ETFE substrate films, it would be desirable to use ETFE films with an improved dimensional stability in order to be more flexible regarding the process parameters. Stretching of polymeric films at elevated temperatures is a common method to improve their mechanical properties [24].

During these studies, however, an alternative method was considered: Before the deposition of barrier layers, the ETFE film (Nowoflon ET 6235 Z, thickness 100 μm) was adhesive laminated with its back side to a PEN film (Teonex Q 51, thickness 125 μm) which exhibits a large dimensional stability [14]. Consequently, the resulting laminate should be strained in the lacquering machine significantly less than the single ETFE film.

In order to confirm this assumption the PEN / ETFE laminate was coated on the ETFE surface with ORMOCER® / ZTO (thickness 150 nm). As described earlier, this structure with a similar ZTO thickness of 160 nm on top of a single ETFE film showed a loss of the barrier performance after winding at 120°C. On top of PEN / ETFE, in contrast, the oxygen permeability measured after winding is below $0.4 \text{ cm}^3 \text{ m}^{-2} \text{ d}^{-1} \text{ bar}^{-1}$ and therefore more than two orders of magnitude lower than on a single ETFE

film. This allows to conclude that the dimensional stability of ETFE films is significantly improved by lamination with the PEN film.

Very low WVTR values between 0.002 and 0.003 g m⁻² d⁻¹ (23°C, 85% r.h.) were finally measured for the complete Fraunhofer POLO[®] multilayer barrier structure ORMOCER[®] / ZTO / ORMOCER[®] / ZTO even with 150 nm thick ZTO layers when the PEN / ETFE laminate was used as a substrate.

5. Conclusions

Fluoropolymer films exhibit excellent stability against UV radiation and weathering. Therefore they seem to be well suited to be used as substrate films for flexible encapsulation of photovoltaic devices under long term outdoor conditions. A serious drawback is their low dimensional stability at high temperature in combination with mechanical stress which arises during the deposition of the barrier structure and following converting processes.

This study shows how to overcome these difficulties and therefore to be able to deposit barrier structures on ETFE, PVDF and ECTFE substrate films. By adjusting process parameters and layer thicknesses the effect of the dimensional change of the films can be reduced in such a way that the barrier properties of already deposited layers are maintained after the process. Furthermore, it has been shown to be possible to improve the dimensional stability of fluoropolymer films by laminating them to a polyester film having an excellent intrinsic dimensional stability.

Based on these methods multilayer barrier structures with water vapor transmission rates between 0.002 and 0.003 g m⁻² d⁻¹ (at 23°C, 85% r.h. or 38°C, 90% r.h.) were produced on ETFE films or PEN / ETFE laminates. This confirms that the flexible encapsulation of photovoltaic devices with multilayer barrier films based on fluoropolymer substrates is possible.

The developed concepts can be transferred to other applications requiring functional layers e.g. with electrical conductance or UV absorption on top of films which are originally difficult to be converted in roll-to-roll processes. Examples for such applications can be found in the building or automotive sector.

Acknowledgements

The authors thank Eva Heidenreich, Intzi Moufti Chalil, Veronika Prusko, Ulrich Galster and the members of the department of materials development of the Fraunhofer IVV for carrying out the coating trials and material characterizations, Sabine Amberg-Schwab, Karl Deichmann and Mark Mirza (Fraunhofer ISC) for the supply of the ORMOCER[®] lacquer, and Rainer Brandt, Esra Küçükpinar and Sandra Kiese for fruitful discussion. This work was part of the *flex25* project funded by the BMBF within the programme *Validierung des Innovationspotenzials wissenschaftlicher Forschung – VIP* under no. 03V0224.

References

- [1] M. Pagliaro, G. Palmisano, R. Ciriminna, *Flexible Solar Cells*, Wiley-VCH, 2008
- [2] S.R. Scully, M.D.W. McGehee, *Physics and Materials Issues of Organic Photovoltaics*, in: W.S. Wong, A. Salleo, *Flexible electronics: materials and applications*, Springer, 2009, 329–371
- [3] N. Grossiord, J.M. Kroon, R. Andriessen, P.W.M. Blom, *Organic Electronics* 13 (2012), 432–456
- [4] P.F. Carcia, R.S. McLean, S. Hegedus, *Solar Energy Materials & Solar Cells* 94 (2010), 2375–2378
- [5] S. Cros, R. de Bettignies, S. Berson, S. Bailly, P. Maise, N. Lemaitre, S. Guillerez, *Solar Energy Materials & Solar Cells* 95 (2011), S65–S69

- [6] J.S. Lewis, M.S. Weaver, *IEEE Journal of Selected Topics in Quantum Electronics* 10 (2004) 1, 45–57
- [7] J. Affinito, D. Hilliard, A New Class of Ultra-Barrier Materials, *Society of Vacuum Coaters 47th Annual Technical Conference Proceedings*, 2004, 563–593
- [8] H.-C. Langowski, Permeation of Gases and Condensable Substances Through Monolayer and Multilayer Structures, in: O.G. Piringer, A.L. Baner (eds.), *Plastic Packaging - Interactions with Food and Pharmaceuticals*, Wiley-VCH, 2008, 297–347
- [9] O. Miesbauer, M. Schmidt, H.-C. Langowski, *Vakuum in Forschung und Praxis* 20 (2008) 6, 32–40
- [10] G.L. Graff, R.E. Williford, P.E. Burrows, *Journal of Applied Physics* 96 (2004) 4, 1840–1849
- [11] O. Miesbauer, How lag time of permeation through flexible encapsulation materials is affected by their layer structure, *LOPEC*, Munich, 05.03.2015
- [12] J. Fahlteich, S. Amberg-Schwab, U. Weber, K. Noller, O. Miesbauer, C. Boeffel, N. Schiller, *SID Symposium Digest of Technical Papers* 44 (2013) 1, 354–357
- [13] S. Amberg-Schwab, Inorganic-organic polymers with barrier properties against water vapor, oxygen and migrating monomers, in: S. Sakka, (ed.), *Handbook of Sol-Gel Science and Technology - 3. Applications of Sol-Gel Technology*, Springer, 2005, 455–478
- [14] W.A. MacDonald, Flexible Substrates Requirements for Organic Photovoltaics, in: C. Brabec, V. Dyakonov, U. Scherf (eds.), *Organic Photovoltaics*, Wiley-VCH, Weinheim, 2008, 471–489
- [15] G. Oreski, G.M. Wallner, *Solar Energy* 79 (2005), 612–617
- [16] J.G. Drobny, *Technology of fluoropolymers*, CRC Press, Boca Raton, 2001
- [17] Validierung einer Rolle-zur-Rolle-Technologie zur Herstellung einer Verkapselungsfolie für die witterungs- und langzeitstabile Frontverkapselung von Solarzellen (flex25), funded by the German Federal Ministry of Education and Research within the programme: Validierung des Innovationspotenzials wissenschaftlicher Forschung – VIP under no. 03V0224
- [18] G. Guerra, C. De Rosa, M. Iuliano, V. Petraccone, P. Corradini, G. Ajroldi, *Die Makromolekulare Chemie* 194 (1993) 2, 389–396
- [19] C.A. Bishop, *Vacuum Deposition onto Webs, Films and Foils*, Elsevier, 2011
- [20] J. Fahlteich, S. Günther, S. Straach, N. Schiller, *Niederdruck-Plasmatechnologien zur Rolle-zu-Rolle-Beschichtung von Kunststofffolien mit Barrierschichten*, 20. Neues Dresdner Vakuumtechnisches Kolloquium - Beschichtung, Modifizierung und Charakterisierung von Polymeroberflächen, Dresden, 26.10.2012
- [21] K. Vaško, *Schichtsysteme für Verpackungsfolien mit hohen Barriereigenschaften*, Dissertation, TU München, 2006
- [22] *Dyneon Fluoroplastics – Product Comparison Guide*, Dyneon, 2003
- [23] O. Miesbauer, S. Kiese, V. Prusko, I. Moufti Chalil, E. Heidenreich, C. Steiner, J. Fahlteich, K. Noller, *Studies of the Dimensional Stability of Polymeric Films during Coating Processes*, AIMCAL Web Coating & Handling Conference 2014 - Europe, Cascais, 08.-11.06.2014
- [24] G.L. Robertson, *Food packaging: principles and practice*, CRC Press, 2006