Project no.: 013883

Project Acronym: FLEXONICS

Project Title: Ultra-high barrier films for r2r encapsulation of flexible electronics

Instrument: Specific Targeted Research Project

Thematic Priority: Sixth Framework Programme, Priority 3, “Nanotechnologies and nanosciences, knowledge-based multifunctional materials and new production processes and devices”

Publishable Final Activity Report

Period Covered: from 01/02/2005 **to** 30/04/2008

Start Date of the Project: 01/02/2005 **Duration:** 39 MONTHS

Project Coordinator Name: Prof. S. Logothetidis

Project Coordinator Organisation Name: **Revision:** 1.0
ARISTOTLE UNIVERSITY OF THESSALONIKI (AUTh)

PROJECT CO-FUNDED BY THE EUROPEAN COMMISSION
WITHIN THE SIXTH FRAMEWORK PROGRAMME (2002-2006)

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Please, visit our official web site: http://www.flexonics.org/

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Section 1: Project Execution

1.1. EXECUTIVE SUMMARY

The FLEXONICS Project is a project funded under the action line: "Nanotechnologies and nano-sciences, knowledge-based multifunctional materials and new production processes and devices".
The project officially started its activities in February 2005.
The FLEXONICS Consortium is composed of 9 partners, listed in the table below.

Table 1. List of participants

Participant Name	Short name	Country
Aristotle University of Thessaloniki (Coordinator)	AUTh	Greece
Fraunhofer-Gesellschaft POLO Alliance	POLO	Germany
Horiba Jobin Yvon	HJY	France
Applied Materials GmbH &Co. KG	AMAT (AF)	Germany
Isovolta AG	ISO	Austria
Alcan Technology & Management	Alcan	Switzerland
Siemens Aktiengesellschaft	Siemens	Germany
Technical University Graz	TUG	Austria
Konarka	Konarka	Austria

1.2. FLEXONICS PROJECT OVERVIEW

Flexible, customized opto- & **e**lectronic **d**evices (**FEDs**) for communication and visualizing of information, and for generation of electricity through renewable sources (based for example on organic light emitters – OLEDs and organic PV modules, respectively) will have a major impact on our daily life. While there have been numerous research projects dedicated to the fundamentals & to the performance improvement of single OLED & OPV devices, little research was undertaken **to provide industry with the necessary material systems and processes to allow the cost-effective production of complete FEDs**. A missing **process step**, essential for the development and reliability of FEDs is their **encapsulation into a transparent polymeric medium** that will protect FEDs against atmospheric oxygen & water-moisture, which are harmful for their performance & long-term stability. Also the appropriate **flexible materials,** which exhibit the required exceptional barrier and optical properties, and are compatible with a large scale encapsulation process are not available. This is a severe gap as these innovative products can only exploit their full potential if produced on flexible substrates by **large scale roll-to-roll (r2r)** conversion processes, using polymer films in rolls up to 3 meters of width and some km of length.

Fig.2 shows the present performance of flexible transparent materials in terms of their oxygen and water vapor barrier properties as required for different applications. Single polymer films exhibit the highest permeability values (upper right), and are just sufficient for food packaging applications. The deposition of one single inorganic layer increases their barrier by more than 2 orders of magnitude. This leads to the indicated industrial high barrier standards presently achieved for transparent flexible materials via **r2r** processes. Experimental combinations of inorganic layers and layers of inorganic-organic hybrid polymers allow for an improvement of another factor of 1000. However, the requirements in oxygen & water vapor transmission for FEDs ask for values lower by another 3 orders of magnitude. These cannot be obtained by any of the current r2r processes.

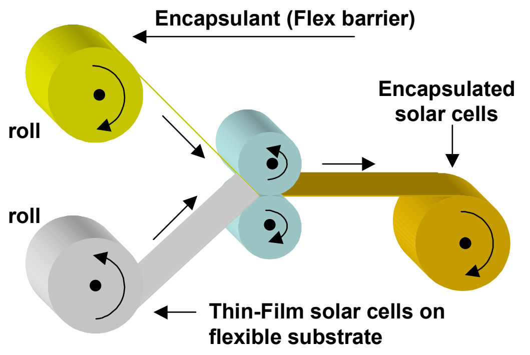


Figure 1. Example: Schematic outline for the concept of large-scale r2r encapsulation of flexible solar modules (roll length ~3000 m & 2 m width.)

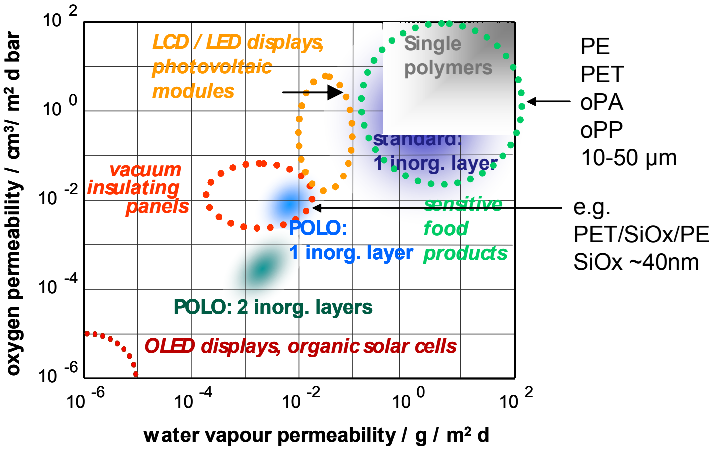


Figure 2. Permeability for oxygen and water vapor of single polymers (upper right), of experimental laminates with 1 & 2 inorganic layers (lower left), and requirements for different application areas (dotted lines)

FLEXONICS research activities performed to **developed the required and missing material systems, processes & their process control** for the production of transparent flexible encapsulation materials **for the new generation of FEDs,** with emphasis to the ultra-barrier films, and will **link the traditional roll-to-roll (r2r)** polymer film conversion industry **& current optoelectronics** industry. **The main objectives** of FLEXONICS are the following:

1) To develop novel ultra barrier material systems in multilayer form (with individual layer thicknesses of a few nm), consisting of preferably not more than 2 pairs of alternating layers from inorganic materials and inorganic-organic hybrid polymers. In addition, the layer systems have to be highly optically transparent in the visible spectral range for OLEDs and in the NIR - UV range for Organic Photovoltaics (OPVs).

2) To establish physical and chemical processes suitable for the deposition of ultra high barrier layer systems, via plasma assisted PVD & CVD processes, for the **fabrication of inorganic barrier layers** & via atmospheric pressure liquid phase coating and crosslinking processes, for hybrid polymeric interlayers, and to **adapt** the appropriate r2r processes (with process speeds up to 5 m/sec) for large scale production.

In order to achieve the required properties of the multi-layer system, **the properties of each individual layer have to be monitored & controlled in-line.**

3) To develop new optical sensing techniques with **sub-nm resolution** to probe organic/inorganic layer and interfaces, and product functionality in **msec time,** and to **integrate them into r2r** processes in order to guarantee maximum uniformity in the intermediate and final product properties.

1.3. PROJECT OBJECTIVES

1.3.1 FLEXONICS General Approach

In this section we give an overview of the overall approach followed and the main results achieved in the Project.

The overall approach proposed, has the following steps: The FLEXONICS project were organised in three Technical Areas (TAs) related to the corresponding technical approaches & objectives. In specific TA1 (Functional materials & processes) includes develops production processes of new ultra-high barrier coatings, consisting of organic/inorganic bilayer and fundamental research on the permeation mechanisms of oxygen and water vapor through the polymeric films and multilayer systems. TA2 (Diagnostics & process control) involves the development of the appropriate optical sensing techniques (SE) and instrumentation to study the optical properties of the barrier-layers and to correlate them with their functional properties based on intelligent methodologies (theoretical approaches, modeling procedures and software) and to deploy/implement them for inline process control. Finally, TA3 include the optimization of material process (inorganic & organic layer deposition), through optical monitoring, for the production of ultra-barrier layers onto flexible substrates. The produced barrier layers should fulfil the strict requirements for the OLED and OPV technologies.

1.3.2 Project Objectives

The objectives of the FLEXONICS Project are the following:

- The development of materials and processes for optimum single barrier layers (inorganic barrier layers, polymeric interlayers), combination of the single layers to layer stacks in lab and pilot scale and to supply a range of complementary coating techniques
- The characterization, with the appropriate optical and non optical methods, of the barrier materials & layers both organic & inorganic and the verification of their applicability and the optical techniques for in-line monitoring.
- The theoretical understanding of the permeation mechanisms through the layer stacks and evaluation of the barrier properties of multi layer structures from the data of single layers and the combined layers in order to select the best layer systems.
- The identification and r2r lab-scale production of multi-layer stacks that allow for a later production of flexible ultra high barrier materials under conditions appropriate for marketable products.
- The development of a very fast spectroscopic units probing matter in IR & FUV range and the growth of theories decoding polarized light interaction with matter in Specular reflection mode Proof that theories & units can analyze complex flat organic/inorganic systems & can be used in large-scale applications and finally the testing of units and theories in lab processes, verification and assessment for transferring
- The verification of principal approach using polymeric & inorganic layers in stacks, achievement of improved figures needed for production of flexible ultra high barrier materials

- The practical verification of the approach via multi layer stacks, preparation of small scale demonstrators relevant to the later production of encapsulated flexible displays and organic photovoltaic modules.

1.4. PROJECT EXECUTION

1.4.1. TECHNICAL AREA 1

The TA1 focuses on the development of materials and processes for optimum single barrier layers (inorganic barrier layers, polymeric interlayers) and for combination of the single layers to layer stacks in lab and pilot scale. These materials will be characterized with the appropriate optical and non optical methods whereas their applicability and the optical techniques for in-line monitoring will be verified. Moreover, theoretical understanding of the permeation mechanisms through the layer stacks and evaluation of the barrier properties of multi layer structures from the data of single layers and the combined layers in order to select the best layer systems will take place. Finally, the identification and r2r lab-scale production of multi layer stacks will allow for a later production of flexible ultra high barrier materials under conditions appropriate for marketable products.

Production Processes & performance evaluation of individual layer (WP1)

For the development of optimum barrier layers the selection of the appropriate substrates was the first important step. Out of 7 PET and respectively PEN films the two most appropriate substrates, namely Melinex 401 (50µm) and Melinex ST 504 (125µm) were chosen for oxide coating. However, all samples were, when normalized in respect to their thickness, in general in the same range concerning oxygen and water vapour transition prior to oxide coating.

Melinex 401 gave the best results concerning initial barrier values after oxide coating. Permeability values down to 0,02 for WVTR and respectively OTR were achievable in lab scale. Compared to Melinex 401, Melinex ST 504 has higher initial barrier values, but it is more suitable for processes where dimensional stability is an issue.

Figure 3 and 4 show a TEM measurement of the surface of Melinex 401 and Melinex ST 504. It can be clearly seen that the surface is smooth for both PET-films

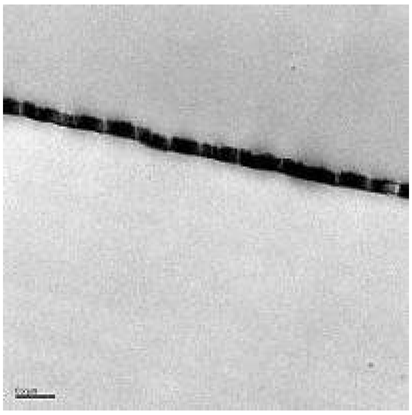


Figure 3 Melinex 401

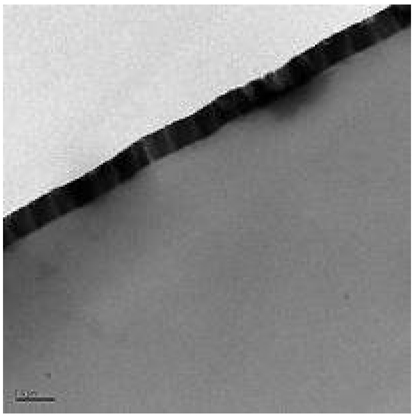


Figure 4 Melinex ST 504

Samples were coated with AlOx by sputtering (AMAT) and with SiOx by Electron Beam evaporation (ALCAN), with both companies putting a lot of effort into the optimization of their oxide layers. Values in the low 10^{-1} region for OTR and WVTR were achieved with single oxide layers in pilot- and production scale. Similar oxide coating trials were carried out by POLO-IVV and AUTh.

For the selection of the most suitable ORMOCER® barrier lacquers 7 candidates were available. Out of the tested lacquers FI H 38% and FI I 33% were chosen for the further optimisation of the barrier properties, because high initial barrier values were measured for these two. With the incorporation of silicon oxide particles the inorganic network degree of the ORMOCER® layers was further increased. TEM measurements proved thereby that the SiOx particles are distributed homogeneously and that no real agglomerates can be found.

Atomic force microscopy revealed a surface roughness of ORMOCER® coatings on PET-SiOx of typically 0,3nm (rms roughness) and respectively 2,2 to 3,4nm (peak to valley).

Characterization of the barrier layers (WP2)

In order to optimize the oxide layers, the growth and the properties of the layers were studied by Spectroscopic Ellipsometry. The results of these measurements were compared with the barrier properties to allow for an inline characterisation of the barrier quality of oxide layers. From the SE spectra the refraction index can be derived. A lower refraction index is thereby consistent with a lower density of the films. Also the content of nanoparticles can be derived with SE. The refractive index is then an indication of the surface quality and the particle content.

Infrared spectroscopy gave interesting results concerning the bonding structure between SiOx and and ORMOCER®. Thus the mechanisms which take place during the bonding of ORMOCER® can be studied. For AlOx the situation is more difficult because AlOx exhibits IR-bands at wavelengths below 1000cm^{-1}.

The two processes thermal treatment and UV-curing, which are used for the ORMOCER®s do not have an influence on the chemical structure of the substrate as it can be clearly seen from Figure 5.

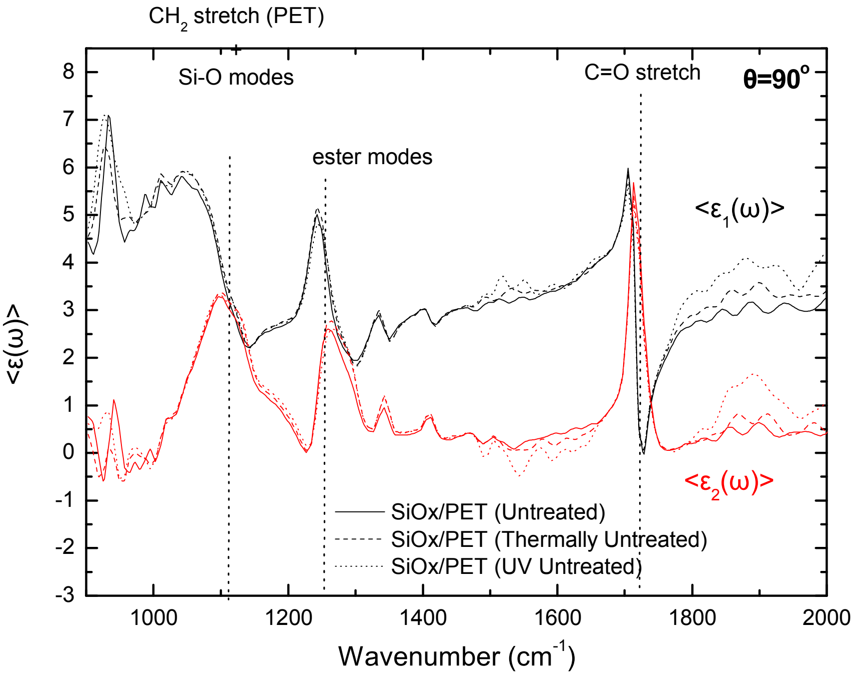


Figure 5 Real <ε$_1$(ω)> & Imaginary <ε$_2$(ω)> part of the SiOx layer (120 nm) deposited onto PET Melinex 401 (50 µm), subjected to Thermal treatment and UV treatment, in correlation to the untreated sample.

Despite the chemical structure, the surface roughness of PET-SiOx was significantly changed by UV-treatment (Figure 6).

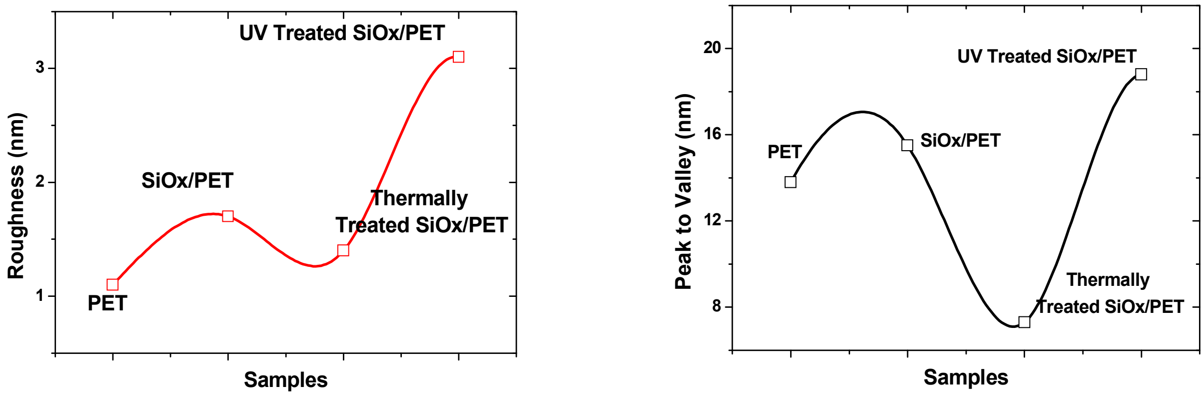


Figure 6 Surface roughness and peak to valley distance of PET, SiOx/PET, UV treated SiOx/PET and thermally treated SiOx/PET.

This may also have an influence on the quality of ORMOCER® layers during curing. However, the ORMOCER® coating itself has a positive effect on the surface roughness. It can be reduced by coating e.g from 1,8µm down to 0,3µm with a 5µm thick coating on 12µm PET. For thicker PET the roughness before coating is lower, end results are comparable. Additionally the surface energy of PET SiOx and PET AlOx was estimated via Contact Angle measurement. These measurements revealed that AlOx is the more hydrophobic surface.

The second step after optimizing the oxide layers and also the ORMOCER® layers was the setup of two and four layer stacks. These stacks can be very different in the sequence of their single layers.

Possible setups (exemplary):

- PET / Oxide / ORMOCER® / Oxide / ORMOCER®
- PET / ORMOCER® / Oxide / ORMOCER® / Oxide
- PET / Oxide / ORMOCER® / Adhesive / ORMOCER® / Oxide / PET

The combination of different oxides with different ORMOCER®s, adhesives and additives can lead to very different results. All components in such two and four layer stacks have to be optimized in order to achieve optimum barrier properties. At the same time the parameters transparency and UV-stability were under investigation. These properties have to fulfil also strict requirements in addition to the barrier properties.

The ORMOCER® FLH38% showed thereby comparably good results for hydrolytic and UV-stability. For the UV-curable ORMOCER® FL Ib 33% some yellowing prior to UV-testing and also the hydrolytic stability was to observe. After UV-testing the yellowing was even more severe. Best results concerning UV- and hydrolytic stability were achieved with the ORMOCER® FL Da 48%. A minimum of yellowing and a good hydrolytic stability was to observe. At the same time the ORMOCER® FL Da 48% was found to be the one with the most hydrophilic surface, due to the lowest contact angle.

For the ORMOCER®s in general it has been found that their hydrophobic properties and their surface free energy were not affected by the oxide layer below the ORMOCER®. Each ORMOCER® type showed the same surface energy independent if there is an oxide layer present or not.

The first roll to roll coating trials were carried out with the ORMOCER® s FL H38% and FL I 33%, which were already mentioned above. These trials proved that it is possible with roll to roll coating to achieve comparable results as in lab-scale. During the project the quality of these coatings was continuously improved, which will be shown in the subsequent work packages.

Development of Ultra-Barrier Testing Systems

"Graz University of Technology" (TUG) has developed a measuring system for automated ultra-barrier testing. During the FLEXONICS project, the prototypes were continuously improved and used in routine measurements of samples provided by the consortium. Thus, the concept proved its capability and round robin tests confirmed its accuracy. From repeatability assessments, an OTR limit of detection in the regime of 10^{-5} [$cm^3\ m^{-2}\ day^{-1}\ bar^{-1}$] is concluded. The method has potential for further improvement and according concepts are at hand.

Figure 7 shows a schematically drawing of the system. The central innovation of the measuring approach is based on the consumption-free yet very sensitive oxygen detection performed by an opto-chemical sensor.

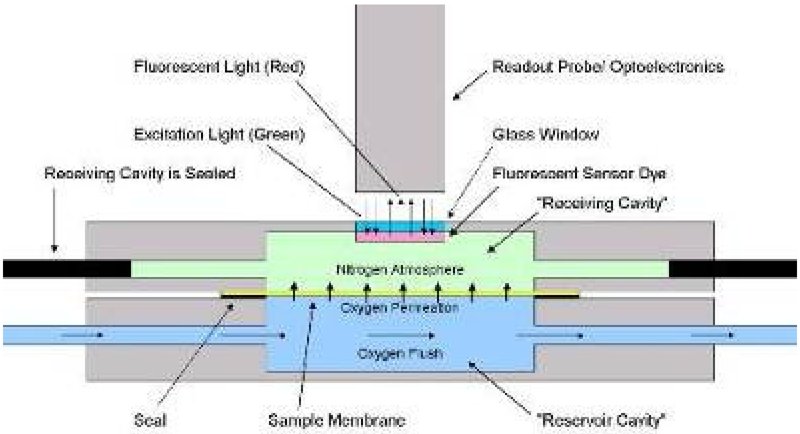


Figure 7 The Principle of the OTR Testing System. Oxygen is passed through the "reservoir cavity". The oxygen sensitive element in the "receiving cavity" is continuously monitoring the increasing oxygen concentration, resulting from permeation through the sample membrane.

POLO was also developed a sensitive measurement systems for water vapour permeation. This system is based on the modification of a gas chromatograph (see Figure 8). Permeating water e.g. is trapped at -50°C and by heating the trap up to elevated temperatures all the permeated water is released to a gas chromatograph. Calculation versus time leads then to a permeation value. Lowest values measured so far are in the 10^{-5} region.

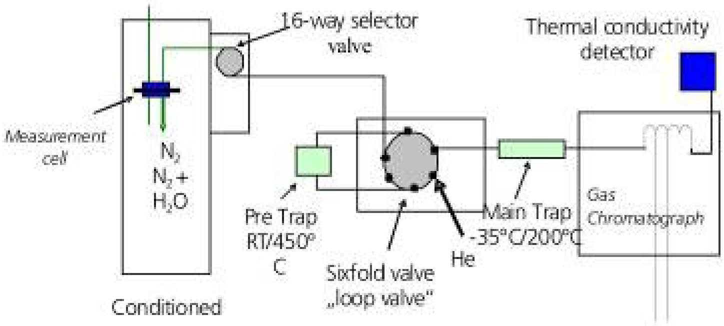


Figure 8 The measurement device for detecting ultra-low water vapour permeation that was developed during the FLEXONICS project (schematic principle).

POLO was also out to develop sensitive measurement systems for water and oxygen. This system is based on the modification of a gas chromatograph. Permeating water e.g. is trapped at -50°C and by heating the trap up to elevated temperatures all the permeated water is released to a gas chromatograph. Calculation versus time leads then to a permeation value. Lowest values measured so far are in the 10^{-3} region.

Konarka focused at the same time on the development of highly sensitive methods for the measurement of water vapour and oxygen through ultra-barrier materials for lab applications. The measurement is based on the electrical Ca-Test, where the formation of CaO or CaOH is monitored online by the change in electrical resistance. Values in the 10^{-5} region could be estimated for special samples. Acceleration factors at elevated temperature and humidity were also derived from ongoing measurements. Figure 9 shows the acceleration factors estimated.

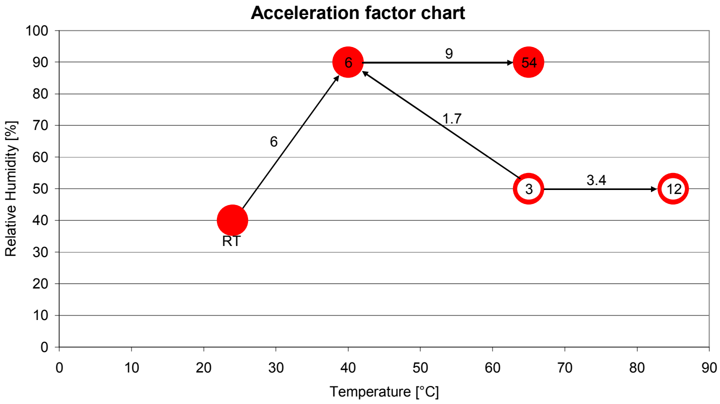


Figure 9 Various stress conditions for accelerated degradation tests and the average measured acceleration factors measured. The direction of the arrows indicates the condition with the faster degradation. Numbers inside the circles represent the accumulated acceleration factors relative to RT. Humidity of the circles with white filling was not controlled and is estimated at ca. 50%.

The suitability of the layer properties for an end user was tested e.g. by Siemens for OLED devices. In this case different functional layers are deposited onto the barrier material. Therefore also dimensional stability of the barrier material is of special importance. The material must be resistant against acids, solvents and short-term UV-radiation, as well as against adhesives. The transparency of such a material has to be above 90%.

Current rigid OLED devices achieve a lifetime of 1000 to 10000 hours. Flexible OLEDS must be in the same order of magnitude if they want to enter the market.

Similar demands are valid for Organic Photovoltaic Devices, in order to allow for a lifetime of at least 3-5 years. With such a lifetime a product acceptable for end-users could be produced.

Theoretical understanding of the permeation mechanisms (WP3)

By means of this sophisticated tests (for low permeation rates) as well as by commercial systems (for higher permeation rates) a great number of experimental permeation data were gained during the project. These data were used as input for establishing a theoretical model for the permeation of water vapour and oxygen through ultra-barrier multilayer stacks. Based on this model, a simulation tool using Fick's law and a Finite-Differences approach was developed. Due to the vast amount of available experimentally gained permeation data, the model correlates extremely well with the measured reality. Hence, it was used successfully as a forecast tool for:

- the barrier properties of multilayer material
- the influence of each layer, e.g. of the defect structure of the inorganic layer to the total barrier
- giving advice how to further improve barrier properties
- both for H_2O and O_2

The calculated defect structures (average pinhole diameters and pinhole distances) can supersede a measurable characteristic necessary for evaluating the quality of inorganic layers. The average pore diameter and distances are certainly no real physical property of the inorganic layer as they were the result of simplifications. However, they showed sufficient significance for being used to comparing/classify different inorganic layers. E.g. for the typical SiO_x layer used in the FLEXONICS project (e-beam) ca. 190 nm for the pinhole diameter and values of ca. 29 µm for the pinhole distance were calculated, whereas the pore diameters for the sputtered AlO_x were much smaller (ca. 50 nm).

Selection of suitable barrier layer stacks (WP4)

The most promising systems of the structure “polymer film/SiO_x/hybrid polymer” and “polymer film/SiO_x/hybrid polymer” have be applied on a pilot coating roll-2-roll machine and additionally be coated with SiO_x and AlO_x nano-layers.

Thus, WVTR values of 0,001 with the system ORMOCER® FL H38% mod.2 (SiO_2-particles incorporated) on Melinex 401 PET with SiOx coating could be achieved. The same coating led to OTR values of 4×10^{-4}. The thickness of the ORMOCER® layer was thereby in the range of 3-4µm, as it can be clearly seen from Figure 10. According to the Ca-mirror test of Konarka best results were achieved with the SiO_2-particle-containing system Fl H38% mod.3 (see sample ISC 5).

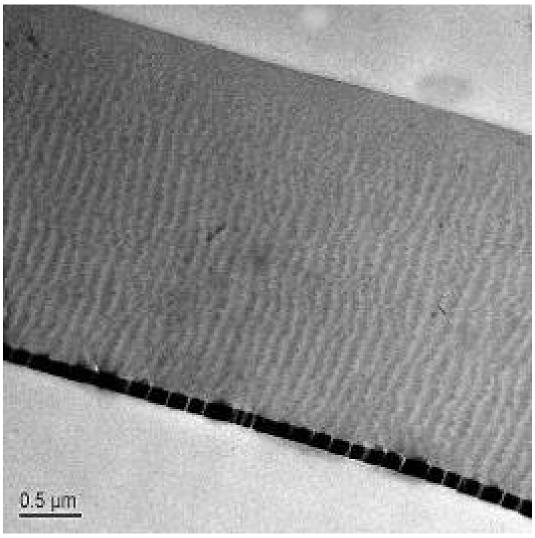


Figure 10 Melinex 401, SiO_x Ormocer Fl 1b (26kx)

However, in general the thickness of the ORMOCER® layer does not have a direct influence on the barrier quality. Another way to improve the barrier properties of ORMOCER®s is the incorporation of fluorosilanes. With this, at the very beginning of the trials, WVTR values below 10^{-2} could be achieved.

1.4.2. TECHNICAL AREA 2

The goal of TA2 is to develop new optical sensing techniques with sub-nm resolution to probe organic/inorganic layer and interfaces. The measurement time scale targeted is the msec range to be compatible with the r2r processes in order to guarantee maximum uniformity in the intermediate and final product properties. To achieve this goal a dedicated **Spectroscopic Ellipsometer** has been developed and fully tested during the project (WP5). Then the system has been installed first in the lab scale secondly on a r2r deposition machine (WP7). To achieve the real-time monitoring goal, several methodologies have been developed (WP6) to be able to monitor all the needed sample properties (thickness, optical properties…). Finally, when the system has been validated, we have started the evaluation on the pilot scale production by controlling the different step of the production barrier layer stack (WP8).

Development of prototype stand alone optical units (WP5)

During this project, a new detector for the Spectroscopic Ellipsometer has been developed which is able to acquire a full spectrum from 3eV to 6eV in less than 100ms. This high measurement rate is needed due to the speed of the r2r processes (5m/s). The Far UV spectral range (3eV to 6.5eV) is needed due to the transparency of the PET under 3 eV. Indeed, we want to minimize the influence of the optical fringes provided by the PET substrate. This substrate is also highly anisotropic. The anisotropic effect on the measurement is minimized by avoiding the transparency region of the PET substrate. Yet, to well understand and taking into account the remaining effect a methodology for taking into account the anisotropy has been studied in the WP6.

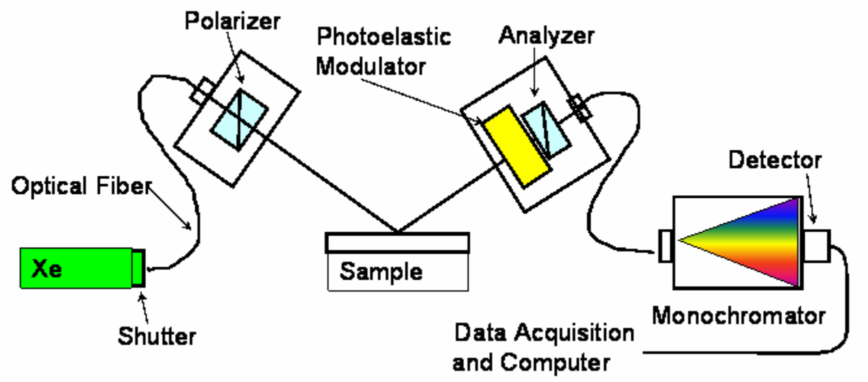


Figure 11 FUV multiwavelength detector (60ms mesurement rate)

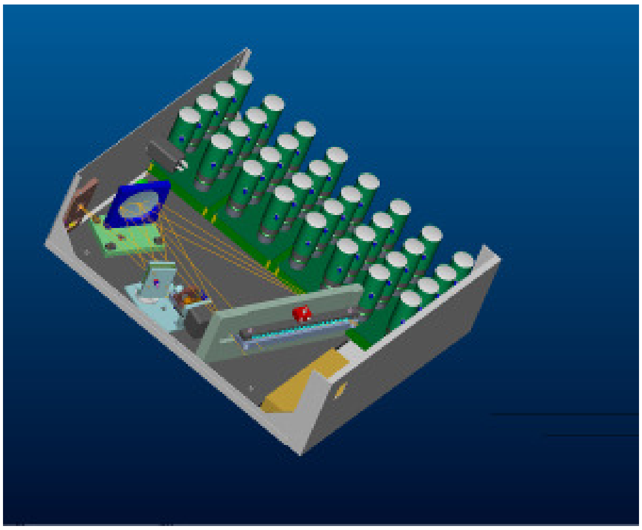


Figure 12 FUV multiwavelength detector (60ms mesurement rate)

The Multiwavelength detector is based on dispersive grating used to focus the spectral range on 32 optical fibbers connected to 32 photomultiplicators (PMT). This 32 detectors are then coupled on an acquisition board with is able to perform a simultaneous measurement each 90ms.

Real-time spectroscopic ellipsometric software has been developed to be able to drive the complete system. This software includes: electronics firmware optimisation, real-time communication between hardware and the software, dedicated algorithm to control the PMT amplification (Electrode High Voltage).

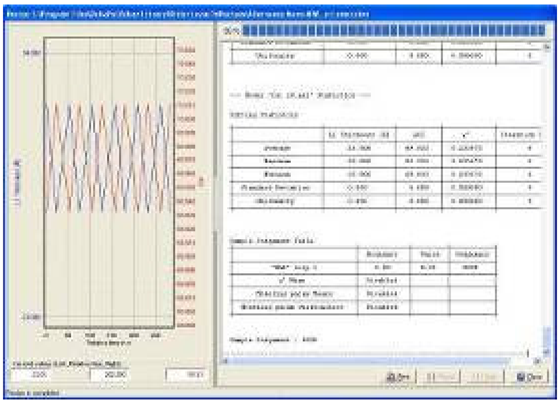


Figure 13 Validation of the new acquisition routine

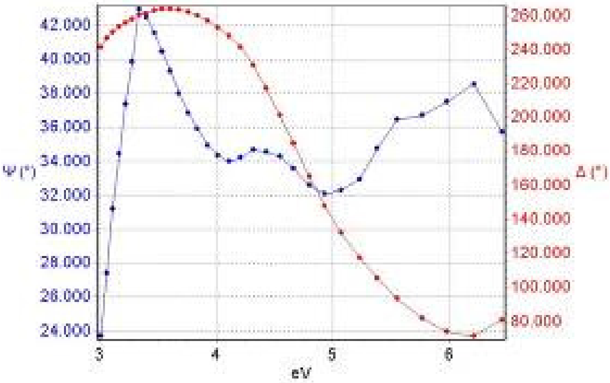


Figure 14 Validation of the new detection system on a static sample 150 A° Oxide on Si

With this real time acquisition software real-time modelling software has been developed indeed the ellipsometry is not a direct technique. A result is always obtained by making a comparison between a measurement and a model through a fitting procedure.

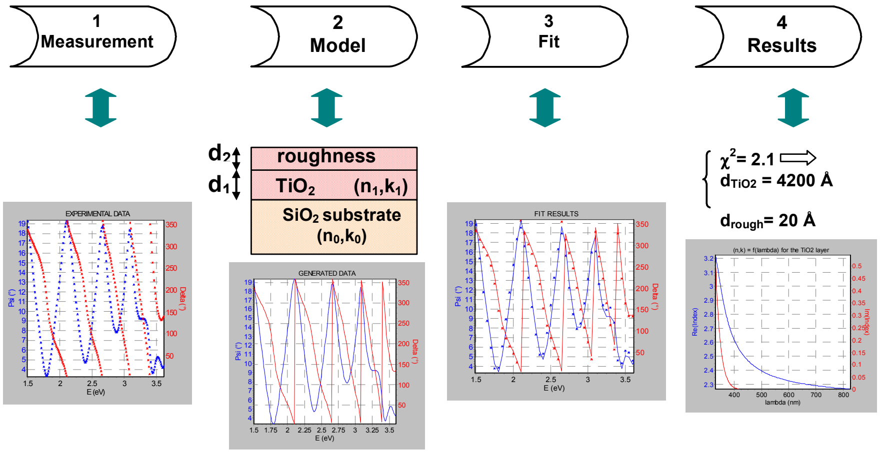
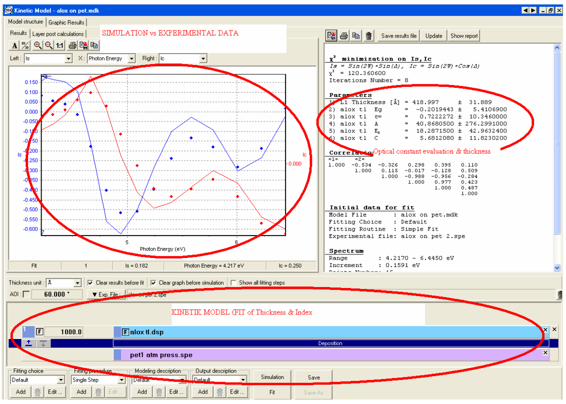


Figure 15 Ellipsometric flow chart

The goal of a real time modelling software is to be able to make this fitting function in real-time.



```
χ² minimization on Is,Ic
Is = Sin(2Ψ)×Sin(Δ), Ic = Sin(2Ψ)×Cos(Δ)
χ² = 120.360600
Iterations Number = 8

Parameters
1) L1 Thickness [Å] = 418.997     ±  31.889
2) alox tl  Eg      =  -0.2019443 ±   5.4106900
3) alox tl  ε∞      =   0.7222272 ±  10.3460000
4) alox tl  A       =  40.8680500 ± 276.2991000
5) alox tl  E0      =  18.2871500 ±  42.9632400
6) alox tl  C       =   5.6812080 ±  11.8230200

Correla
=1=    =2=
1.000  -0.534  -0.326   0.298   0.395   0.110
        1.000   0.115  -0.017  -0.128   0.509
                1.000  -0.988  -0.956  -0.284
                        1.000   0.977   0.423
                                1.000   0.487
                                        1.000

Initial data for fit
Model File        : alox on pet.mdk
Fitting Choice    : Default
Fitting Routine   : Simple Fit
Experimental file: alox on pet 2.spe

Spectrum
Range          : 4.2170 - 6.4450 eV
Increment      : 0.1591 eV
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Figure 16 Kinetic model window

The development of an optical sensor to fulfil the r2r measurement has been performed during the project. This tool has been then deeply tested.

Prototype implementation and testing

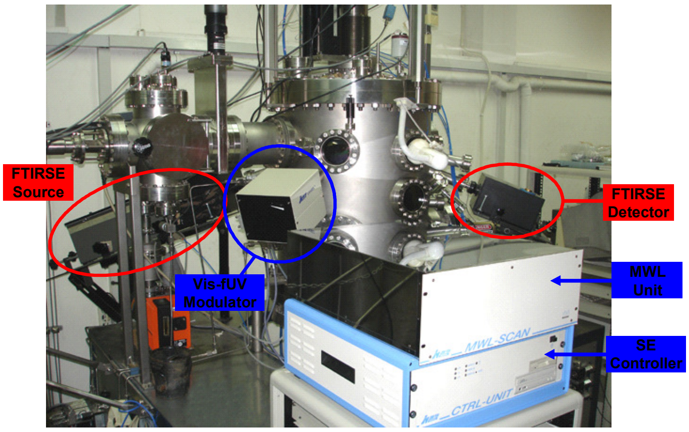


Figure 17: Ellipsometer on the UHV Auth Chamber

The full system has been installed on the AUTh ultra high vacuum chamber for a deep test program. The reliability and the measurement rate have been tested and help for the final system optimisation.

Table 2 Measurement time

Sampling Time (ms)	Integration Time (ms)	Spectra	Estimated Time of Measurement (s)	Real Time of Measurement (s)	Measurement Speed (ms)
80	40	200	16	18	90
90	45	200	18	18	90
100	50	200	20	20	100
120	60	200	24	24	120
150	75	200	30	30	150
300	150	200	60	60	300
500	250	200	100	100	500
1000	500	200	200	200	1000
2000	1000	200	400	400	2000
90	45	1000	90	90	90
120	60	1000	120	120	120

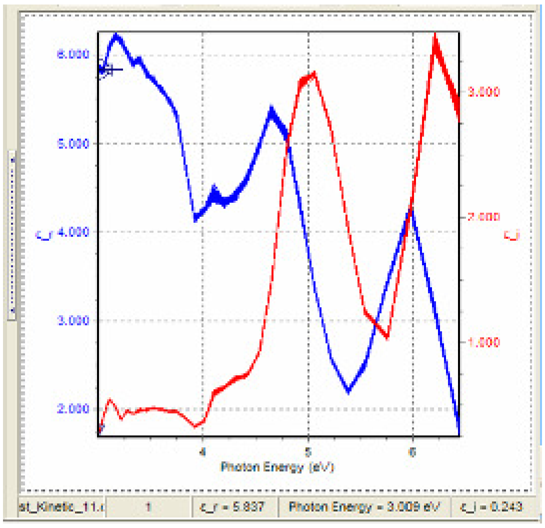


Figure 18 The MWL spectra of a PET Melinex ST504 (125 μm) obtained with real-time kinetic measurements using the prototype SE unit (ST:90, IT:45, Spectra:200)

The system has been validated and then a new prototype has been manufactured for being installed on the r2r deposition chamber of AMAT.

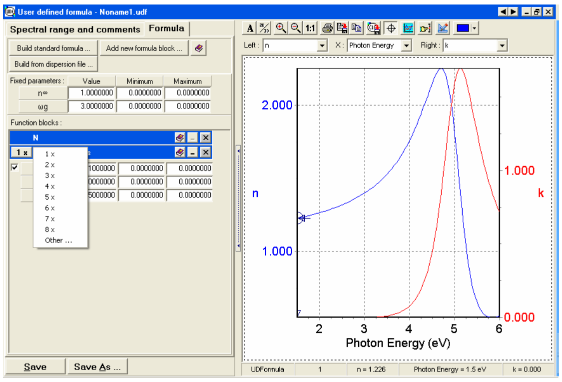
Development of Methodologies & Verification for envisaged applications (WP6)

As explained previously the ellipsometry is not a direct measurement technique. It needs the use of a model which represents the sample characterized. The measurement of the FED sample needs two main issues:

- A dispersion formula which represents the optical properties of the material (organic & inorganic layer)
- An anisotropic model for describing the PET substrate which is highly biaxial.

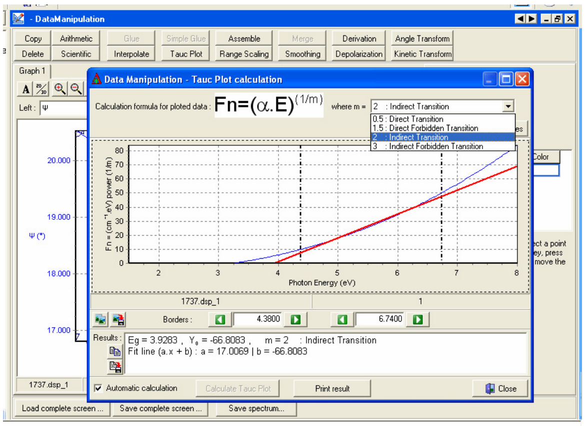
Dispersion formula

A new dispersion formula mode has been developed in the modelling software. This tool is used for creating any kind of dispersion formula for describing any kind of materials. This feature has increased significantly the power of the Spectroscopic Ellipsometry technique.



Fixed parameters :	Value	Minimum	Maximum
n∞	1.0000000	0.0000000	0.0000000
ωg	3.0000000	0.0000000	0.0000000

UDFormula | 1 | n = 1.226 | Photon Energy = 1.5 eV | k = 0.000



1737.dsp_1 | 1

Borders : 4.3800 | 6.7400

Results :
Eg = 3.9283 , Y_0 = -66.8083 , m = 2 : Indirect Transition
Fit line (a.x + b) : a = 17.0069 | b = -66.8083

Figure 19 Interface Menu for the creation of any Dispersion formula

Figure 20 Interface Menu for the Data Manipulation

Anisotropic Model

The flexible substrate PET or PEN are anisotropic biaxial material. This material has been intensively studied by Auth to be able to characterize the barrier layer deposited on them.

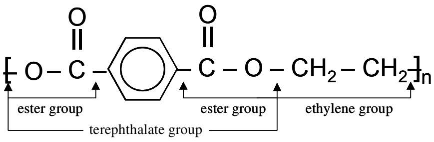


Figure 21 Molecular structure of the Poly(Ethylene Terephthalate) (PET) repeat unit

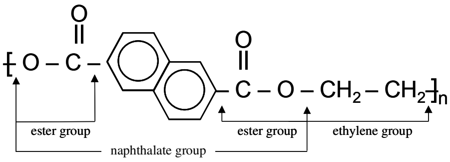


Figure 22 Molecular structure of the Poly(Ethylene Naphthalate) (PEN) repeat units

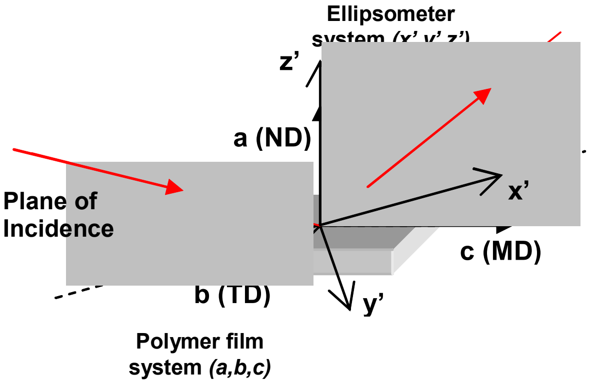


Figure 23 Coordination Axis system for the SE measurements

This analysis has permitted to implement in the modelling software the capability to describe complex anisotropic model.

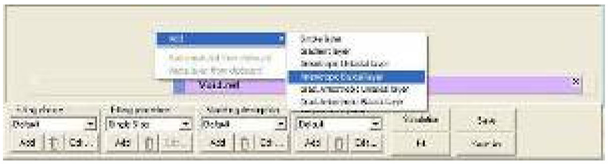


Figure 24 Anisotropic model

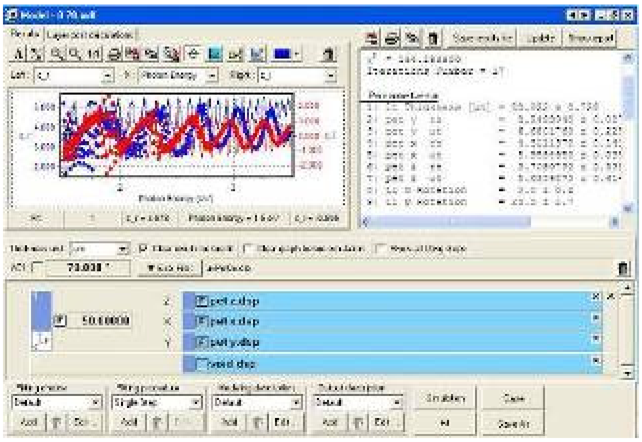


Figure 25 Biaxial model

Methodology for FED

A methodology to characterize the different layers deposited on PET and PEN has been also prepared. The overlying layer is represented by a dispersion formula based on 3 or more Tauc Lorentz oscillators. During the real-time monitoring the thickness, the fundamental band gap E_g and Penn gap E_0 of the layer are monitored.

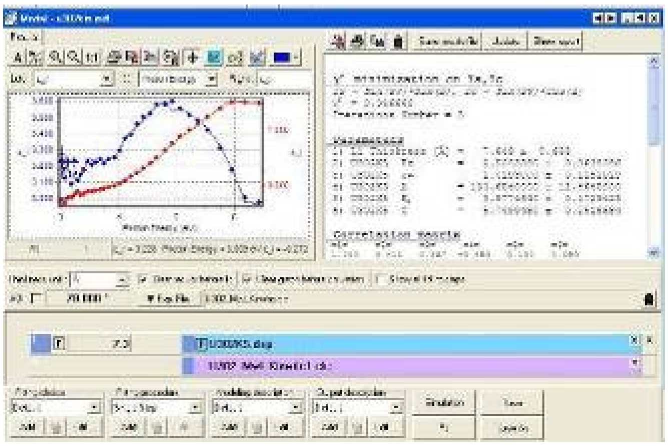


Figure 26 Analysis screen

This methodology has been used in real-time for monitoring the thickness and the optical properties of the layer deposited.

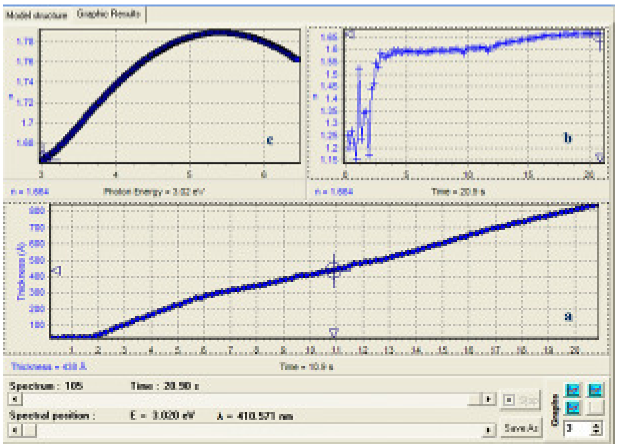


Figure 27 Results of the analysis of spectra of SiO_x thin film onto PET. Evaluation of: thickness with deposition time (a), refractive index with deposition time (b), refractive index with photon energy for whole time of deposition

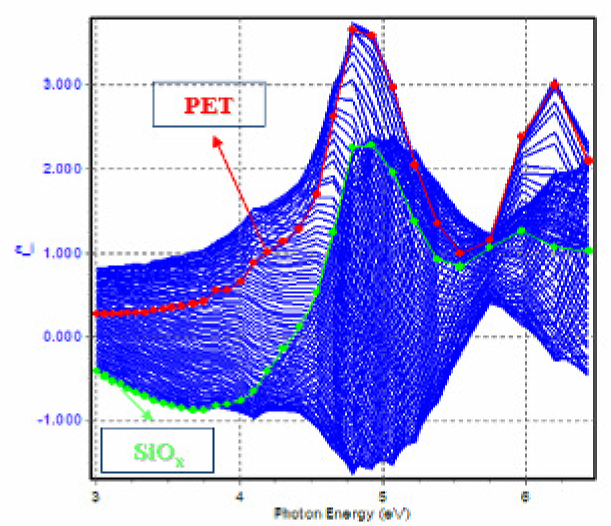


Figure 28 The <$\varepsilon_2(\omega)$> spectra recorded in real-time during the deposition processes of a SiO_x coating on polymeric PET Melinex 401. The curve plotted with red circles corresponds to the <$\varepsilon_2(\omega)$>before the SiO_x deposition, and that plotted with green circles to the final <$\varepsilon_2(\omega)$> measured by MWL Vis-fuv SE

The final goal of the monitoring is to be able to monitor the barrier properties by using the correlation of the barrier and the optical properties. For achieving this goal a deep comparison between the optical properties (E_g and E_0) has been performed.

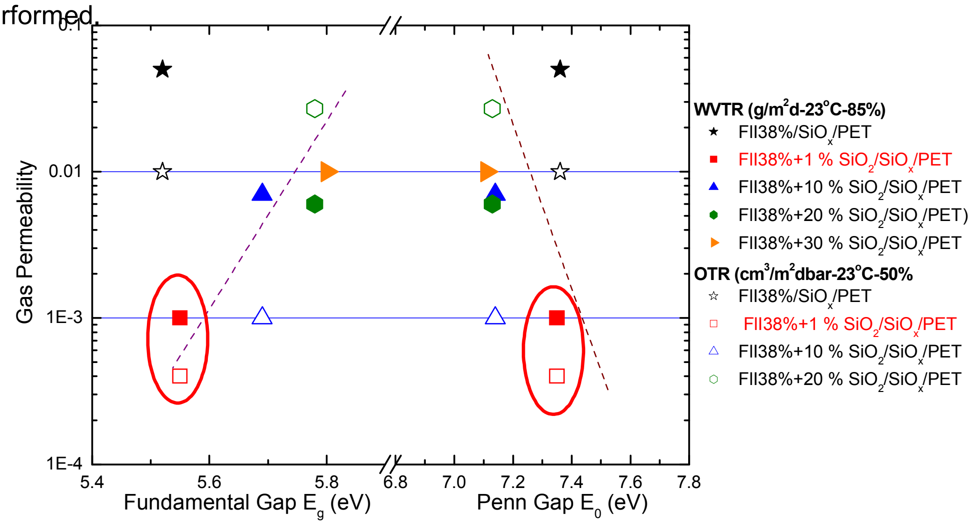


Figure 29: The correlation of Fundamental Gap E_g and Penn Gap E_0 with the WVTR and OTR for the FIH38%+SiO_2 coatings onto SiOx/PET Melinex 401.

This study has shown that there is possibility to correlate the barrier properties to optical properties. This is adding to the thickness monitoring capability of SE the possibility to check the barrier properties of the deposited layers.

Deployment of Units & Testing into real-time Lab process (WP7)

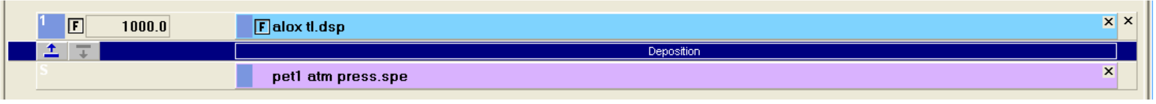
The optical sensor has been installed on the Smart Web machine by AMAT in Alzenau, Germany. The optical sensor employs the measurement methodology developed and validated as a lab scale by AUTh.

Figure 30 Adapted SE unit onto roll-to-roll machine

Figure 31 Adapted SE unit onto roll-to-roll machine

The system has been tested on AlOx and SiOx processes. Real-time monitoring of thickness and optical properties has been performed.

Example of AlOx deposited on PET substrate.



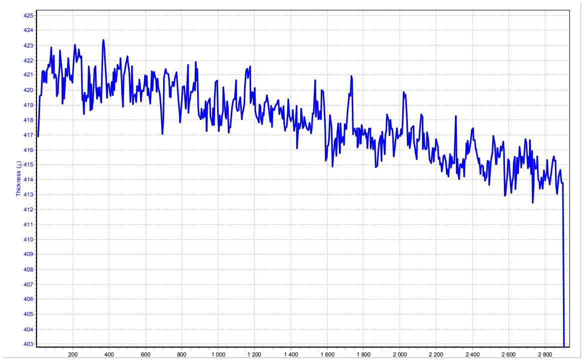


Figure 32 Thickness of AlOx layer in real time

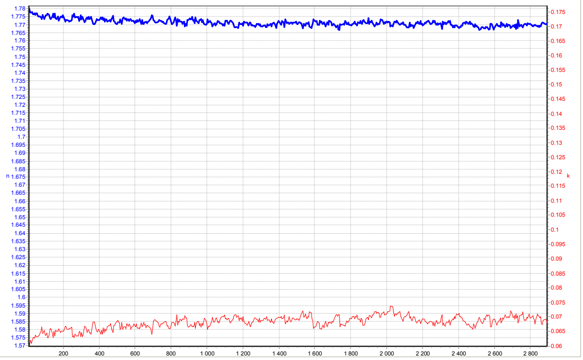


Figure 33 Optical properties of AlOx in real time

To check that the system is robust against to process variations, the stability has been checked. The robustness to the thickness measurement has also been verified. These tests show that the technology is therefore compatible with production processes.

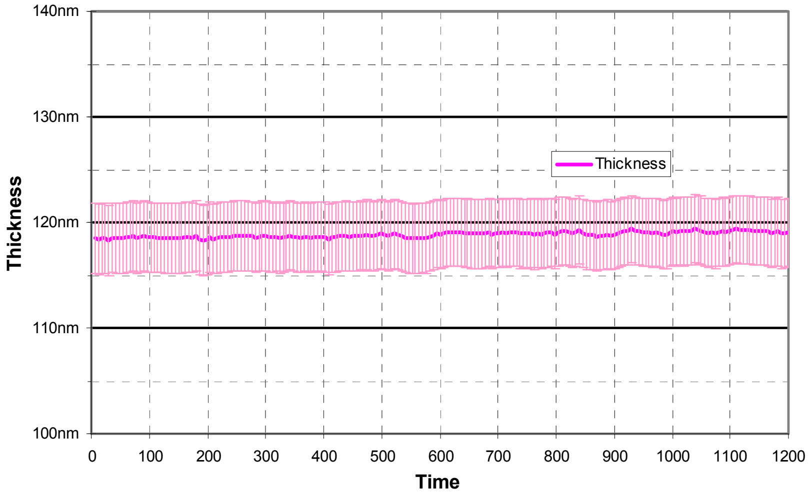


Figure 34 Stability test of AlOx layer on Melinex

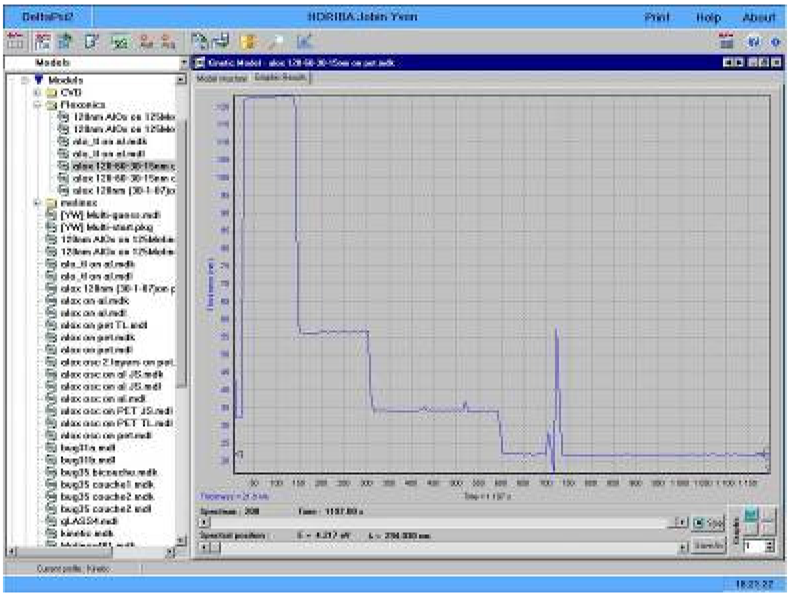


Figure 35 Real-time monitoring of 120nm-60nm-30nm-15nm AlOx layer on Melinex

Conclusion on TA2

The collaborative work performed within Technical Area 2, has permitted the successfully development of an optical sensor for the real time monitoring of layers on flexible substrate on r2r deposition machines. This has been achieved by developing hardware, software, modelling methodology and integration of the Ellipsometer in an R2R pilot machine prior to rugged testing under real process conditions.

This tool is therefore ready to be used for both in-line quality control on the r2r machine for the production phase but also during the R&D phase for the process development.

1.4.3. TECHNICAL AREA 3:

The goal of Technical Area 3 is the controlled production of barrier layer stacks and the verification of principal approach using polymeric & inorganic layers in stacks, as well as the achievement of improved figures needed for production of flexible ultra high barrier materials. Also, TA3 focuses on the Testing & Performance of the encapsulation system that includes the practical verification of the approach via multi layer stacks, preparation of small scale demonstrators relevant to the later production of encapsulated flexible displays and organic photovoltaic modules.

Controlled production of barrier layer Stacks (WP8)

During the FLEXONICS Project, several samples have been developed, starting from the plain PET substrate, to the final multilayer structure. Each multilayer consisted of a polymer substrate + inorganic coating + hybrid coating + inorganic coating + hybrid coating. A pair of one inorganic and one hybrid coating is called dyad. Within this project, a maximum of 2 dyads were produced. The following two diagrams (Figures XX and YY) show the improvement of the gas barrier properties with every further coating step on top of the PET substrate (please note the logarithmic scale).

The experimental results of the multilayer structures prove the tendency that was forecasted by the theoretical model and the simulations with regard to the barrier improvements for each step:

- barrier improvements are the largest for the 1st inorganic coating on top of the PET and the 1st hybrid coating on top of the 1st inorganic layer (the 1st dyad)
- both the 3rd and 4th layer (the 2nd dyad) do bring lower improvement factors
- each dyad brings a lower improvement factor than the one before

Furthermore, it becomes obvious in Figures 36 and 37 that the final barrier of the complete multilayer structure depends strongly on the quality of the inorganic layer. Even if already broad process parameter studies were performed at the beginning of the FLEXONICS project (by the inorganic coating partners AMAT and ALCAN), these permeation results suggest further research on how to further improving the quality of the inorganic layers (i.e. their intrinsic barrier).

These two diagrams also represent one important advantage of the FLEXONICS project: The big amount of ca. 1500 permeation data that could be gained due to the cooperation of several measuring partners, helped to really know the possible and the typical barrier improvements for each coating step and the deviations from these typical or best results that occur during the fabrication of the ultra-barrier multilayer structure – whereas similar projects or research groups often only report one single best value without explaining about their **reproducability**.

According to the results in Figures 36 and 37, the best results achieved are:

- for **oxygen barrier**: 0.00032 $cm^3/(m^2\ d\ bar)$ at 23°C and 50% RH,
  i.e. **$3*10^{-4}\ cm^3/(m^2\ d\ bar)$**
  which is 2 orders of magnitude lower than in former EU projects

- for **water vapour barrier**: 0.0019 $g/(m^2\ d)$ at 23°C and 85→0% RH,
  i.e. 0.0011 $g/(m^2\ d)$ at 23°C and 50→0% RH,
  i.e. **$1*10^{-3}\ g/(m^2\ d)$**
  which is 1 order of magnitude lower than in former EU projects

These results are **appropriate to encapsulate** sensitive organic electronic devices, like **organic photovoltaic cells (OPVs)**. Life time tests with OPVs (later described in this report) confirmed these results. As both the encapsulation material as also the functional organic layers of the OPVs can be produced **with roll-to-roll coating processes**, the 1st target product of this project, the OPVs, is achieved.
For the 2nd target product, the OLEDs, these achievements are still to low at this point. But with ca. 500 h of life time in best cases (see later chapters) of necessary minimum 1000 h, at least one aspect can be gained from the OLED tests: as life time measurements show a better performance than expected (regarding the best results), the always reported necessary 10^{-6} range must maybe not be achieved when using permeation tests that refer with the permeation result only to the stationary state of the permeation mechanism (e.g. for gas chromatic or fluorescence methods). The period of time that passes until the non-stationary state is finished may be one key aspect in developing ultra-barrier encapsulation material.

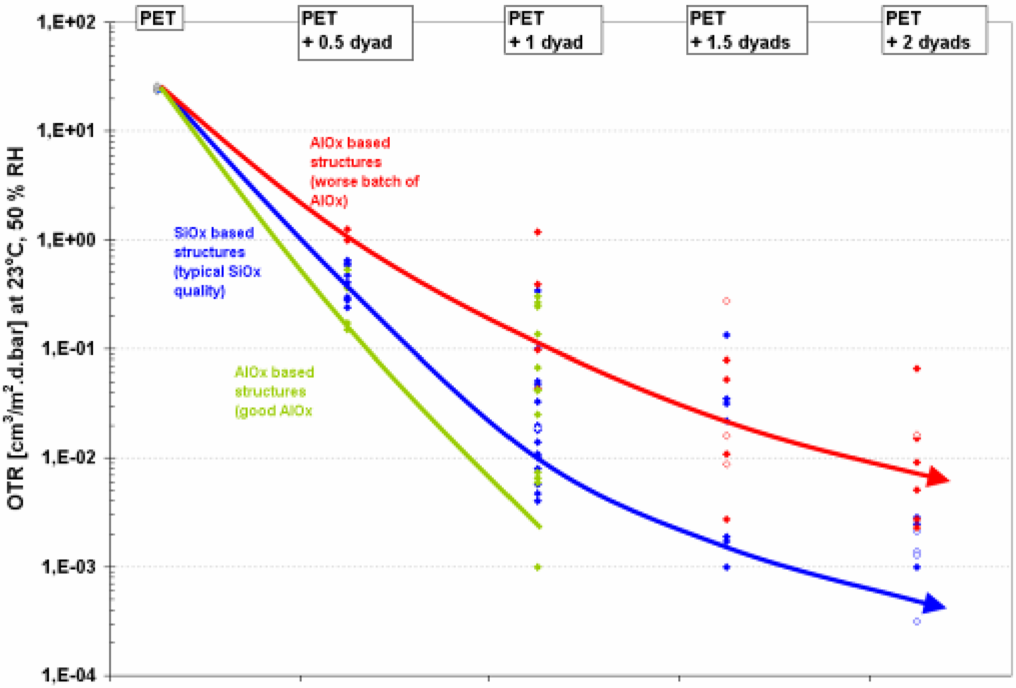


Figure 36 Oxygen transmission rates (OTR) of multilayer material, produced in pilot scale during the project.

Explanations:

Each small rectangle represents one single OTR result. Red and green data refer to AlO_x based structures, with AlO_x layers of two different qualities (green = good one; red = worse). Blue data refer to SiO_x based structures. Filled rectangles are results measured at Fraunhofer IVV (commercial systems, electrolytic method), non-filled were measured at TU Graz (fluorescence method). The multilayer fabrication on top of the good AlO_x coated substrate (green curve) had to be stopped after 1 dyad due to a lack of material.

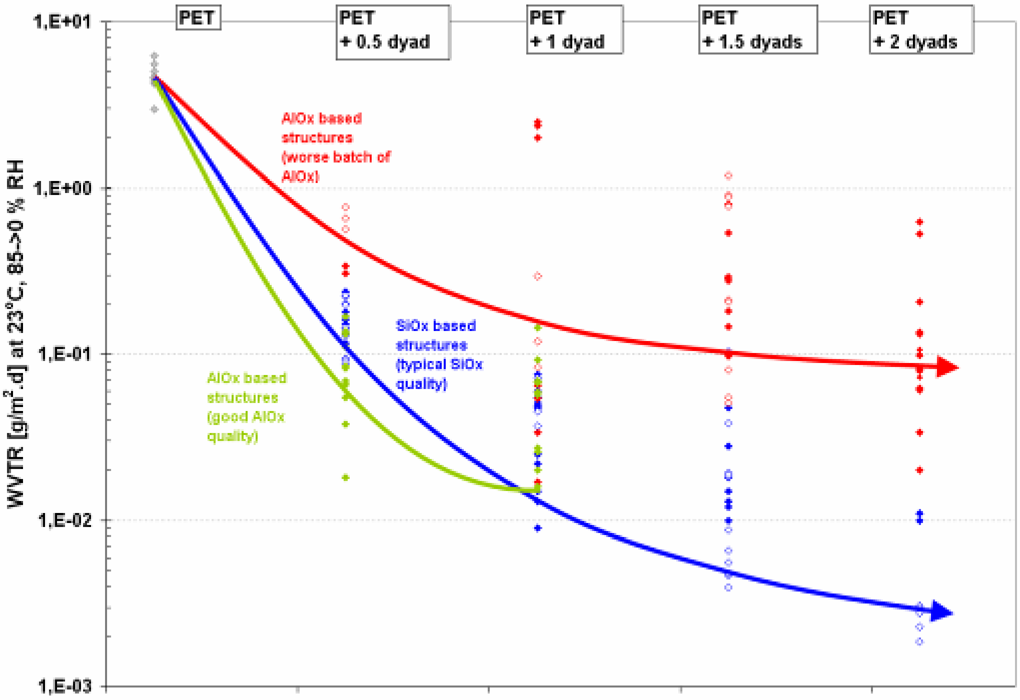


Figure 37 Water vapour transmission rates (WVTR) of multilayer material, produced in pilot scale during the project.

Explanations:

Each small rectangle represents one single WVTR result. Red and green data refer to AlO_x based structures, with AlO_x layers of two different qualities (green = good one; red = worse). Blue data refer to SiO_x based structures. Filled rectangles are results measured at Fraunhofer IVV (commercial systems, electrolytic method + newly developed gas chromatic system), non-filled were measured at Siemens and Konarka (both Ca mirror test). The multilayer fabrication on top of the good AlO_x coated substrate (green curve) had to be stopped after 1 dyad due to a lack of material.

Monitoring of materials and the coating processes by the in-situ SE unit

The AlO_x coating in the multilayer barrier coatings has been performed by AMAT and successfully monitored using an ellipsometer. AMAT characterized the **optical stability of Melinex ST 504**. Optical stability is a basic requirement for steady modelling results i.e. the optical response of the substrate must be constant. The following figures show the measurements before and after monitoring of pilot production processes.

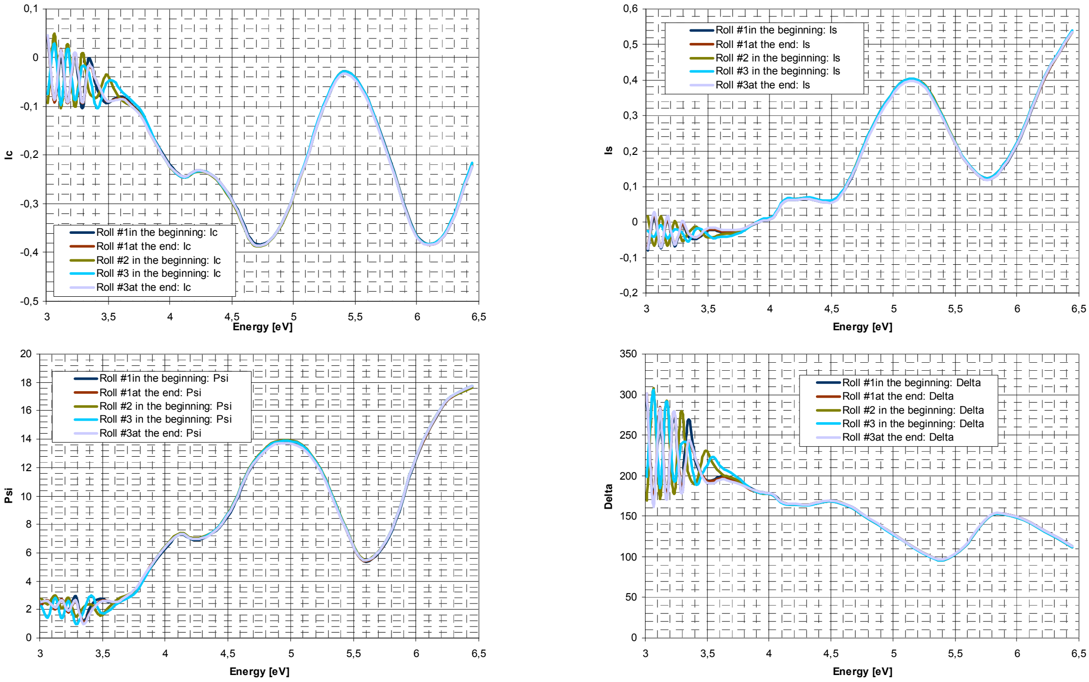


Figure 38 Ic, Is, Ψ, Δ, for start and finish of three different PET rolls

AMAT have also evaluated the coating parameters for an AlOx-coating process. The objective of this evaluation is, to find a stable AlOx-coating process with a deposition rate as high as possible. A typical example for the evaluation of the AlOx coating process is given in Figure 39.

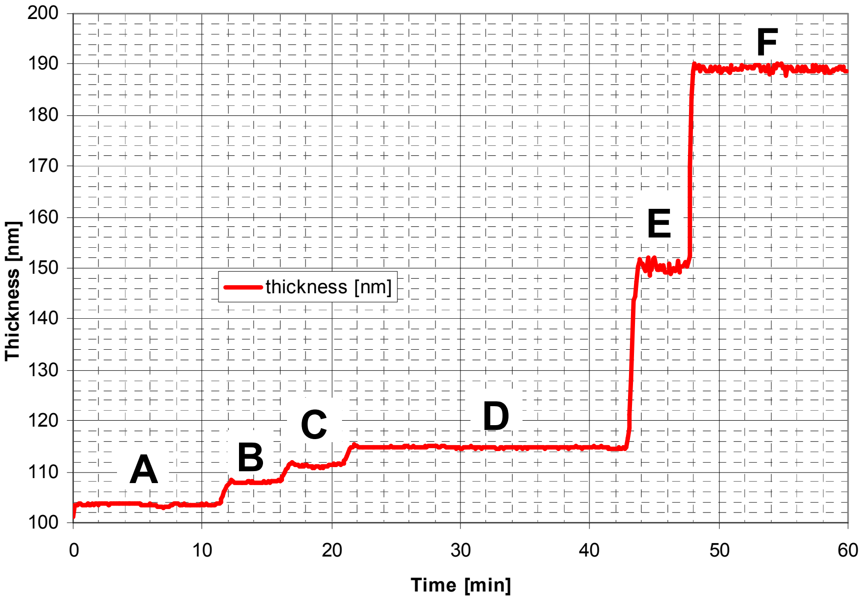


Figure 39 AlOx-thickness for different process-parameters during the evaluation phase. The AlOx-thickness is detemined by inline-ellipsometry

The Monitoring of the pilot production process for the first roll is displayed in figure 40. To get a stable AlOx-coating process, certain experimental parameters have been chosen. After 10min with 20cm/min web speed for conditioning, the web speed was increased to 56cm/min. The goal objective was a 40nm layer thickness.

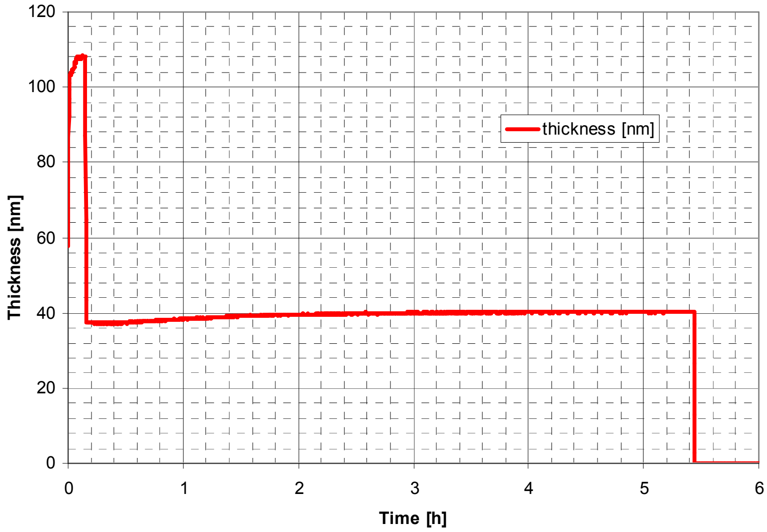


Figure 40. AlOx-thickness for pilot production process #1, film thickness by ellipsometric in line monitoring

Besides the barrier measurements, the surface quality of some of the coatings of the produced multilayer stacks have been evaluated. All of the tested AlO_x coatings and all of the tested Hybrid coatings had a very smooth surface resulting in surface roughnesses of ~1 nm (Table. 3 and Figure 41).

Table 3 AFM results of selected surfaces of the multilayer stacks, Ra and RMS being two differently calculated means values of the surface roughnesses.

		Ra,whole			øRa	±	RMS,whole			øRMS	±
PET M 401 + SiOx	50µm, 120nm	3,7	9,2	9,8	**7,6**	3,4	5,8	15,3	16,4	**12,5**	5,8
PET M 401 + SiOx + Hybrid#1	50µm, 120nm, 3µm	0,9	1,0		**0,9**	0,1	1,1	1,3		**1,2**	0,1
PET M 401 + SiOx + Hybrid #2	50µm, 120nm, 3µm	0,5	1,1		**0,8**	0,4	0,7	1,3		**1,0**	0,4
PET M 401 + AlOx#1	50µm, 40nm	0,9	1,0		**0,9**	0,1	1,1	1,3		**1,2**	0,1
PET M 401 + AlOx#2	50µm, 40nm	0,8	1,1	1,0	**0,9**	0,1	1,0	1,4	1,4	**1,3**	0,2
PET M 401 + AlOx#3	50µm, 40nm	0,2	0,5		**0,4**	0,2	0,2	0,7		**0,5**	0,3

The roughnesses of the tested SiOx coatings were higher which can already be seen on the AFM pictures (Fig. 41).

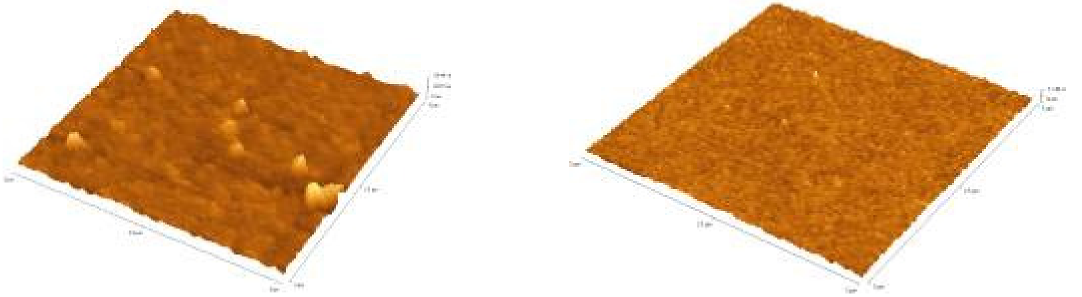


Figure 41 AFM picture of the inorganic surface of PET/SiOx (left side) and PET/AlOxMay06 (right side).

Nevertheless, the difference of the roughnesses of the two types of inorganic coatings are not correlated to barrier properties (as expected).

For the visualization of surface defects on barrier foils a combination of SE ("**S**econdary **E**lectrons") and BSE images ("**B**ack-**S**cattered **E**lectrons"). As a result of an additive overlay of the SE and BSE images, the defect sites appear dark (with good contrast) while dust particles become considerably brighter in comparison. All in all, a more explicit idea of the surface relief is obtained. The example in Figure 42 shows two micrographs of a PET substrate coated with an Al-layer.

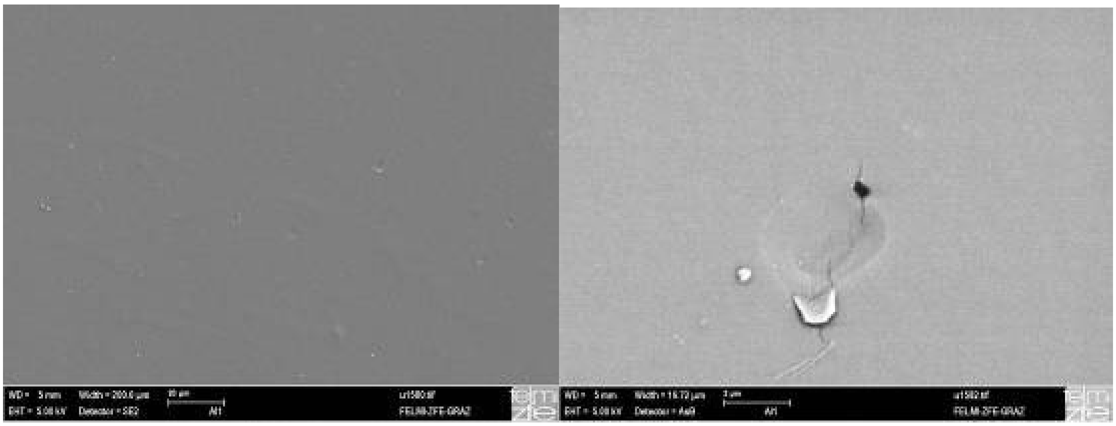


Figure 42 Micrographs of the surface of PET coated with an Al-Layer

In addition to the micrographs shown, a number of images were obtained showing no significant impairment of the surface integrity, apart from the presence of dust particles. As it is seen in Figure 42, defects intrinsic to the surface barrier layers appear to be absent. The defects shown seem to have their origin in mechanical stress or damage. It cannot be said whether the defect formation occurred during the production process, shipping & storage or the sample preparation procedure of the microscopic investigation (although care was taken to the greatest possible extent not to introduce “artificial” defects in the course sample preparation). On the surface of Al-coated samples the defect density appears to be lower than in case of AlO_x and SiO_x-coated samples.

Testing & Performance of encapsulation system (WP9)

Barrier performance of new film samples

A large number of barrier foils have been tested for their **Oxygen transport properties (OTR)** at 0% humidity.

The **Water Vapour Transition Rate (WVTR)** values of numerous samples delivered by the partners has been evaluated. The results of the barrier analysis are summarized in the following Table. Most of the films had to be measured by Mocon Testing (lower measuring limit 10^{-2} g/m^2/d). Four samples could be investigated by the much more sensitive Ca Mirror Testing (F277, F278, F279, FZ 5). Good barrier properties are obtained for the 3-layer system F78 and the laminated films PB07-007 with WVTR values of 0,1 g/m^2/d. The films F277 and F278 have a 5-layer barrier coating and display - depending on the interpretation of the Ca-test results - moisture permeation rates in the 10^{-2} - 10^{-3} g/m^2/d range!

Table 4 Water vapour transmission rate of different multilayer samples in g/m^2/d (test conditions: 38°C / 90% r.h.)

Sample	Source	d (µm)	Mocon	Ca-Test
F43	IVV (4/07)	55	0,24	
F78-6	IVV (4/07)	53	0,1	
F79-6	IVV (4/07)	54	0,27	
F91-2	IVV (4/07)	54	0,55	
P91-3	IVV (4/07)	52	0,54	
F92	IVV (4/07)	54	3,1	
ISC_1	ISC (6/07)	ca. 130	0,13 / 0,06	
ISC_2	ISC (6/07)	ca. 130	0,10 / 0,16	
ISC_3	ISC (6/07)	ca. 127	0,20 / 0,09	
ISC_4	ISC (6/07)	ca. 130	0,18 / 0,11	
F277	IVV (6/07)	ca. 53		0,0039 and 0,02 *
F278	IVV (6/07)	ca. 53		0,0027 and 0,012 *
F279	IVV (6/07)	ca. 53		0,25
FZ 5	Alcan (7/07)	54	0,19 / 0,26	0,077
PB07-007	Alcan (7/07)	54	0,1	

* Two characteristic regimes in the 1/R versus t-curves.

Characterization of general processing & application relevant properties

Previous investigations revealed relatively low dimensional stability for unstabilized standard PET films such as Mylar 401. Dimensional stable substrates are required for the preparation of flexible OLED displays. For OLED lighting panels based on the “small molecule” technology the dimensional stability is somewhat less critical, but shrinkage values below 0,25 % at 100°C are nevertheless required.

Due to the insufficient thermal stability of Mylar 401 in the view of the SIEMENS process conditions, it was decided to develop also barrier coatings for heat stabilized PET grades in order to provide barrier substrates for high performance OLED applications. The PET grade Melinex ST 504 – 125 µm was selected for this work, and first samples with a two-layer barrier coating system were provided by ISC (samples ISC 1 – ISC 4, see Table 5). As is clear from Figure 43, the films display relatively low shrinkage at 150°C and 180°C. For comparison, the shrinkage of standard PET grades is up to 2 % in this temperature range.

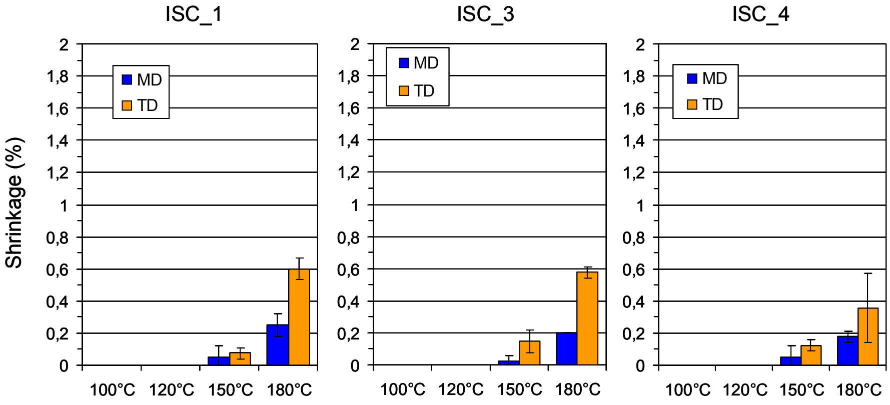


Figure 43 Shrinkage of heat stabilized PET films with a 2-layer barrier coating.

Deposition of ITO layers

For the preparation of flexible OLEDs it is necessary to deposit a transparent electrically conductive electrode layer on top of the barrier coating. The standard anode material is Indium-Tin-Oxide (ITO) which may be applied by sputtering onto polymer films. Several companies offer ITO coated PET, PEN or PES films on a commercial scale, however, barrier films with an ITO layer are not yet available. Therefore SIEMENS applied ITO on four PET barrier films in a batch process using in house sputtering facilities. The substrate size was 5 x 5 cm^2. The thickness of the ITO layer is about 125 nm as measured on a co-processed glass-substrate. The resulting surface conductivity was found to be in the target range (below 100 Ohm/sq, Table 5).

Visual inspection of the coated samples revealed significant differences between the Mylar 401 and Melinex ST 504 based barrier films. The latter displayed no apparent bending after the sputtering process, whereas pronounced warpage was observed for the Mylar 401 based samples F66 and F78-6, respectively (see Figure 44). Although there might be a different result when ITO is deposited on a roll-coater, our findings demonstrate again the importance of mechanically stable substrates for OLED applications.

Table 5 Surface conductivity of ITO coated film samples

Sample	Thickness (µm)	Soure	Conductivity (W/sq)
F 66 (Substrate = Melinex 401)	52	IVV	Ca. 90
F 78-6 (Substrate = Melinex 401)	53	IVV	Ca. 100
PET 125 / AlOx / Hybrid (Substrate = Melinex ST504)	127	ISC	Ca. 80
PET 125 / AlOx / Hybrid+ np (Substrate = Melinex ST504)	127	ISC	Ca. 90

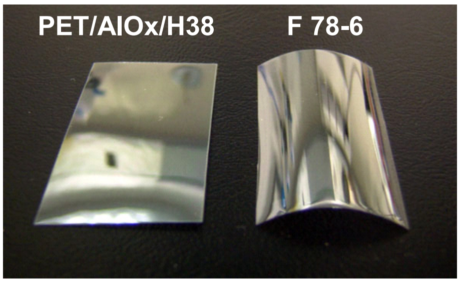


Figure 44 ITO coated film samples; Mylar 401 based samples display warpage after the sputter process.

Testing of the environmental stability

The environmental stability especially of the SiOx/Hybrid layers on PET has been evaluated by UV testing and Damp-Heat-Testing. The UV – Testing has been performed by Atlas Test (750 hours) and by QUV-B Test (750 hours).

The test device for the Atlas-Test is called Atlas-Weatherometer. According to DIN EN ISO 4892-2 a Xenon arc lamp is used for testing. The irradiance is 0,50 W/m² at 340nm, which corresponds to an irradiance of 550 W/m² in a wavelength range of 280 – 800nm. This is done at 65°C at rh. of 65%. One test cycle comprises 18 minutes irradiation under moisture followed by 102 minutes irradiation under dry conditions.

In the QUV-B test the material is irradiated with a fluorescent tube with its emission maximum at 313nm (UV-B). The testing is done accordingly to DIN 53384. 4 hours of irradiation are followed by 4 hours of bedewing, both at 50°C.

- The Damp-Heat-testing has been performed at 85°C and 85% rh (1250 hours)

The testing assembly consist of two counter-laminated barrier foils and is displayed in Figure 45

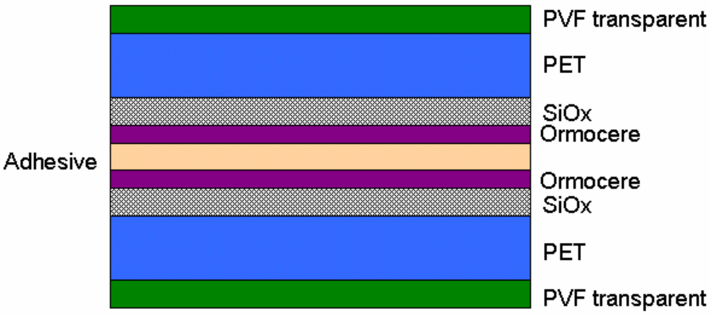


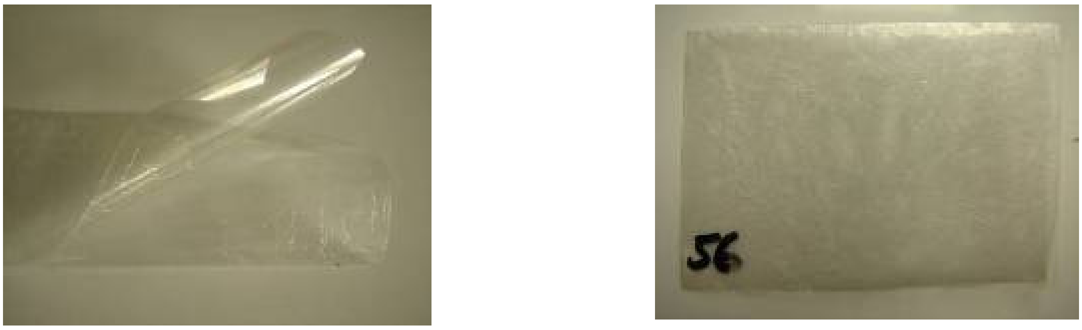
Figure 45 Test assembly for environmental stability at ISOVOLTA

The assessment of the environmental impact on the samples was performed by visual inspection. The evaluated samples and the results of the UV-Testing are displayed in Table 6, the results of the Damp-Heat-Testing in Table 6.

Table 6 Results of the UV-Testing

Sample	Curing	Testing	Comment / Observations
Hybrid #1	Thermally		No coloring
		QUV – B (750 h)	Severe delaminations, formation of crystalline sections, no yellowing
		Atlas-testing (750 h)	Severe delaminations, formation of crystalline sections, no yellowing
Hybrid #2	UV		Visible yellowing after curing, not acceptable
		QUV – B (750 h)	Proceeding yellowing, formation of crystalline sections in connection with delamination within the irradiated area
		Atlas-testing (750 h)	No remarable changes
Hybrid #3	Thermally		No yellowing before testing
		QUV – B (750 h)	No yellowing, formation of crystalline sections within the irradiated area
		Atlas-testing (750 h)	Formation of crystalline sections as before, in connection with severe delamination

Exemplarily the samples after UV-Testing are displayed in Figure 46:



QUV – B

Atlas-testing

Figure 46 Results of the UV-Testing of F1 H38%

Table 7 Results of the Damp-Heat-Testing

Sample	Curing	Testing	Comment / Observations
Hybrid #1	thermally	85°C / 85% r.h. 1250 h	Severe delamination starting at the edges and also in the middle of the sample, - not acceptable -
Hybrid #2	UV	85°C / 85% r.h. 1250 h	Delamination to alower extent than in first sample possibly caused by mechanical stress
Hybrid #3	thermally	85°C / 85% r.h. 1250 h	No delamination, slight yellowing Best result of the 3 samples

Overall, Hybrid #3 displayed the best stability in Damp-Heat-Testing, in the UV-Testing all samples have no sufficient stability.

Testing of WVTR by Konarka

Barrier films were tested by **Konarka** for the WVTR using the Ca-test. Samples were stored under 65°C/85 % humidity and permeation rates were evaluated after at half time of the complete failure of the Ca-sensor.

Further WVTR testing by SIEMENS

The barrier foils from Alcan (sample 1 – 10) and IVV (F337, F338, F369, F370) already tested by Konarka for the WVTR evaluation were delivered to SIEMENS too, in order to perform Ca-Testing (electrical and optical inspection) at differing conditions (40°C / 92% r.h.) (second series of the SIEMENS WVTR testing).
Additionally IVV provided a multilayered barrier sheet F70, consisting of two inorganic and two hybrid polymer layers. For the results of the tested samples please see Table 8 and Table 9.

The IVV-films IVV F337, IVV F338 were tested only in the Mocon testing, due to their modest barrier performance. As reference system a UTG-glass (100 µm) encapsulated Ca-mirror testing assembly has been used. UTG glass substitutes in the reference assembly the barrier foils to be tested, all other components and processes are identical.

All processes in the preparation of the test assembly have been performed in a glove box under nitrogen atmosphere. Due to the evident change of the water permeation rate of the tested barrier foils during the climatic testing, SIEMENS switched to a more detailed reporting:
Up to six assemblies per barrier foil type have been tested in the climate chamber (min. 4 assemblies), the results of the best and the worst sample have been reported as follows: Maximal and minimal permeation rate (respective time in brackets (hours)) and time of the complete breakdown ("time of death") of the testing assembly (See Table 8)

Table 8 Evaluation of WVTR at SIEMENS by Ca-mirror testing @ 40°C / 92% rh (electrical testing)

Sample	**Permeation rate best sample**			**Permeation rate worst sample**		
	Min [g/m^2*day]	**Max [g/m^2*day]**	**Time of death [hours]**	**Min [g/m^2*day]**	**Max [g/m^2*day]**	**Time of death [hours]**
Glass UTG reference	$9,20\cdot10^{-5}$ (225)	$3,4\cdot10^{-4}$ (15)	interupted (360h)	$2,00\cdot10^{-4}$ (75)	$6,00\cdot10^{-4}$ (230)	interupted (360h)
Alcan: sample 1 CX07-094	$1,90\cdot10^{-3}$ (2)	$8,00\cdot10^{-3}$ (113)	163	$6,30\cdot10^{-3}$ (2)	$2,33\cdot10^{-2}$ (45)	55
Alcan: sample 2 CX07-095	$2,00\cdot10^{-5}$ (0)	$1,10\cdot10^{-2}$ (192)	230	$1,10\cdot10^{-3}$ (160)	$5,84\cdot10^{-3}$ (19)	163
Alcan: sample 3 CX07-096	$1,40\cdot10^{-3}$ (90)	$4,64\cdot10^{-3}$ (80)	165	$2,58\cdot10^{-3}$ (84)	$9,79\cdot10^{-3}$ (54)	165
Alcan: sample 4 CX07-097	$2,80\cdot10^{-4}$ (1)	$8,40\cdot10^{-3}$ (44)	132	$3,60\cdot10^{-3}$ (1)	$1,67\cdot10^{-2}$ (14)	62
Alcan: sample 5 CX07-098	$1,70\cdot10^{-3}$ (0)	$5,21\cdot10^{-3}$ (20)	300	$4,45\cdot10^{-3}$ (0)	$2,57\cdot10^{-2}$ (14)	140
Alcan: sample 6 CX07-099	$6,42\cdot10^{-3}$ (14)	$3,15\cdot10^{-2}$ (2)	87	$9,35\cdot10^{-2}$ (0)	$2,3\cdot10^{-1}$ (1.6)	8
Alcan: sample 7 CX07-100	$7,45\cdot10^{-4}$ (0)	$1,07\cdot10^{-2}$ (99)	155	$2,70\cdot10^{-3}$ (0)	$2,33\cdot10^{-2}$ (19)	122
Alcan: sample 8 exCX07-038	$1,45\cdot10^{-4}$ (2)	$1,30\cdot10^{-2}$ (191)	213	$3,26\cdot10^{-4}$ (0)	$1,20\cdot10^{-2}$ (100)	167
Alcan: sample 9 exCX07-039	Problem	during	encapsulation			
Alcan: sample 10 exCX07-018	$9,20\cdot10^{-4}$ (0)	1,50·10-2 (20)	93	$8,20\cdot10^{-3}$ (5)	$2,20\cdot10^{-2}$ (12)	45
IVV 369	$1,85\cdot10^{-4}$ (2)	$1,40\cdot10^{-2}$ (68)	133	$3,00\cdot10^{-4}$ (4)	$1,40\cdot10^{-2}$ (78)	112
IVV 370	$5,30\cdot10^{-4}$ (0)	$1,18\cdot10^{-2}$ (58)	69	$6,40\cdot10^{-4}$ (0)	$1,20\cdot10^{-1}$ (18)	25
IVV F70	$2,27\cdot10^{-4}$ (5)	$4,3\cdot10^{-3}$ (483)	After 500h Test still ongoing	$3,95\cdot10^{-4}$ (405)	$2,76\cdot10^{-3}$ (8)	After 500h Test still ongoing

He reference assembly supplied the best results with water vapour transmission rates of $9,20\cdot10^{-5}$ up to 6,00e-4 g/m^{2}*d (see Figure 47), the test has been stopped after 360 hours. All newly tested barrier foils delivered by Alcan and IVV supplied higher water vapour transmission rates. So we can be sure, that this effect is mainly due to the barrier properties of the foils. The best barrier properties of foils supplied by Alcan were CX07-95 and Alcan exCX07-38 with best permeation rates in the 10^{-4} g/m^{2}/d range (starting values), but with the disadvantage of the short term stability of barrier performance (see Figure 48).

IVV F70 showed overall the best barrier properties among the tested foils up to now (see Figure 49**).**

All other barrier foils showed a higher defect density giving rise to higher permeation rates and thus lower barrier properties. This was confirmed by optical analysis of the degradating Ca mirrors. Example of this optical inspection is given in Figure 50 for the best foils tested.

IVV F70 showed overall the best barrier properties among the tested foils up to now (see Figure 49). As the foil F70 has been glued PET-face to the Ca-mirror, maybe a further improvement of the barrier properties of these foils could be realizable by an additional thermal pre-treatment of the foil in order to remove residual water traces in the PET. We see an additional benefit in using such counter-laminated barrier foils in the protection of the barrier layers against mechanical impact under handling and r2r-processing.

All other barrier foils have been glued with the barrier layers faced to the Ca-mirror. They showed a higher defect density giving rise to higher permeation rates and thus lower barrier properties. This was confirmed by optical analysis of the degradating Ca mirrors. Example of this optical inspection is given in Figure 50 for the best foils tested.

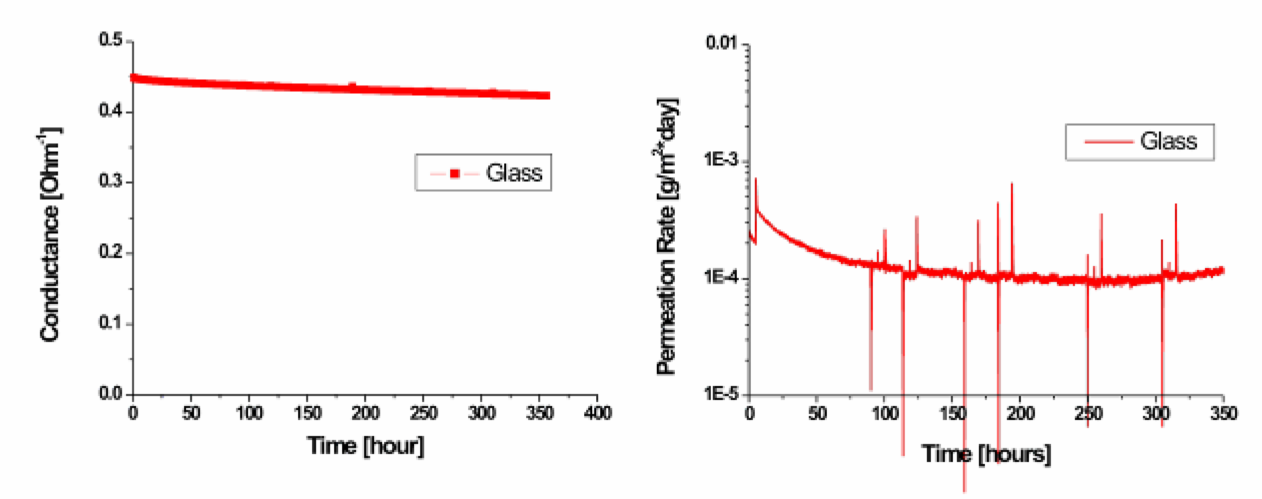


Figure 47 Conductance and water vapour permeation rate of the Glass-UTG reference assembly

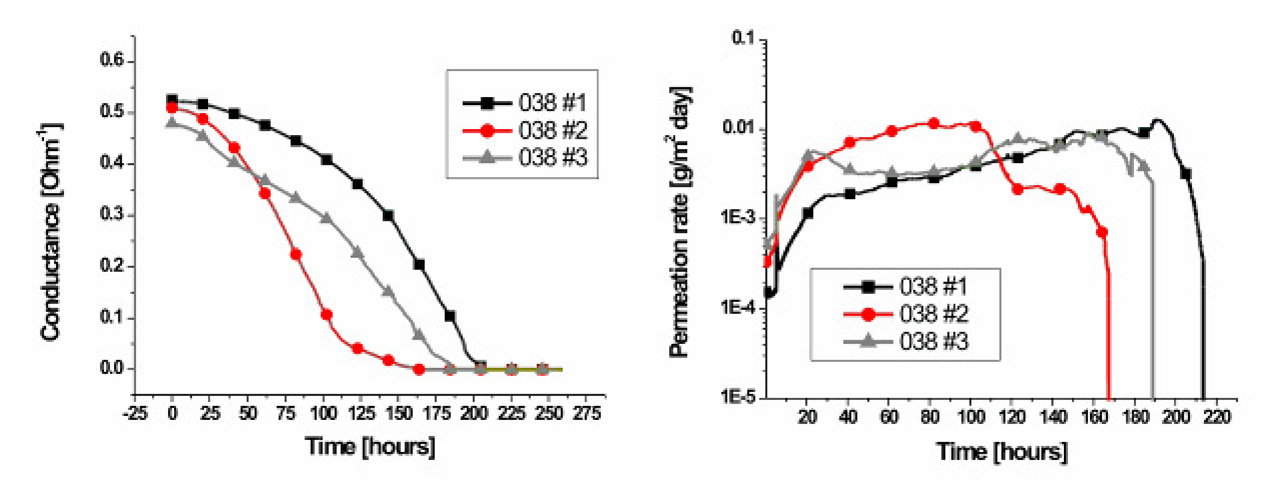


Figure 48 Conductance and water vapour permeation rate of the Alcan ex CT07-038 - foil

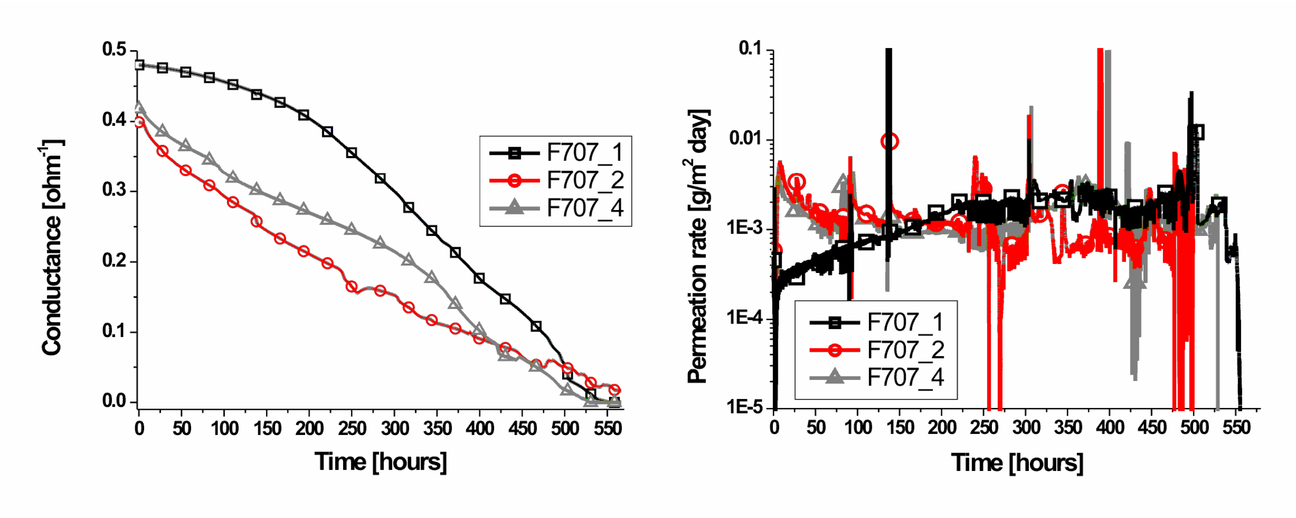


Figure 49 Conductance and water vapour permeation rate of the IVV F70 – foil

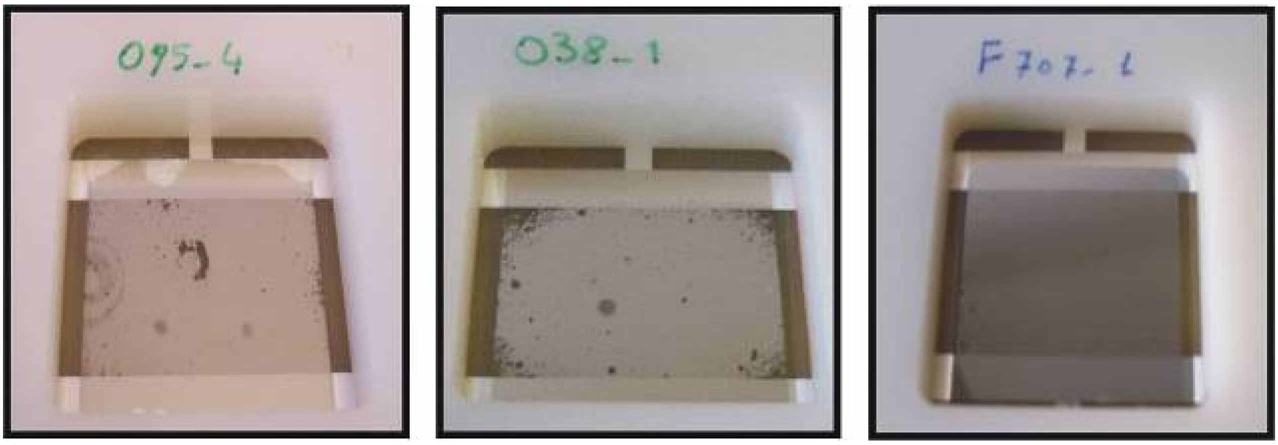


Figure 50 Optical inspection of the the most promising foils (Alcan CX07-95, Alcan exCX07-38 and IVV F70 respectively) after ~100h Climatic chamber 38°C/90rH.

1.5. DEMONSTRATORS - EVALUATION AND VALIDATION

1.5.1. Flexible OPV Device Demonstrator

Manufacturing of demonstration PV sample by r2r processes & performance durability tests

Encapsulation of OPV devices with Flexonics barrier samples of the barrier films submitted to date two films were selected, using available quantities and barrier performance as the selection criteria, for performance testing. The two films selected were a barrier material from IVV and the 4-ply laminate from Alcan. In a first test the materials were used as encapsulation films for OPV cells manufactured on glass. This type device configuration is called “semi-rigid” due to its combination of flexible and rigid materials. The performance of such devices was monitored over time at room temperature (“shelf life”) and at 65°C/85%rh (“damp-heat”). The results obtained for this test series are shown in Figure 52. At room temperature (shelf life test), no degradation is observable for the samples with IVV barrier encapsulation, while there is a minimal amount of degradation visible in the samples encapsulated with Alcan barrier. Similarly during the damp-heat test the samples encapsulated with IVV material show a significantly improved lifetime over the samples encapsulated with the Alcan film. Defining lifetime of a device as the time it takes until the efficiency has dropped to 80% of its original value, then in the damp-heat test on average the devices encapsulated with Alcan barrier have a lifetime of 400hrs, and the devices encapsulated with IVV material have an extrapolated lifetime of ca. 1000hrs. Despite these excellent results, still a significant number of individual devices failed during the test, resulting in unsatisfactory yield. As the degradation progresses the distribution of efficiencies increases**.**

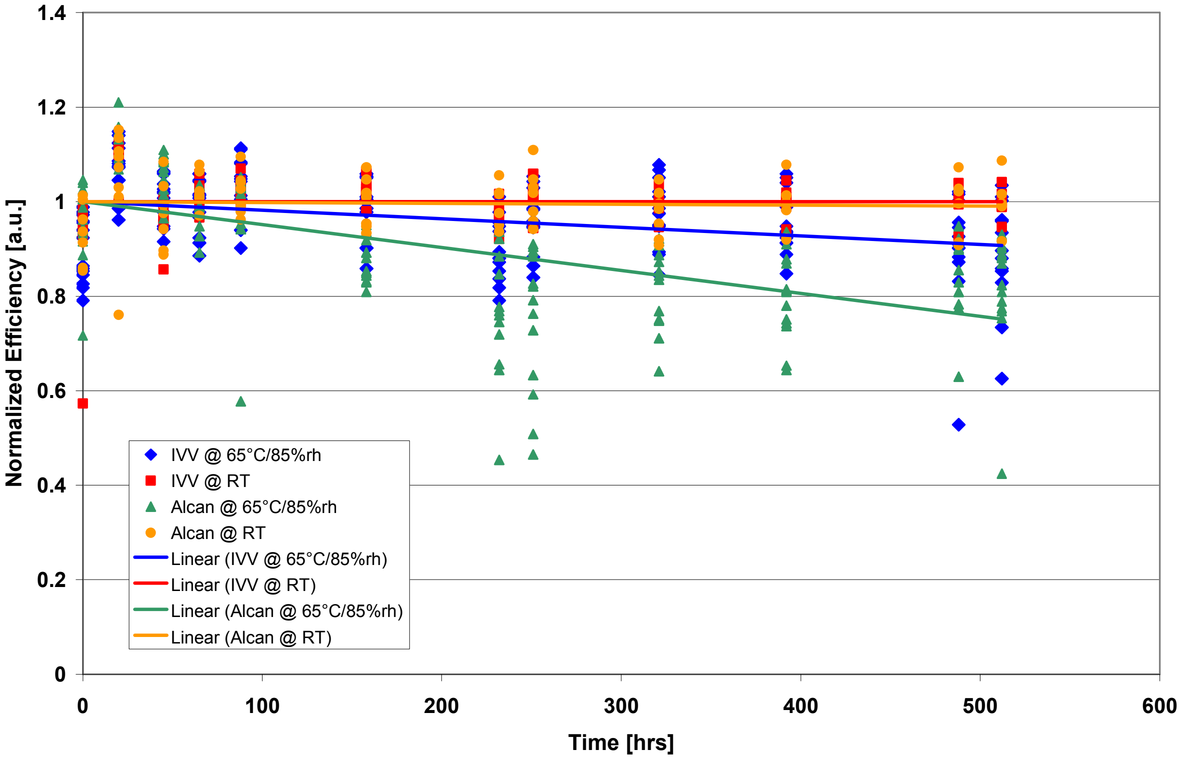


Figure 52 Normalized efficiency over time for glass OPV cells encapsulated with the flexible barrier films from IVV and Alcan. The cells were stored at room temperature and at the accelerated testing climate of 65°C/85%rh.

As a next step, fully flexible solar cells were prepared and then encapsulated with the Alcan barrier film on the front and the back. These devices were stored at the damp-heat condition 65°C/85%rh. The degradation results obtained with these samples are shown in Figure 53. The average lifetime for the cells in this test was very comparable to the lifetime obtained with the semi-rigid devices. Unlike in the semi-rigid devices, the spread of the cell performance did not increase over time. The likely reason for this are improved processing conditions that also lead to a better stability for these cells. It is interesting to observe that the degradation rate for fully flexible cells does not increase by a factor of two (as would be expected since water can enter the package from top and bottom, in comparison to only one side as is the case in semi-rigid cells. There are two possible explanations for this: a) the underlying transparent electrode has a better barrier performance than the barrier film itself b) the permeation is dominated by lateral permeation through the adhesive. Both mechanisms are conceivable**.**

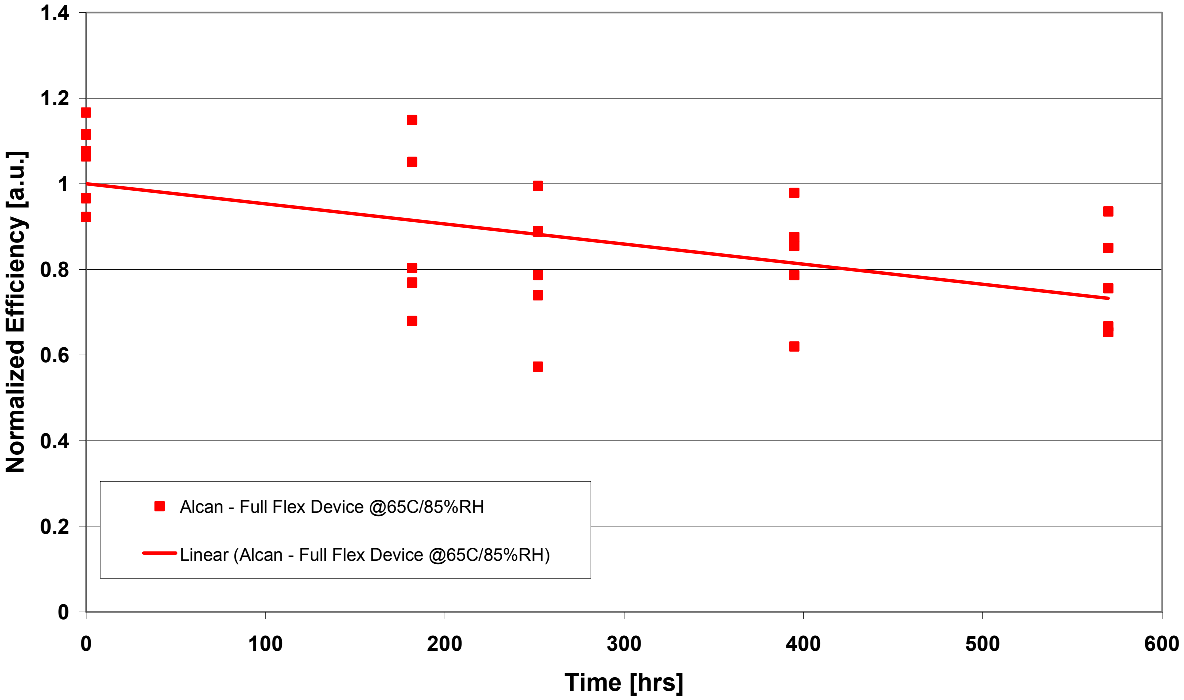


Figure 53 Normalized efficiency over time for fully flexible OPV cells encapsulated with the barrier film Alcan. The cells were stored at the accelerated testing climate of 65°C/85%rh.

Using the data obtained in the accelerated degradation testing it is possible to extract a rate of degradation from the data and to correlate this with the WVTR rates measured in Ca-tests. This is shown in Figure 54. It is apparent in Figure 54 that degradation of OPV cells correlates directly with the permeation rate of the encapsulation films. This is a powerful tool for predicting lifetimes of devices and determining necessary permeation rates for achieving a desired lifetime. The results indicate an acceleration factor of ca. 30 for the damp-heat condition of 65°C/90%rh over storage at room temperature. Therefore the current flex cells will have a shelf lifetime of ca. 12000hrs.

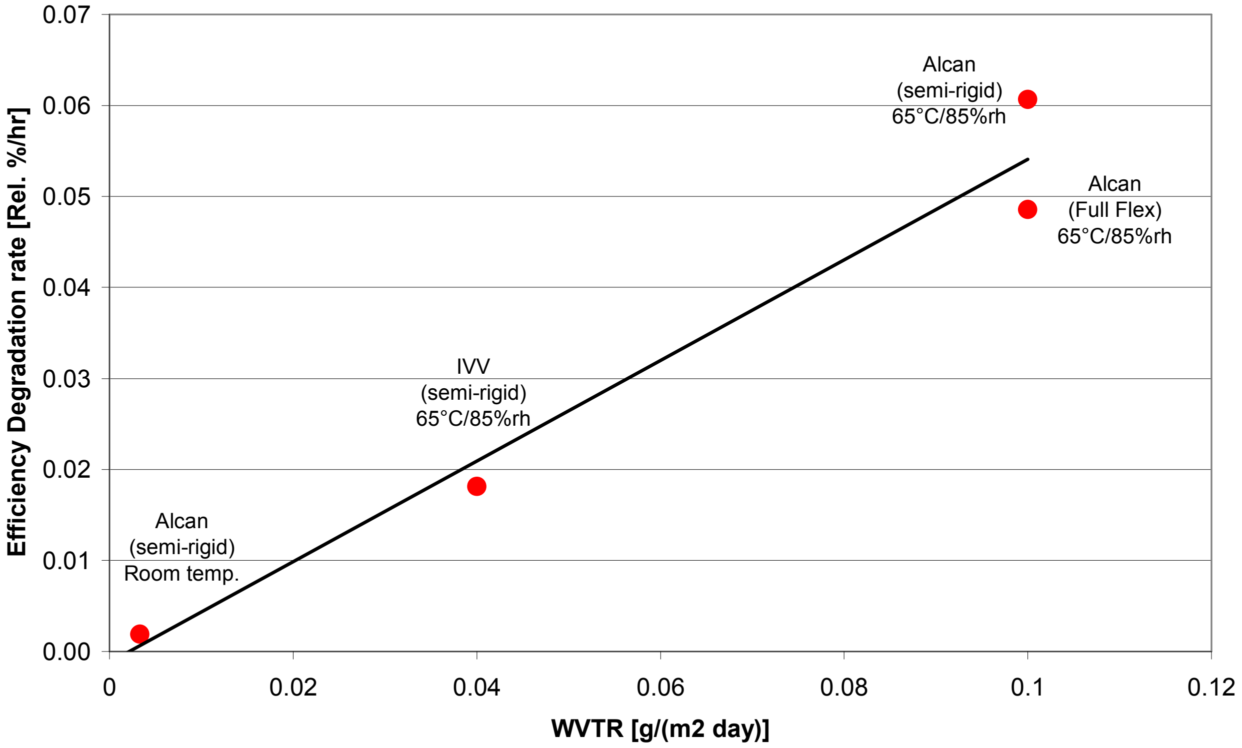


Figure 54 Rate of degradation obtained from semi-rigid and fully flexible cells vs. the measured WVTR rate for the encapsulation films.

Additional packaging trials were performed together with **ISOVOLTA**, in order to evaluate the suitability of the ISOVOLTA packaging process and study the performance of the OPV cells after packaging.
Standard OPV devices were packaged with different barrier films and 400 μm thick EVA material from Etimex. The following stacks were prepared:

Stack 1: Alcan barrier **|** EVA **|** OPV cell **|** EVA **|** Alcan Barrier
Stack 2: Icosolar 2716 (Alu laminate) **|** EVA **|** OPV cell **|** EVA **|** Icosolar 2754 (ETFE/SiOx)
Stack 3: IVV Barrier **|** EVA **|** OPV cell **|** EVA **|** IVV Barrier

A fast cure type EVA was used as embedding material for the cells and modules with different types of barrier materials on the outside. The EVA packaging was done under a pressure of 1 bar at 140°C for 20 minutes). Several packaged devices were produced which were submitted to lifetime testing at 85°C / 85%rh. In Figure 9-3.4 the evolution of the device efficiency versus testing time is plotted for the different packaging materials.

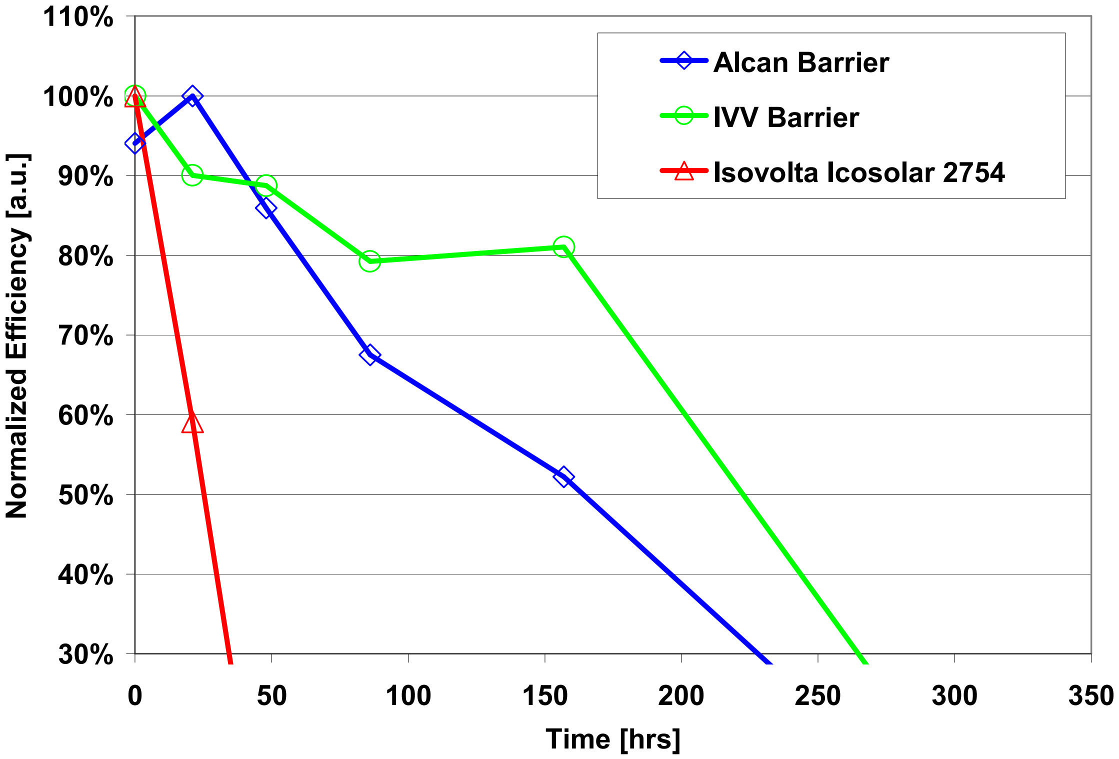


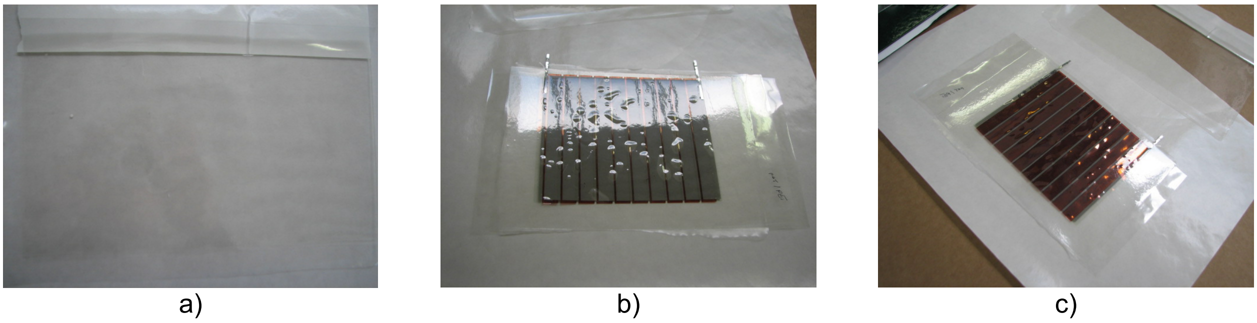
Figure 55 Efficiency decay of devices packaged at Isovolta upon storage at 85°C / 85%rh.

Figure 55 shows that the efficiency decay scales with the barrier properties of the applied packaging films. However, working with different adhesives and thinner layers, significantly longer lifetimes have been observed for OPV-devices packaged with Alcan. This indicates that the EVA material, especially when 400 µm thick may be the limiting factor for the observed lifetimes.

Before starting the encapsulation trials, the Konarka encapsulation material was laminated against itself, in order to test the suitability of the lamination process with this material. The laminates remains clearly transparent after the lamination process. No bubbles or wrinkles could be observed.

However, the lamination of an OPV-module (160 x 130 mm) caused problems:

On the reverse side of the OPV-module a reaction between the conducting layer and the EVA took place causing the formation of bubbles being approx. 5 to 10mm in diameter. In turn the bubbles on the reverse side caused certain unevenness. No chemical reaction could be observed there. These result can be seen in figure 56.


a) b) c)

a) Laminate with Konarka encapsulation material
b) Laminated OPV module from the reverse side
c) Laminated OPV module from the front side

Figure 56: Konarka OPV modules encapsulated with Konarka encapsulation material

1.5.2. Flexible OLED Device Demonstrator

Manufacturing of small scale test OLED display and encapsulation such OLED samples into the flexible, ultra-barrier layers developed in WPs 7 & 8. OLED performance/durability tests.

4 different packaging concepts for OLEDs are currently discussed at **SIEMENS**
For the state-of-the art encapsulation, a glass lid is glued onto an OLED device processed on a glass substrate as schematically shown in Figure 56 (a). The hermetic sealing is realized via an adhesive rim. As an additional protection, a moisture getter pad is placed inside the OLED device in order to absorb remaining humidity and outgasing products of the adhesive.
Thin film encapsulation represents another packing concept for OLED. Here, alternating layers of inorganic and organic material are deposited onto the OLED substrate (Figure 56 (b)). To some extent, the thin film encapsulation process resembles the development of barrier layers in the Flexonics project with the difference that in the thin film encapsulation process the barrier coating is applied directly on a device whereas in the Flexonics project the focus is on a semi-finished product (polymer based barrier film). SiOx and AlOx are typical materials for the inorganic layer, and UV curable epoxy or acrylic coatings are used for the organic layer. In principle, this concept can also be used for flexible devices provided the barrier coating displays sufficient adhesion to the substrate and high flexibility.
For fully flexible devices two other concepts are discussed in literature. A flexible barrier film can be applied on a flexible OLED substrate either via a rim sealing adhesion layer, or over its entire surface in a lamination process as shown in Figure 56 (c) + 3 (d). In principle, the barrier film for the backside encapsulation can be transparent or non transparent. Cost effective solutions for non-transparent protective films are thin metal films or metal/polymer laminates. Candidates for transparent encapsulation films are the film materials which are developed in the Flexonics project. The big challenge for this packaging concept is to find suitable barrier adhesives with sufficient flexibility.

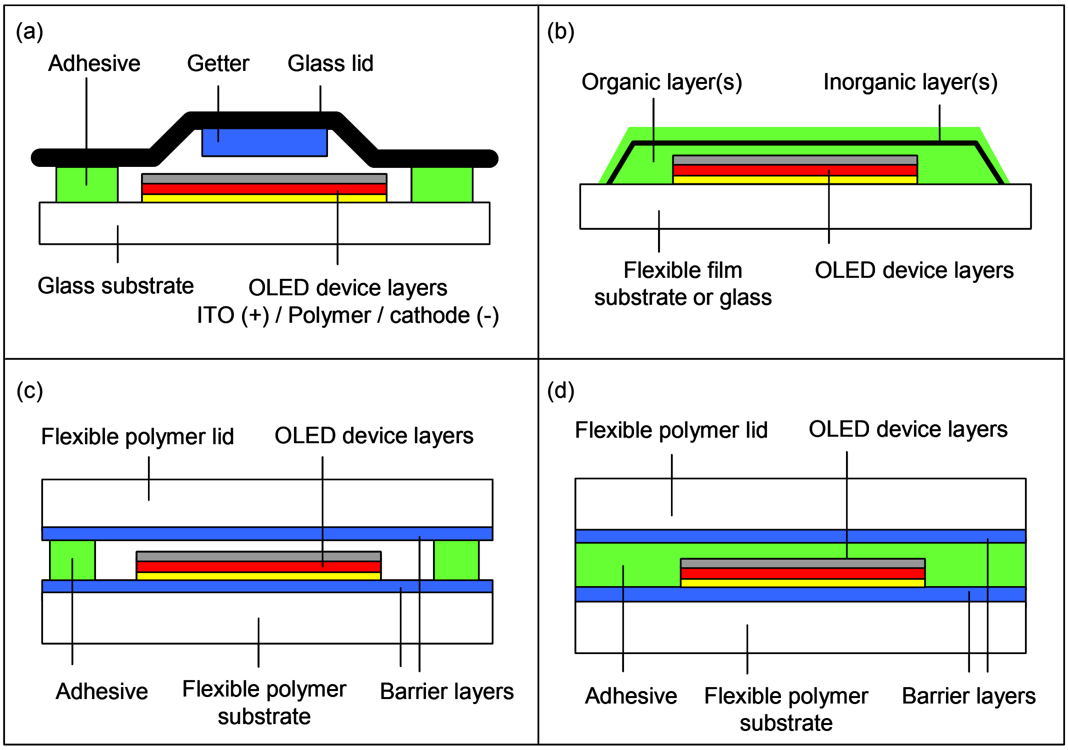


Figure 56 Packaging concepts for OLED: (a) Standard glass lid encapsulation for rigid OLED, (b) Thin film encapsulation, (c) rim sealing for flexible devices and (d) lamination of a barrier film on a flexible OLED substrate.

Preparation of OLED devices
The films F277, F278 and PB07/007 were used for the preparation of small OLED lighting devices. In a first step, the barrier films were used as a protective lamination film for OLEDs processed on glass substrates. This procedure resembles to the device concept depicted in Figure 56 (d). The barrier films were glued on the OLED using an UV curable adhesive. All the samples displayed sufficient stability for handling of the devices at ambient conditions (Figure 57). The functionality of the OLED samples has been checked periodically over time to analyze the performance of the barrier films.

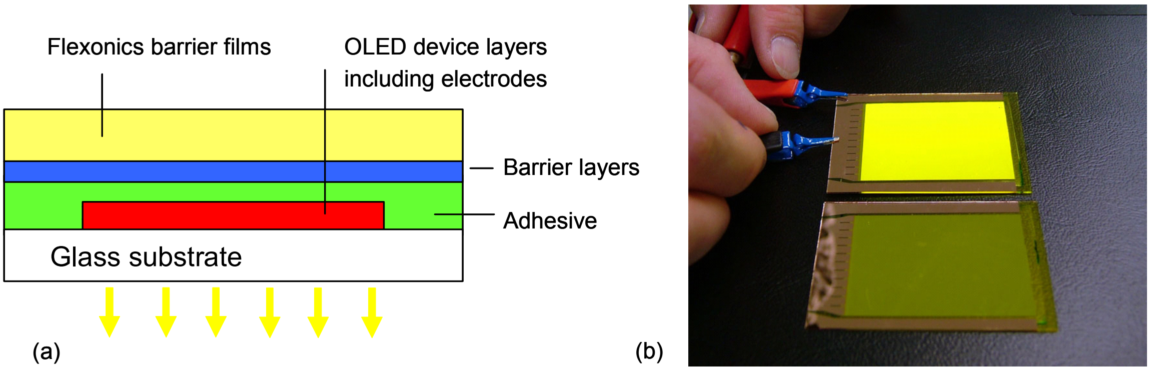


Figure 57 (a) OLED device architecture, (b) OLED with backside barrier film encapsulation

Several OLED devices have been stored at ambient conditions in the lab over time. Representatively the stability of two devices encapsulated with F277 and PB07 are presented in Figure 58. The defects in both samples are starting from the border of the OLED fields.

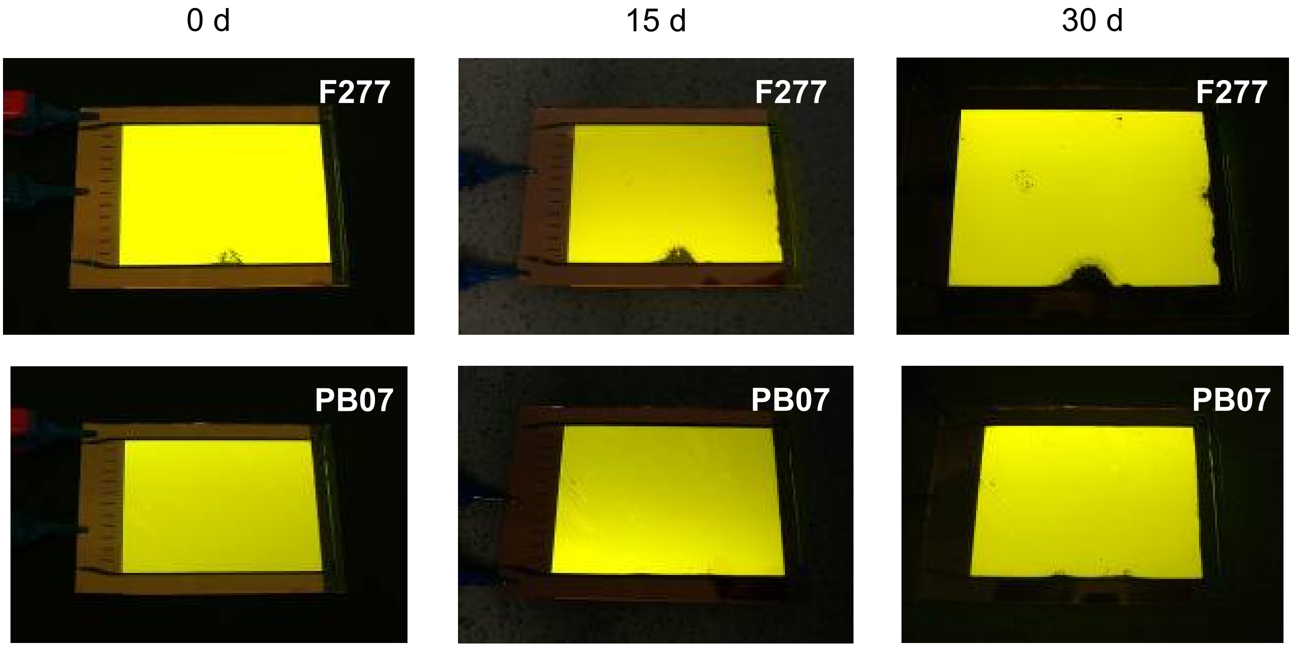


Figure 58 Time dependent OLED device performance

Integration of an OLED and an Organic Photodetector (OPD) for the realization of a positioning sensor.

One highlight in within SIEMENS has been the realization of a demonstrator where a positioning sensor has been realized by integrating an OLED and an OPD.
Figures 59a and 59b show the encapsulation concepts adopted in Flexonics for the OPD demonstrators. A total flexible and a semi-rigid OPD are depicted respectively. Candidates as encapsulation films have been foils which showed better results with Ca-mirror testing (IVV 70, Alcan CX07-095 and Alcan exCX07-038).

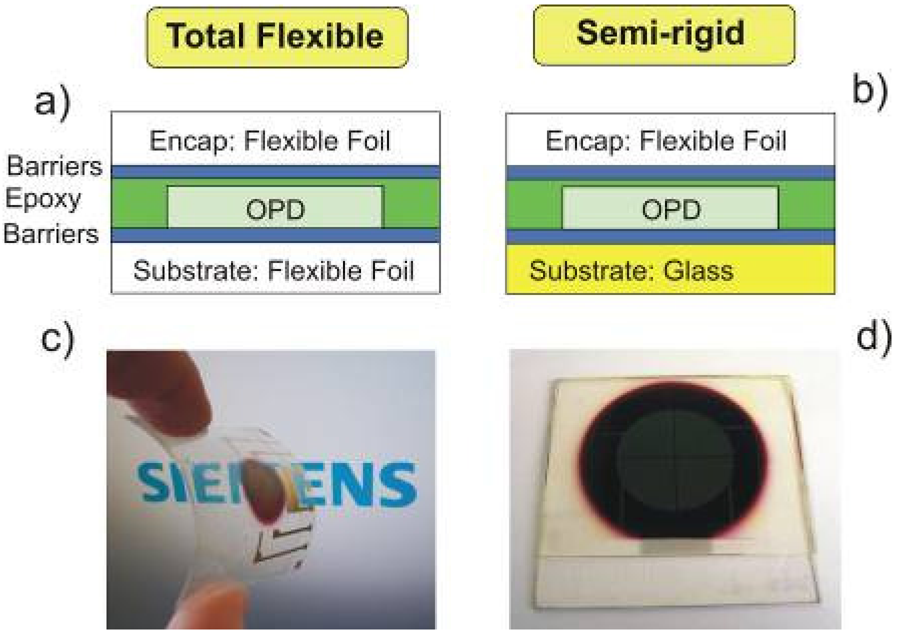


Figure 59. Encapsulation concepts used in Flexonics for the realization of OPDs a) Schematic view of the layer stack for a total flexible OPD. b) Layer stack for the semi-rigid concept. c) and d) show the images of the OPDs for both flexible and semi-rigid encapsulation.

Figures 59c and 59d show optical images of the devices realized as flexible and the semi-rigid OPD, respectively.

OPDs with an active area 4mm^2 have been used to test packaging quality of the different foils (semi-rigid approach). Accelerated lifetime tests have been performed by ageing the OPDs in a climatic chamber under 85°C/85rH conditions (accelerating factor ~65). OPDs with 1cm^2 active area have been processed to fabricate 4-quadrant OPD sensor.

Figure 60 shows an example of electro/optical characterization of semi-rigid OPDs encapsulated with different barrier coated foils. All samples show a good rectification behavior and low dark current densities at reverse bias (<10^{-3} mA/cm^2 @ -5V) as well as high External Quantum Efficiencies (EQEs) approaching 70% (@ -5V). These measurements have been performed 24h after the processing of the devices.

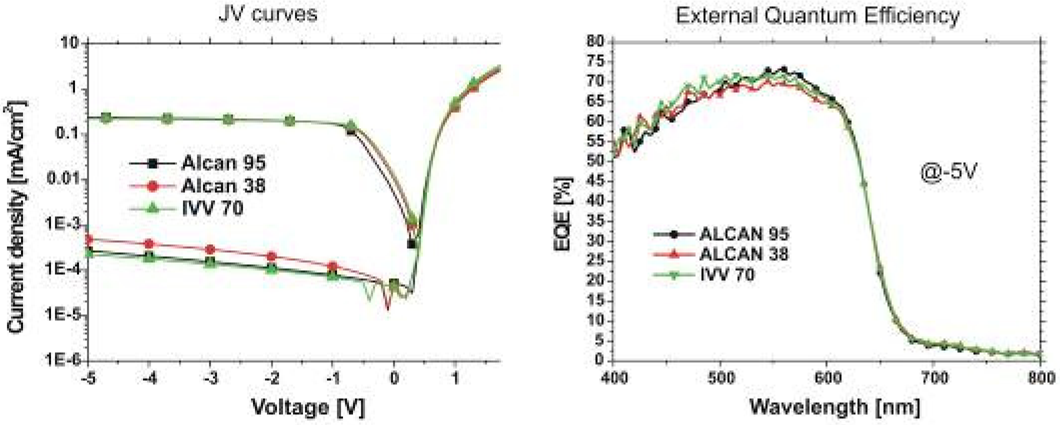


Figure 60. Characterization of semi-rigid OPDs encapsulated with different barrier coated foils (IVV 70, Alcan CX07-095 and Alcan exCX07-038) a) Dark and light JV curves and b) External Quantum Efficiencies (EQEs) for the foil encapsulated OPDs. All measurements have been performed 24h after processing

The demonstrator has been presented at the final FLEXONICS meeting (Halkidiki, 21/22 April 2008). Basic concept of this demonstrator is the integration of an OLED and an OPD for the realization of a positioning sensor. The working principle of the system is rather simple and is shown in Figure 61. The light coming out from an OLED is focused with a lens system into a spot.

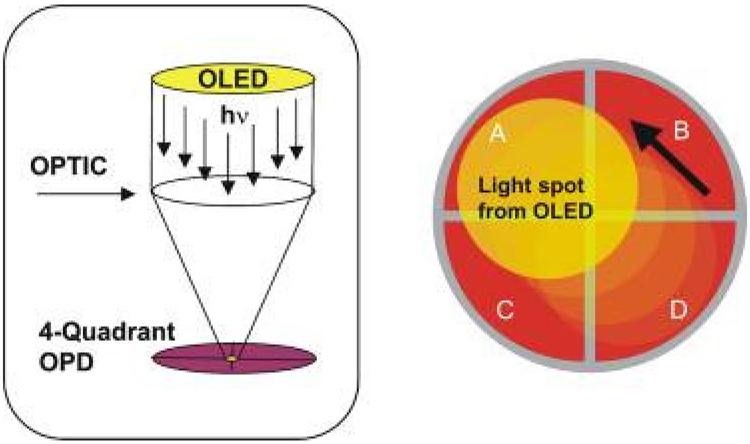


Figure 61. Working principle of a 4-Quadrant positioning sensor. Light coming from an OLED is focused into a spot which is projected onto a 4-Quadrand OPD sensor.

This light spot is then projected onto a 4-quadrant OPD sensor (OPDs A, B, C, D) mounted onto an X-Y table. The light spot is in the center of the division bar cross between OPDs only if the light signals coming from the 4 OPDs are identical. Different photocurrents are measured with the light spot moving away from the center (e.g. turning the X wheel of the X-Y table). Thus, X and Y positions of the light spot onto the sensor are calculated according to following formula:

$$Y = \frac{(A+B)-(C+D)}{(A+B+C+D)}$$

$$X = \frac{(B+D)-(A+C)}{(A+B+C+D)}$$

An image of the demonstrator is shown in Figure 62a. The photocurrents of each individual OPD segment is read-out by an appropriate readout electronic circuit (copper box in Figure 62a) and the digitalized data is transferred to a PC with a home-built Labview program. Figure 62b shows the movement of the center of the light spot.

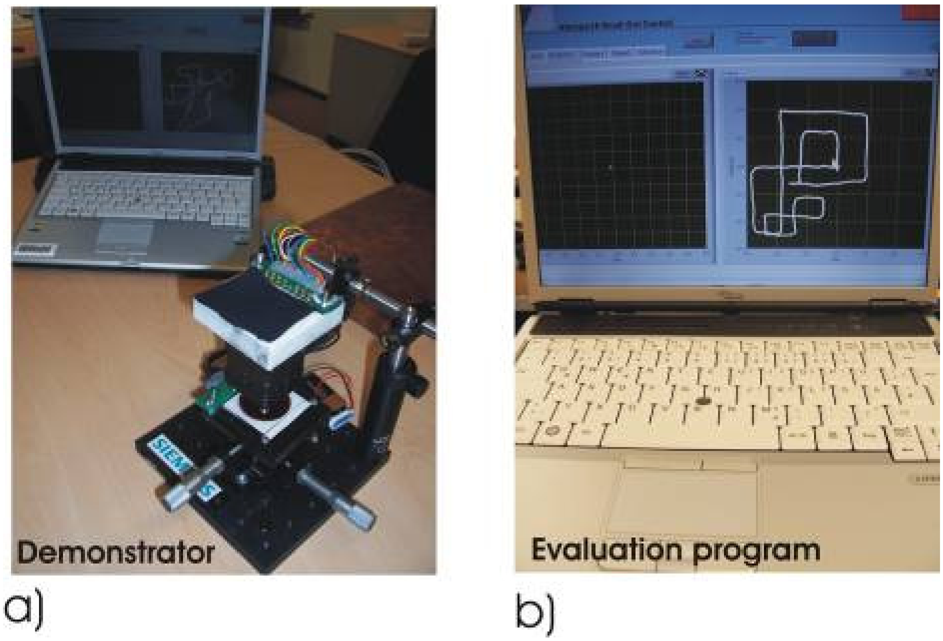


Figure 62. a) Picture of the 4-quadrant positioning demonstrator setup. b) On the screen of the PC it is possible to follow in real time the position of the spot.

Lateral resolution of less than 50µm has been achieved with this demonstrator (portable version).

- Literature13091309

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[Bra_01] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Plastic Solar Cells*, Adv. Funct. Mater. **11**, 15 (2001).

IMPACT

1.6. IMPACT OF THE PROJECT

FLEXONICS deals with the development of a new generation of flexible, transparent, ultra-barrier layers and the adaptation of the production process for the encapsulation of flexible opto-& electronic devices (FEDs) with high precision, quality and uniformity, through intelligent optical monitoring & process quality control. FLEXONICS research activities were performed to develop the process step that is missing, essential for the development and reliability of FEDs (OLED-based displays & OPV modules), that is their encapsulation into a transparent polymer medium, in order to protect FEDs against atmospheric oxygen & water-moisture which are harmful for their performance & long-term stability.

The S&T prospects of the research that were performed in FLEXONICS in the above fields are all focused to achieve ultra high barrier properties on polymer films that will lead to a new generation of radically innovative products, for industrial use and for consumer applications. FEDs will be used for communication and visualizing of information, and generating electricity through renewable sources (based on OLEDs and OPVS modules, respectively) and will have a major impact on our daily life. The above generated knowledge of FLEXONICS, in order to be used for further research and development and to reach other production applications was and will continue to be disseminated according to a specific policy and plans.

FLEXONICS serves one of the most rapidly growing sectors in today’s industry. Related manufacturers of materials, process & monitoring equipment for different industries (Displays, Solar Energy Devices) & their suppliers (mainly SMEs) are presently covering about one million of direct working places. The high level of sophistication in material systems, production processes & equipment will generate several tens of thousands of highly specialized, knowledge intense workplaces. Synergies will be achieved & sustained from lab scale up to all stages of the production chain & from RTD to commercialization. This will have a major impact on EU competitiveness since it will benefit society through knowledge integration in a new multidisciplinary area, by promoting knowledge & learning capabilities due to requirement for the implementation & dissemination to potential user groups. The Environmental EU policy is addressed by the increased use of new types of higher efficiency lightweight OPVs requiring less input of resources, and by reduced waste (~50%) of r2r production processes. Finally, the controlled production lines & improved visualization of information will potentially improve the EU citizens Quality of life.

The market of optoelectronic & electronic devices is one of the most rapidly growing sectors in today’s industry. The production technology for OLED displays on flexible polymer substrates through r2r technology will expand this already flourishing market towards a series of new applications. PV devices are another fast-growing sector of optoelectronic industry. Again, the introduction of flexible PVs produced by r2r technology on polymer substrates will substantially expand the market far beyond the figures foreseen for rigid PVs.

The deployment of in-line process control on r2r machines results both in the improvement of product properties & higher process stability and in reduction of production costs by minimizing & avoiding rejects, as well as in lower costs for exploitation, maintenance & quality control. Therefore, the whole strategy behind FLEXONICS represents the transition from resource intense industries (using e.g. glass, thick plastic parts, metal) towards knowledge-based industries (e.g. by incorporating intelligent & controllable processes that deliver materials with high functionality). Finally, the new optical monitoring units and platforms will also be available for other industrial sectors, such as semiconductors, biochips etc. These developments will drive sales in specialized machine systems, by a factor of some tens above the sales for the optical equipment alone, due to their enhanced performance and thus will boost the market share of European manufacturers of r2r film conversion equipment. Such a trend will strengthen the competitiveness of the participating companies and especially their customers (mainly SMEs) on an international level, maintain technical & economical leadership and improve employment across Europe.

FLEXONICS contributes to the standardization by defining typical figures of merit, for example: First, in efficiency & power generation for solar cell test-devices. The development of new fabrication methods will have a positive impact on quality standards and environmental norms for industrial production. Second, new standards in the measurement limits, modeling & analysis methodology established. Third, expand the current limits for water vapor transmission & establish new standards in the measurement resolution. Finally, new methodology for the offline measurement of oxygen & water vapour at low permeation that is based on a photochemical sensing system.

Section 2: Dissemination and use

Website

The FLEXONICS website has been created to act as a permanent dissemination channel, updated with reports on progress and results emerging from FLEXONICS. It also provides a mechanism for interested parties to contact the appropriate FLEXONICS partners in order to find out more about the Project or its results. The website is: **http://www.flexonics.org**

Welcome to STREP Project FLEXONICS Website

The objective of FLEXONICS is the development of Ultra-high barrier films for r2r encapsulation of flexible electronics.

Project duration is from February 1st, 2005 to January 31st, 2008.

The Project Consortium consists of 9 partners of 5 EU Countries and it is coordinated by Aristotle University of Thessaloniki (AUTh) - LTFN, Greece.

FLEXONICS is funded under the NMP priority within the 6th European Framework Programme.

30-11-2006: 71st International Exhibition Thessaloniki-Greece

08-11-2006: Technical Meeting at Freising, Germany in 13.11.06

21-04-2008: Flexonics Final Meeting in Halkidiki, Greece

Webmaster: alask@physics.auth.gr

Website designed & powered by: pzate@physics.auth.gr

Best viewed in: Internet Explorer 6+ or Mozilla Firefox 1.5+ at 1024 x 768 (True Color)

Publishable Results (PR) of the Final plan for using and disseminating the knowledge

PR1: ULTRA BARRIER MATERIALS SYSTEMS

New barrier lacquer systems based on hybrid polymers with better barrier properties in multilayered structures compared to barrier materials from the state-of-the-art.

In order to further improve the barrier properties, different concentrations of silicon oxide particles (synthesized at Fraunhofer ISC) have been incorporated into two lacquer systems from the state-of-the-art. This method is one possibility to increase the inorganic network degree of the ORMOCER® based polymers and thus led to an improvement of the oxygen and the water vapor barrier.

Table 1. Best barrier improvements obtained with particle-modified systems in comparison to the state-of-the-art system FI H 38% (achieved with OTR and WVTR measurement devices)

Film sample	WVTR (23 °C, 85 % r. h.)	OTR (23 °C, 50 % r. H.)
PET M 401 / SiOx (uncoated)	0,1	0,2
PET M 401 / SiOx / H 38%	0,05	0,01
PET M 401 / SiOx / H 38 % mod. 1	0,003	0,004
PET M 401 / SiOx / H 38 % mod. 2	0,001	0,0004

WVTR in (g/m^2), measured at 85 % r. h., 23 °C; OTR in (cm^3/m^2 d bar), measured at 50 r. h., 23 °C

Advantages: Improved barrier properties with additional properties as better mechanical stability of the coated polymer films.

Products envisaged:

- Multilayered structures consisting of the polymer film being coated with two inorganic and two hybrid polymer layers:

Barrier films for technical applications, e. g. the encapsulation of flexible electronic devices

- Two-layer structures consisting of the polymer film coated with one inorganic and one hybrid layer: Barrier films for pharmaceutical applications (packaging of oxygen and water vapor sensitive products).

Market applications:
The improved barrier materials are suitable for technical applications and special packaging materials required for oxygen and water vapor sensitive products.
The expected time to market for the first product (encapsulation material for photovoltaics) is estimated for the end of 2009 (common project with ISOVOLTA).
Further research:
The achieved results will be used as base for further research projects also dealing with the development of flexible encapsulation materials with ultra barrier properties for electronic devices. Moreover, these results are useful for the development of flexible encapsulation materials or functional barrier coatings for the construction industry, e. g. vacuum isolation panels or membrane constructions.
Stage of development:
The above reported results have been achieved in laboratory scale. The new coating materials were applied on DIN A4 sheets of PET/SiOx and PET/AlOx films.

Collaboration sought or offered:
The achieved results will be offered to potential customers who could use the new materials for the manufacturing of new products and who are able to finance further optimization work which would be necessary to bring new products on the market.
Collaborator details:
Potential customers could be film converters and companies that develop and sell functional coating materials or use functional polymer films for their product manufacturing.

Intellectual property rights:
Fraunhofer ISC and IVV have already some patents for protecting their know-how concerning the synthesis of hybrid polymer based barrier lacquers and the required coating and application technology.

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PR2: FLEXIBLE BARRIER LAYER SYSTEMS

Flexible material with superior barrier properties that can be processed in large scale and via roll-to-roll processes. Its improved properties result from a combination of optimized barrier structured deposited on top of each other on a polymer film. This film material will thus allow producing flexible PV modules and Flexible Electronic Devices via roll-to-roll processes which is currently only possible with technological compromises for the PV modules.
This product will probably be very interesting for companies who aim to manufacture flexible electronic devices, like flexible solar cells or flexible displays, in mass quantity. Also, for the production of vacuum isolation panels this barrier material will be interesting as an encapsulation material. With some optimisation existing coating technologies can be used - which enables producers of refined flexible films to start the production of this encapsulation material with little costs. During the FLEXONICS project, the ultra-barrier material was produced in pilot plant production in large scale with good reproducibility. Thus, the material is ready for now going into the production at industrial scale.
As Fraunhofer is a non-profit organisation for research and development we are now very interested in transferring the knowledge gained within FLEXONICS to production at industrial scale, together with an industrial partner. One cooperative project already started with ISOVOLTA.

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PR3: MULTI-LAYER BARRIER DESIGN TOOL

Tool for the simulation of permeation processes through multilayer barrier structures targeting greater understanding of the influence of process conditions and strategy to the final barrier properties and, thus, reduced time and cost consumption during the experimental development of multilayer barrier structures.
During the FLEXONICS project, this tool already proved to be able to realistically forecast the total barrier properties of a multilayer material towards either oxygen or water vapour. For the forecast it is possible to virtually change the order of inorganic and organic/hybrid layers as well as the material characteristics of each layer and thus to gain knowledge concerning the influence of each part of the structure to the total barrier. From this systematic understanding, advice can be concluded how to further the total barrier.
Due to this great use for the experimental development of ultra-barrier material, we are of course going to further use this tool for our future research activities. However, this tool should be very interesting for other companies or research institutes working in the field of ultra-barrier development and using the principle of multilayer stacks. We, too, would be interested in such collaboration as we are always trying to gain more knowledge about multilayer production and to introduce this into the simulation tool.

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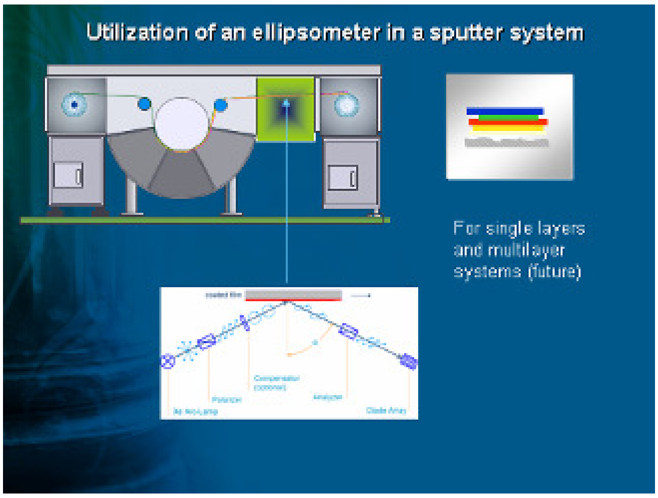
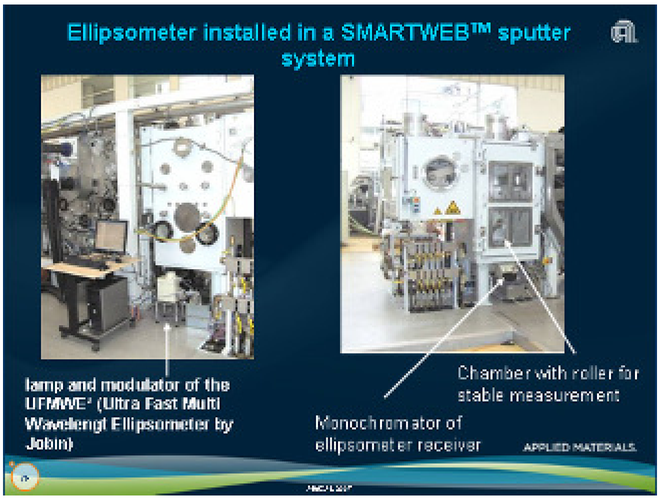
PR4: R2R graded ultra-high barrier coating process

Results description

Integration of an FUV Ellipsometer from HJY in the AMAT SMART WEB^{TM} sputter coating production system.


Utilization of an ellipsometer in a sputter system

For single layers and multilayer systems (future)

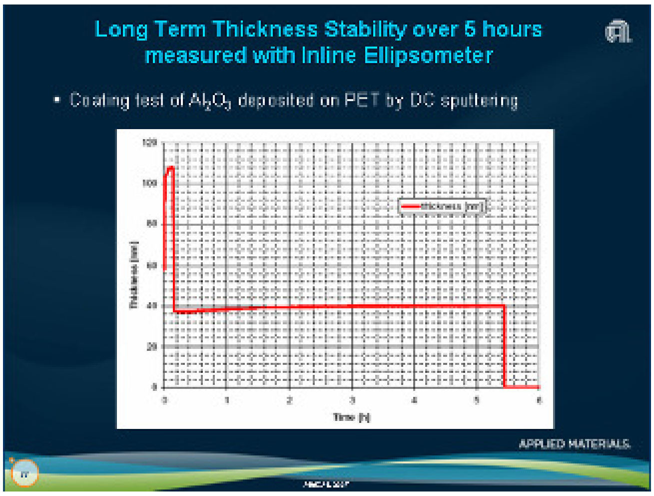

Ellipsometer installed in a SMARTWEB™ sputter system

lamp and modulator of the UFMWE¹ (Ultra Fast Multi Wavelengt Ellipsometer by Jobin)

Chamber with roller for stable measurement

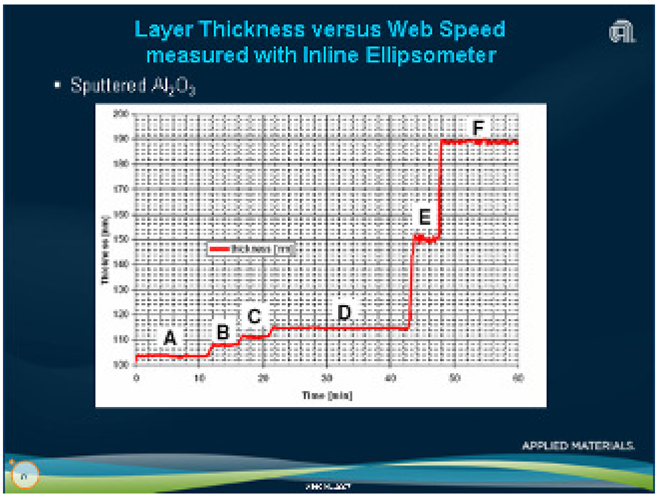
Monochromator of ellipsometer receiver

An in-line real time monitoring Spectroscopic Ellipsometer working in the FUV range from 3ev to 6,5 ev with a sampling time of 100 ms including hardware, software acquisition and modelisation. Monitoring of thickness and optical properties (n, K) of coated inorganic layers e.g. Al_2O_3 or SiOx.



Long Term Thickness Stability over 5 hours measured with Inline Ellipsometer

- Coating test of Al_2O_3 deposited on PET by DC sputtering



Layer Thickness versus Web Speed measured with Inline Ellipsometer

- Sputtered Al_2O_3

The measurement and inline control by Ellipsometer of the thickness of the sputtered Al_2O_3 layer on a PET film was achieved.

Possible marked application
End-user for the production of flexible products for FE, PV and high barrier encapsulation films.
Stage of development
The product is ready for commercialisation.
Collaboration
This system has been developed in collaboration between HJY, AUTH, AMAT
Intellectual property rights
Patents for the Ellipsometer , ellipsometric model and measuring method's have been filed by HJY, AUTH

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PR5: WVTR MEASUREMENT SYSTEM

Measuring device for the detection of very low water vapour transmission rates (WVTR). Thus, the barrier properties towards water vapour of ultra-barrier materials can be measured down to WVTRs of 10-5 g/(m2 d) - something that is impossible with commercially available systems. Up to now, the most recent of these state-of-the-art systems (e.g. “Aquatran”, market release 2008) can not measure WVTRs lower than 10-3 g/(m2 d).

Thus, companies producing measuring devices for permeation measurements could be interested in offering such a measuring device for companies working in the fields of ultra-barrier development or ultra-barrier production. As the system uses existing gas chromatic devices (in a clever combination) the whole measuring device would not cost more than approx. 100,000 Euro. Additionaly, the manufacturing of such a device can be started with little costs.

Up to now, the market for such a device is still a niche market. But as soon as the production of flexible electronic devices rises, the need for a controlling device for the encapsulation material (income check / production control) is going to rise, too.
For collaboration please refer to:

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PR6: Measuring System for Routine OTR Testing on Ultra-Barrier Membranes

The rapidly growing demand for ultra-barrier membranes showing very low oxygen and water vapour transmission rates has brought about intensive scientific activities in this field. However, according research is handicapped by the absence of commercially available instruments which are sufficiently sensitive for ultra-barrier characterisations. The best devices on the market have limits of detection lagging behind the demands of typical ultra-barrier applications (e.g. OLED-encapsulation) by orders of magnitude.

Lacking other alternatives, according tests are commonly performed by means of sensitive but highly complicated methods (”Calcium Degradation Tests”) which involve labour and equipment-intensive sample preparation procedures and are therefore not particularly suitable for routine measurements. Furthermore, these methods are not able to discriminate between oxygen and water vapour permeation – two processes which often obey to fundamentally different mechanisms.

In the framework of FLEXONICS, the ”Graz University of Technology” (TUG) has developed a stand-alone-system capable of performing highly sensitive and automated routine measurements of oxygen transmission rates (OTR) through ultra-barrier membranes. The constructed prototypes have an extrapolated limit of detection for OTR testing of around 10^{-5} $cm^3m^{-2}day^{-1}bar^{-1}$ and thus perform with sensitivity superior to anything on the market - with the potential for further improvement. In addition, the demonstrators (see Fig. 1) retain the convenience known from commercial systems, with respect to sample preparation, device operation and data processing. The development reached the stage of a ready-to-use application, which has been shown in routine tests on a large number of FLEXONICS barrier membranes. Thus, the technology is highly ready for the transfer to an industrial manufacturing partner.

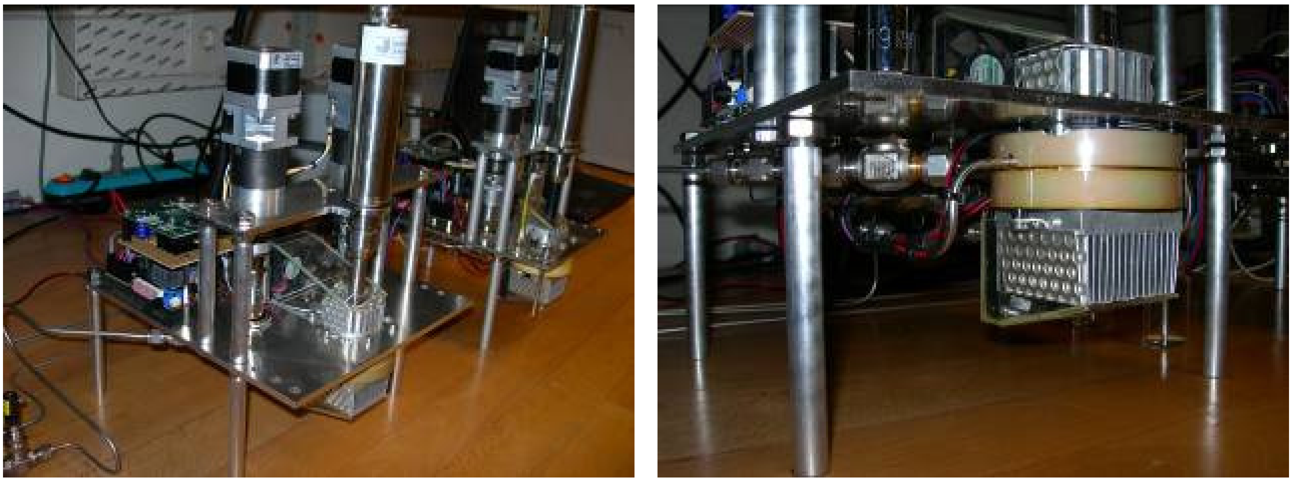

Figure 1. The Stand-Alone, Automatically Operating, Software-Controlled Laboratory Prototypes Capable of OTR Testing with Superior Sensitivity.

Unlike commercial instruments which commonly function according to ASTM, ISO and DIN standards with their strict requirements for coulometric oxygen sensors, an innovative approach involving the highly sensitive yet consumption-free oxygen detection by opto-chemical means was followed. The sensing technique is based on the luminescence quenching effect displayed by a number of organo-metallic complexes in the presence of molecular oxygen.

The feasibility of such OTR measurements, based on opto-chemical sensors, has been shown on a laboratory scale by Winnik et al. [1]. The principle, as outlined elsewhere [2], involves the steady monitoring of the increasing oxygen concentration inside a measuring cavity into which permeation through the sample membrane occurs. The continuous observation of the oxygen accumulation relieves the demands in detector sensitivity but requires a means of *consumption-free* detection. As indicated, opto-chemical sensors show this capability, besides further advantages which simplify the architectural complexity of the small-volume, perfectly airtight measuring cavity. The integrated opto-chemical detection system was established by Joanneum Research GmbH (Graz, Austria), a close research partner of TUG. It is successfully employed in a number of technical applications.

The developed technology has an interesting potential for commercialisation due to the superior sensitivity and expectedly cost-effective production, with justifiably small efforts in re-engineering, since comprehensive know-how has been generated in the project. Although the method is yet not covered by ASTM, ISO or DIN standards, it produces comparable results.

The market for ultra-barrier testers is, at the time, estimated to only some 1000 units worldwide but likely to be growing in the future. Although the system is capable of detecting also higher OTRs (typically encountered in the food and medical packaging industry), the extraordinary sensitivity provided is not required in this application segment. The primary potential is therefore constrained to ultra-barrier research and related quality control, where commercial devices fail to serve the demands.

Nevertheless, the opto-chemical approach may offer a more cost-effective alternative to established systems operating in the range of higher transmission rates. Furthermore, similar technology may be used for the permeation rate measurement of gases such as water vapour, carbon dioxide or ammonia. According sensors are either already existing or under development.

In the future, the Graz University of Technology will continue to use the prototypes in the analysis of barrier samples. Thus, ultra-barrier OTR testing on a consultancy-basis is possible and welcome.

As mentioned, the technology is ready to be commercialised with little re-engineering efforts by an industry partner. Although respective interest has been indicated, no manufacturer was found as yet. In co-operation with Joanneum Research Forschungs-GmbH, we are therefore inviting interested, potential industry and sales partners to talks about an according technology transfer.

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References:

[1] Y Rharbi, A. Yekta, M.A. Winnik, *A Method for Measuring Oxygen Diffusion and Oxygen Permeation in Polymer Films based on Fluorescence Quenching*, Anal. Chem., 71 (1999) 5045-5053.

[2] M. Tscherner, C. Konrad, A. Bizzarri, V. Ribitsch, F. Stelzer, *Opto-Chemical Oxygen Permeability Measurements*, Proceedings of the 7th Int. Conf. on Optical Technologies, Optical Sensors & Measuring Techniques (OPTO), Nürnberg (2006) 79-84.

PR7: Inline FUV ellipsometer, for monitoring & correlation to material properties

Result description

In-line and real-time monitoring Spectroscopic Ellipsometer working in the FUV range from 3eV to 6.5eV with a sampling time of 90ms including hardware, software acquisition and modelisation for monitoring thickness and optical properties for material and process analysis. The Ellipsometer has the ability for analysis of ani-

sotropic samples (organic & polymeric materials) and specimens with irregular surfaces. Also, via the in-line control the establishment of correlation between optical, intermediate (thickness, density) & functional barrier properties is possible.
Finally, the deployment of in-line process control on r2r machines results both in the improvement of product properties & higher process stability and in the reduction of production costs by minimizing, detecting & avoiding rejects.

Possible market
The possible customers of this innovation are Deposition machine manufacturer (r2r, standart machine PECVD, MBE, ALD…), End user (materials and process developers: university and industry, R&D laboratory; Production: industry).

Stage of development
The product is ready for the commercialisation.

Collaboration
This system has been developed in collaboration between HJY, AUTH, AMAT.

Intellectual property rigths
Patens have been filled to protect this system and the methodology.

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PR8: Flexonics Thin Film Encapsulation system

With results out of the FLEXONICS project Isovolta is ready to work on implementing the production processes for high barrier materials on pilot scale and on its own production lines. Selected barrier materials based on hybrid systems were tested using methods such as Damp Heat, QUV, Atlas, transmission measurements etc., being investigated on a standard basis in the photovoltaic industry. Consequently these high barrier materials are to be about to start with tests on a pilot and furthermore a production line. Collaboration between Isovolta and Fraunhofer Gesellschaft has been established out of this project to improve properties in means of barrier in lab scale and larger scale.
As soon as a product is available in larger quantities, improvement of properties on a large scale can also be introduced. This is at least of the same importance as the improvement of barrier properties.
Intellectual property rights: A patent pending on the use of oxide (SiOx, AlOx) combined with hybrid layers as barrier material for photovoltaic applications.

PR9: Flexible Organic Solar Cell

Result description
Packaging materials produced within the Flexonics project were used to encapsulate organic solar cells from Konarka. The packaged devices were characterized in terms of performance and stability. A picture of a packaged 10 stripe module and a typical jV-curve are shown below. The manufactured devices have shown

good lifetimes under accelerated conditions and lifetimes of ~500 hours under 65°C/85 % rh could be achieved.

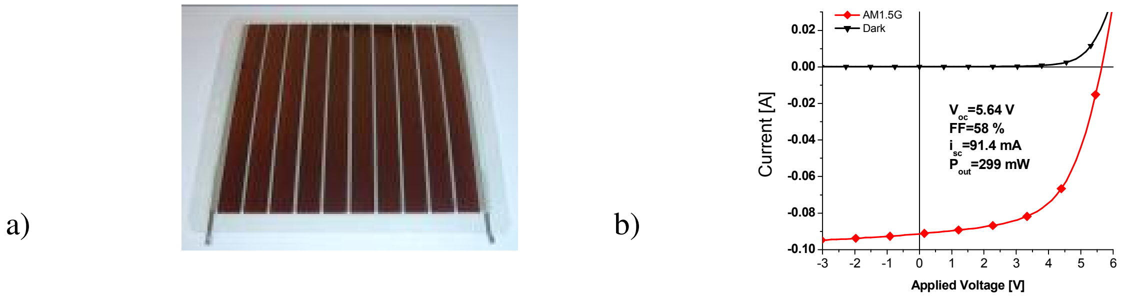

Figure 1: a) Encapsulated, flexible module; b) typical jV-curve

The observed lifetimes are compatible to the requirements for various portable electronic devices and indoor applications, which could be first markets for organic solar cells.

Figure 2: Possible Organic Solar Cell Applications

For roof-top applications further efficiency and lifetime improvements may be required.
Konarka is currently commercializing roll-to-roll manufactured flexible organic solar cells. Konarka will continue to work with the FLEXONICS partners to develop appropriate packaging solutions for various OPV applications.

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PR10: OLED based displays and Lighting devices, Organic Photo detectors

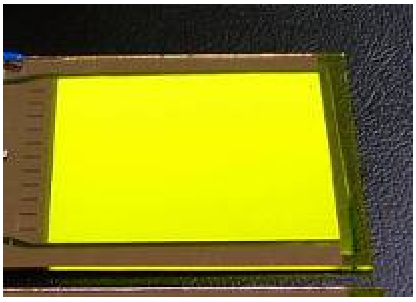
Displays based on organic light-emitting diodes (OLEDs) are on the brink of the consumer market. OSRAM achieved new levels of efficiency and lifetime for OLED lighting: efficiency of 46 lm/W, 5000 hours life time and a brightness of 1,000 cd/m2 for warm white OLEDs. These new light sources approach the values of conventional lighting solutions.
However, one of the most promising properties of the functional OLED stack is not utilized in these applications: its inherent flexibility. Material and process development for flexible organic displays is at the focus of many current research activities. The two main strategies that seem viable for flexible substrates are ultra-thin glass (UTG) and polymeric foils. While the glass substrates show excellent temperature and chemical stability and very good barrier properties, they cause severe handling problems and also have limited flexibility. For the ultimate flexible application of a roll-in/roll-out display, polymeric foil substrates appear more promising. The most serious obstacle to the commercialization of flexible displays on foils is the high moisture and oxygen permeation rate through organic polymers. It is estimated that for a device lifetime of 10,000

hours, the water vapour transmission rate (WVTR) must be below 10^{-6} g/m²day and the oxygen transmission rate (OTR) below 10^{-5} cc/m²day.

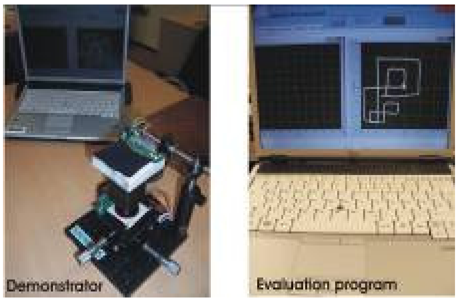
Within Flexonics barrier foils with improved OTR- and WVTR-properties have been developed and produced in r2r-technique. The best barrier foils have been used in the lab-scale setup of semi-rigid and fully flexible OLED- and organic photodiode (OPD) demonstrators.

At the final stage of Flexonics, Siemens fabricated an integrated OLED-OPD-demonstrator with position sensing functionality.

a) Fully flexible OPD with quadrant sensor layout



b) semi-rigid OLED



c) Demonstrator with integrated OLED and OPD for position-sensitive sensing

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ANNEX A: LIST OF DELIVERABLES PRODUCED BY THE CONSORTIUM

Table 11 Deliverables List

Del. No	Deliverable Name
1	**POLO, AMAT, Alcan:** a ranking of production methods for barrier and intermediate layers and data for layer stack modelling.
2	**POLO, AMAT, Alcan:** samples for offline characterization
3	**AUTh:** Overall Report on optical and non-optical characterization results
4	**POLO:** Prototype WVTR measurement system & detailed report on performance, recommendations
5	**TUG:** OTR measurement system & detailed report on performance, recommendations
6	**POLO:** Software for prediction of barrier properties in multi layer stacks
7	**POLO:** Modelling of produced layer stacks & failure analysis
8	**AMAT, Alcan:** Ranking layer stacks under given market & cost constraints
9	**HJY:** Prototype Stand-alone Ellipsometer & Assessment for in-line transfer of stand alone units
10	**AUTh, HJY:** Mathematical Modelling & Data Modelling in FIR to FUV optical investigations
11	**AUTh:** Report on establish correlations & testing
12	**Amat, HJY, Alcan:** Evaluation for large scale applications
13	**AUTh, HJY:** Evaluation Units in Lab processes, Assessment for Transferring
14	**Alcan/AMAT (AF):** High performance ultra high-barrier films
15	**Konarka:** Performance feedback
16	**ISO, Konarka:** Demonstration sample of flexible encapsulated PV modules
17	**Siemens, Alcan:** Flexible encapsulation of OLED display
18	**AUTh:** Progress Reports