Project Name: NANOMEND - Nanoscale defect detection, cleaning and repair for large area substrates

Duration: 48 months *Start Date*: 1st Jan 2012

Project Website: http://www.nanomend.eu/

The NANOMEND Project: Final publishable summary

NanoMend Executive Summary

NanoMend was an industry-led collaboration where the primary aim was to develop pioneering technologies for in-line detection, cleaning and repair of micro and nano-scale defects on thin films used in applications covering flexible photovoltaics PV and paper-board food packaging films. The project ran from January 2012 to December 2015 and comprised of 14 partners across 6 European countries.

Further aims for the project included demonstrating the ability to implement roll to roll atomic layer deposition (ALD) coating technologies to produce ultra-barrier coatings for both flexible photovoltaic (PV) modules and polymer coated paper. To test the functionality of the barriers a traceable water vapour transmission rate (WVTR) instrument was built in the consortium. Allowing the lowest detectable WVTR's to be traceably measured.

Early experimental work in the project led to a deeper understanding of the nature of substrate defects in both the flexible PV and polymer coated paper products. From this research defect classification systems were developed which led the research teams to understand the size and morphology of critical substrate defects, which were detrimental to the film functionality. By understanding and targeting the measurement and local cleaning of the most critical defects of the substrates under study the consortium were able to design specify and develop two technology demonstrator systems for the PV and Paper industries and a further two proof of concept measurement systems for direct measurement of PV film layers, coated fibre products, ALD Al_2O_3 barrier coatings and embossed holographic film respectively.

In terms of impact it is predicted that the demonstrator capabilities will be seen to have significant advantages in their application sectors following further optimisation and as such, be implemented into full-scale manufacturing lines, thus facilitating significant manufacturing efficiency gains for end user industries. Through a comprehensive dissemination exercise the technology suppliers within the consortium have gained new knowledge to facilitate access to new markets in coated paper and printed electronics in the area of defect detection and substrate cleaning.

Glossary of Terms

ALD	Atomic Layer Deposition
BIPV	Building-integrated PV
BOS	Balance of System
CCD	Charge-coupled device
CIGS	Cu(InGa)Se2
EURAMET	European Association of National Metrology Institutes
FOV	Field of View
GW	Gigawatt (10^9 watts)
ICCG	International Conference on Coatings on Glass and Plastics
LFS	Liquid Flame Spraying
MCR	Measurement Cleaning and Repair
MeOx	Metal oxide
NIST	National Institute of Standards and Technology (UK)
OLED	Organic Light Emitting Diode
PTB	Physikalisch Technische Bundesanstalt (Germany)
PV	Photovoltaic
PVSEC	European Photovoltaic Solar Energy Conference and Exhibition
R2R	Roll-to-roll
RES	Renewable Energy Sources
TFPV	Thin Film Photovoltaics
TW	Terawatt (10^{12} watts)
WVTR	Water Vapour Transmission Rate
Si PV	Silicon Photovoltaic
BGIP	Background IP
FGIP	Foreground IP
SGIP	Side ground IP
MB	Management Board
AFM’s	Atomic Force Microscopy
SEM’s	Scanning Electron Microscopy
H/W	Hardware
S/W	Software
QFD	Quality Function Deployment
SWOT	Strengths, Weaknesses, Opportunities, and Threats
PESTEL	Political, Economic, Social, and Technological analysis
PUD	Plan for Use and Dissemination

Project Partners

No	Name	Short name	Country	Project entry month[10]	Project exit month
1	THE UNIVERSITY OF HUDDERSFIELD	HUD	United Kingdom	1	48
2	ISOVOLTAIC AG	ISO	Austria	1	48
3	LAPPEENRANNAN TEKNILLINEN YLIOPISTO	LUT	Finland	1	48
4	STORA ENSO OYJ	SE	Finland	1	48
5	TTY-SAATIO	TUT	Finland	1	48
6	FRAUNHOFER-GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V	FRAUN	Germany	1	48
7	ISRA VISION AG	ISRA	Germany	1	48
8	NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHAPPELIJK ONDERZOEK - TNO	TNO	Netherlands	1	48
9	IBS PRECISION ENGINEERING BV	IBSPE	Netherlands	1	48
10	FLISOM AG	FLI	Switzerland	1	48
11	NPL MANAGEMENT LIMITED	NPL	United Kingdom	1	48
12	MICROSHARP CORPORATION LIMITED	MIC	United Kingdom	1	16
13	Centre for Process Innovation Limited	CPI	United Kingdom	1	48
14	Kite Innovation (Europe) Limited	KITE	United Kingdom	1	48
15	ISCENT OY	ISC	Finland	19	48

1.0 Project Context and Objectives

1.1 Context

Europe has many world-class companies that manufacture high volume products using large area substrates. They serve established markets such as paper and packaging products, and emerging market sectors such as flexible electronics. The manufacturing processes often involve the deposition and patterning of multi-layer thin films on large area substrates and foils. For these types of product, increased product performance and functionality can come from an increase in the number of layers, or a decrease from micro- to nano-scale in the thickness of individual layers or size of pattern features. To achieve high yield in the coating and patterning processes, the films must be uniform and possess a predictable functionality over the substrate. However, there is an increased risk of defects forming as the number of film interfaces increases, and the size and deleterious nature of those defects changes as the layer thicknesses shrink to the nano-scale. Layer defects can be caused by surface anomalies e.g. scratches and surface peaks or holes, by contamination in the form of ambient particles or chemical stains and by incorrect process conditions. In order to ensure high product yield, the key challenge is to inspect the foil surface on line and desirably at production speed with sufficient resolution to i) detect the presence of problem defects on the starting foil surfaces and ii) detect defects as they appear as a result of the coating and patterning processes. It is also desirable to clean or even repair substrates in situ in order to avoid excess wastage of substrate before faults can be corrected downstream in the production line.

NanoMend has addressed specific user requirements for better process inspection and control systems for nano- scale thin films on large area foils, and has integrated two exemplar vertical supply chains for **functionalized polymer-coated paper products** and for **low cost flexible photovoltaics**. The aim has been to demonstrate **beyond state-of-the-art in-line detection, cleaning and repair of micro and nano-scale defects.**

End-User Problems - NanoMend has attempted to resolve defect challenges in production of foils and to demonstrate measurable improvements in yield, performance and product life, as well as demonstrating the potential to reduce costs, resulting from better process control. Various critical process stages identified by end users in the project Table 1.1

Demonstration of effective surface inspection was seen as vital to detect defects and enable targeted user response. Important measurement instrument characteristics that determine the performance of surface inspection systems and their suitability for different applications were outlined as: i) the lateral distance defining the area from which a sensor collects data (spatial range); ii) the vertical distance over which surface topography or layer thicknesses can be measured (vertical range - a large vertical range allows an uneven surface or multi-layer to be inspected rapidly); iii) the minimum lateral and vertical dimensions at which the sizes of discrete defects or thicknesses of layers can be measured (lateral or vertical resolution); iv) the time to acquire data from an area of sample v) Robustness in the manufacturing environment vi) For in-line inspection systems the scan speed, is critical.

The NanoMend consortium decided at the outset of the project to utilise optical sensors for surface inspection for several critical reasons

(i) the spatial range and scan speed can be very high using wide area illumination with cameras or microscopes to capture images. This can enable massively parallel data acquisition by pixel arrays incorporating many data-acquisition sensors; (ii) optical methods can have large vertical range and sub-nanometre vertical resolution, e.g. Interferometry (iii) fast data acquisition is possible using optical sensors designed with no moving parts; (iv) low intensity light is a contactless probe that does not damage the substrate surface regions; (v) the lateral resolution of optical methods is generally limited to features greater than 500nm by diffraction effects, but features smaller than the diffraction limit can be detected using emerging optical methods. The effective lateral resolution of fast inspection systems using cameras is determined by the distance on the surface corresponding to one pixel in the image.

Table 1.1: Critical process stages for in-line inspection and control

Stage	**Polymer-coated Paper**	***Flexible PV***
Substrate	Extrusion-*coated paper – to detect smaller defects, particles, stripes*	Polymer *for barrier films – to detect foil surface anomalies causing barrier defects*
Barrier Layers	Need *for source reduction leads to thinner coating, causing more defects in a deposited diffusion barrier* Better *quality barrier needed on polymer for biodegradable packaging*	Avoidance *of defects is critical in very high quality water vapour barrier layers required for protection of long life flexible PV modules* Current *methods to measure performance of barriers are inadequate*
Module fabrication		PV *module yield reduced by particles and pinholes in active layer deposition and by scribing defects during layer patterning*

The NanoMend strategy was to develop novel optical inspection methods by:

I. Enhancing **the effective lateral and vertical resolution** of high speed optical inspection systems **currently used** to scan large area foils, allowing smaller defects and the surface of nano-scale multi-layer films to be measured. This was achieved by using both faster line-scan cameras and novel illumination conditions. The approach allowed variation of key film properties to be mapped with high spatial resolution in real time using high speed data processing.

II. Developing high precision optical interferometric sensors with significantly **higher spatial**

range and speed than existing laboratory interferometers. These are based on compact, robust interferometers using wavelength scanning, i.e. without moving parts. The spatial range and scan speed was enhanced by constructing autofocus elements.
III. Building and test prototype optical instruments that can detect defects or structures which have a spatial size below the diffraction limit by utilizing a priori knowledge of the geometry of the defects and inverse modelling approaches.

The NanoMend **strategy for cleaning** was to decrease defect density and enhance yield by using directional cleaning methods optimized for i) continuous operation to **remove sub-micron defects** from large area foils prior to barrier deposition and ii) **local removal** of particles generated during fabrication of PV modules. **Local repair techniques** were investigated and solutions found for shunt removal in PV modules. Unfortunately as these techniques were not truly local they were not developed on the demonstrator systems. Very high spatial resolution cleaning was not essential to deploy the local systems because their interaction footprints (e.g. the area of the substrate surface affected by a gas stream) is relatively large (>1mm^2). The various sub-systems for defect detection, cleaning that were developed in NanoMend were integrated as appropriate to create systems designed for specific end-user applications. This comprised

- A hybrid high speed low resolution/high resolution low speed, camera based demonstrator system on the coated paper product pilot line.
- A high resolution camera based demonstrator system at the PV production line (TUT)
- A high resolution interferometric proof of concept system (PoC), at CPI
- A laboratory based (PoC) system used to assess defects in holographic coatings

The performance of the measurement systems were verified by traceable measurement calibration procedures and by evaluation on roll-to-roll (R2R) processing tools by end-users.

Key Concepts that had to be addressed

Key Concept 1: Detection and Measurement – NanoMend tackled specific challenges for enhancing lateral and vertical resolution and speed of optical in-line inspection: **1)** it was not possible to "scale" slow lab- based metrology systems for large area nano-surfaces because this would result in very high system costs and low performance. **2)** When using measuring probes for micro/nano-scale surfaces defects the output had to be at the process speed if possible **3)** Existing methods and algorithms for the detection of defects in nano-scale surfaces were not designed for high-speed processing or environmental robustness. **4)** Current in-line sensor outputs are generally not traceable to measurement standards. **5)** In many cases, the knowledge about the defects that have greatest impact on product yield and performance was inadequate. NanoMend initially used lab based methods to characterize and catalogue critical defects affecting substrate performance. This information was required to fully specify the new inspection systems and identify key performance characteristics. The traceability of laboratory based instruments is normally carried out using calibration artefacts that have been measured using a primary at a national measurement institute, usually with a direct link to the definition of the metre. At the start of NanoMend, it was not established how a traceability route could be applied for in-line, large-area measurements and this was a task for the NanoMend project. The Objectives for defect detection and measurement were:

- **Objective 1**: To develop a defect database used to optimize sensor design.
- **Objective 2**: To establish fast inspection methods to detect defects for two different substrate speeds, up to 800m/min (packaging) and down to 10m/min (PV)
- **Objective 3**: To achieve the first in-line deployment of an interferometer to be able to

detect defects with single digit μm spatial resolution.

- **Objective 4**: To prove the feasibility of super-resolution methods that can resolve defects below the diffraction- limit of light.
- **Objective 5:** To establish measurement traceability for the sensor systems.

Key Concept 2: Cleaning & Repair- The efficiency with which directional cleaning methods remove submicron particles in addition to larger particles was initially studied on small area samples and lab-scale pilot lines. Megasonic, laser beam, electrostatic charging techniques and gas jetting techniques were investigated for cleaning foil substrates after patterning during PV module fabrication. Electrochemical methods were investigated for repair of faults in PV modules. Interaction strategies were developed for the cleaning and repair methods in order to link them to inspection and enable the spatially-resolved particle removal. For the polymer coated paper strand the aim of the project was to ALD coat the paper to enhance WVTR/OTR performance. Consequently prior to ALD coating a cleaning method for the edge of the substrates was investigated. The objectives here repair were:

- **Objective 1:** To decrease the defect density in polymer coated fibre products and flexible PV-modules by developing cleaning methods to remove > 90% of detectable particles
- **Objective 2:** To adapt the cleaning methods for particle removal in R2R manufacturing at web speeds of 1 – 10 m/min.
- **Objective 3:** To investigate repair methods for shunts in PV modules on polymer films
- **Objective 4:** To define integration strategies between detection and cleaning.

Key Concept 3: System integration- The various subsystems developed in the project were evaluated for application to R2R equipment. For demonstration, the sub-systems were integrated according to the requirements of the packaging and PV R2R manufacturing processes and installed at pilot or end user production lines. In addition two further systems, a production line proof of concept high precision and a lab based proof of concept system were developed. The high precision system was integrated with a lateral actuation capability at CPI. For defect detection, the sensors or cameras were interfaced to the high-speed-processing units directly. The software algorithms of the high-speed-inspection were integrated either in the high-speed-processing units or in the sub-computers. The objectives for system integration were:

- **Objective 1:** To integrate a full system demonstration of in-line inspection and high precision measurement, local cleaning and investigate repair on a PV production line to deliver multiple benefits in yield and cost savings.
- **Objective 2:** Develop fast inspection methods to detect defects for two different substrate speeds; 10um at 800m/min (packaging) and <5 um at of 10m/min (PV).
- **Objective 3:** To achieve the first in-line deployment of an interferometer able to detect defects 5um width and <10nm vertical resolution operating on a R2R process.
- **Objective 4:** To prove the feasibility of super-resolution methods that can resolve defects below the diffraction- limit of light down to 10nm.
- **Objective 5**: To establish measurement traceability for the sensor systems.

Key Concept 4: R2R ALD Coating and Traceable Water Vapour Transmission Rate (WVTR) Measurement- Ultimately the implementation of in process defect detection, cleaning and repair strategies in PV and Polymer coated fibre products is a means to facilitate improved process yield and improved performance of the substrates in question. To facilitate improved performance consortium members in the NanoMend project developed R2R ALD coating of Al_2O_3 for both the polymer coated paper to improve oxygen and water vapour transmission for paper products and to improve ultra-barrier properties to significantly reduce WVTR in PV barrier films. For PV barrier film the WVTR target was <10^{-4}g/d/m^2. Currently this level of resolution is beyond the best commercial systems and as a result the consortium have developed a traceable WVTR measurement system capable of assessing ultra-low WVTR at levels beyond any system currently available and demonstrated systems capable of accelerated measurement beyond state of the art systems. The objectives for ALD coating and WVTR measurement were:

- **Objective 1:** Development of a R2R ALD coating facticity to produce thin film coatings on polymer coated fibre board products
- **Objective 2:** Development of a R2R ALD coating facticity to produce thin film coatings on polymer sheet to act as an ultra-barrier for flexible PV modules.
- **Objective 3**: Development and testing of traceable WVTR systems capable of ultra-high resolution and accelerated measurement.

2.0 NanoMend S&T Results Foreground

2.1 Introduction

The NanoMend Project was structured around 7 work packages, figure 2.1. The project began with a user need needs analysis (WP1) investigating the current user requirements in the PV and coated paper industries. Specific hindrances to the development of new products and to enhancing current production were highlighted by end users. Addressing these problems took the consortium beyond the state of the art in defect detection cleaning and repair and drove the subsequent science and technology work packages in the project. At the end of the project activities in WP1 concluded with a user benefits analysis to analyse to potential impact of the outputs of from the S&T work conducted in the project.

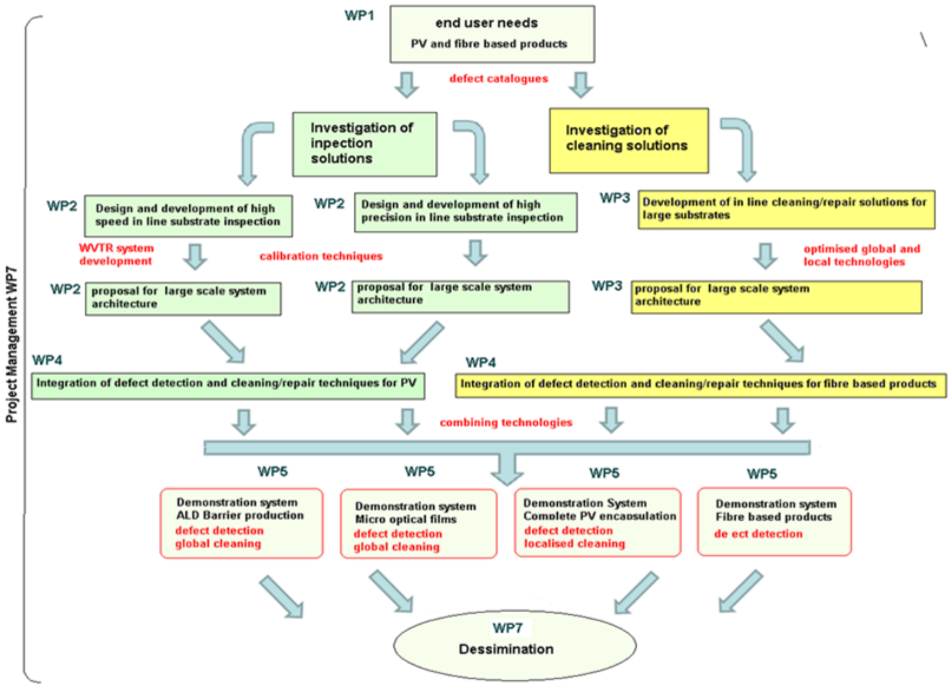


Figure 2.1 Work Package structure in the NanoMend project.

2.2 Developing barrier coatings for target substrates

An underpinning aim in the NanoMend project was to achieve ALD AlO_X coating capability for both the PV and polymer coated paper products. This was to demonstrate the ability of R2R processing to produce enhanced PV life and enhanced shelf life for food packaged using ALD barriers.

For the PV strand ALD barriers on PEN polymer substrates were made at CPI for incorporation into the transparent frontsheet encapsulation for flexible PV modules (ISO). In this application, the main function of the barrier is to prevent ingress of water vapour which degrades efficiency of the PV module. The target water vapour transmission rate (WVTR) for ALD barriers on good quality polymer was $<10^{-4}$ g/m^2/day at 35 °C and 90 %RH. NanoMend aimed to achieve WVTR $<10^{-4}$ g/m^2/day by using only a single ALD AlOx barrier layer in the front sheet assembled at ISO, eventually making possible a reduction in encapsulation cost for end users. The typical ALD coating thickness used in the project was 40nm.

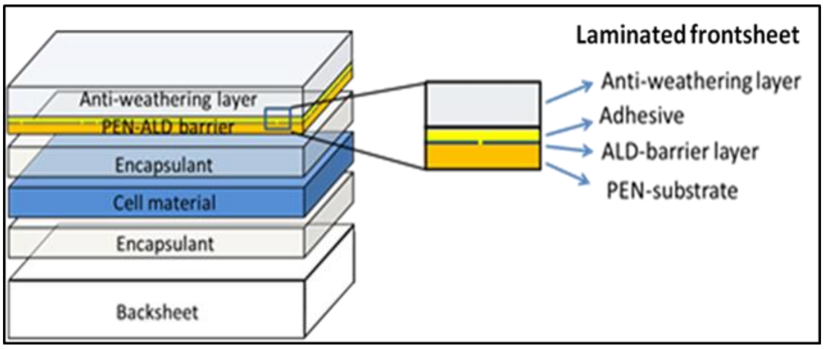


Figure 2.2 – Cross section of the Isovoltaic frontsheet including produced ALD barrier layer

ALD barriers on paper-based substrates were made at LUT and were investigated for use in special food packaging applications. Low values of both oxygen transmission rate OTR and WVTR are required for paper-based packaging when aseptic or extended shelf-life products are in concern. For these applications, the barrier is required to prevent ingress of water vapour and oxygen which can degrade food quality, and therefore, both WVTR and OTR were critical quality indicators. In the project, the specific target to achieve for WVTR was <1 g/m^2/d for biodegradable paper-based packaging by depositing an ALD AlOx barrier layer on paperboard extrusion-coated with poly lactic acid (PLA). Other substrate materials used in the comparative studies of ALD barrier coatings included BOPP film, LDPE coated paperboard. The polymer coating is needed for paper-based substrates as it offers a continuous surface for the ALD coating to bind to. With ALD, both OTR and WVTR of packaging materials can be improved. The thickness range for the ALD coating used was 30 – 50 nm.

2.3 R2R ALD coatings for ultra-barrier for PV applications.

A task for CPI in the project was to develop the technique for R2R ALD coating for the production of single layer ultra-barrier substrates. Currently manufacturers seek to achieve ultra-barrier performance based on multi-layer approaches, either by multi-layer coating or by multi-laminations of coated polymer films. The most well-known method is a multi-layer coating, produced by alternating inorganic barrier materials (providing barrier, usually sputtered AlOx or SiOx) in combination with a separating organic layer (providing separation of the defects included in the barrier layers). The barrier performance is obtained by introducing a 'lag-time' to the permeation between the defected inorganic barrier layers, which, it is envisaged, will be adequate for the life-time of the device applications. These solutions are by definition expensive as they involve multiple processes making their application to flexible PV production uneconomical. The caveat to claimed ultra-barrier performance is that standard measurement techniques for moisture permeation (MOCON) are still to be developed fully for rates $<5x10^{-4}$ $g/m^2/day$, making comparisons at levels below this difficult.

Large area single layer barrier samples for frontsheet encapsulation were at made CPI using a Beneq WCS 500 R2R ALD tool, installed and commissioned during 2014. This tool was a later version of the first WCS 500 R2R ALD tool installed at LUT but with significant design changes to the web winding system and the gas delivery head, see Figure 2.3. AlOx barriers will be deposited on 500 mm wide polymer web using a TMA/water ALD process.

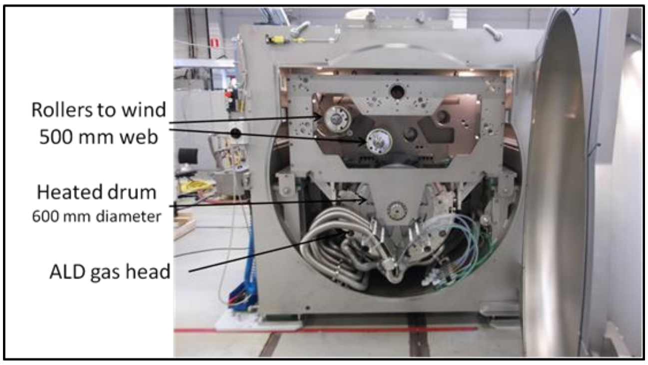


Figure 2.3 – R2R ALD tool (inside vacuum chamber)

Several types of ALD barrier structure relating to PV frontsheet encapsulation were made in NanoMend these included

i. A single ALD barrier layer: AlOx/ PEN. Deposition of AlOx thicknesses in the range 5 – 40nm has been investigated. This basic barrier structure is the main vehicle for measuring the WVTR of ALD AlOx on polymer. In order to maximise reproducibility of barrier properties, an AlOx barrier thickness of 40nm were used for all barriers that CPI supplied to partners for processing and testing.
ii. Single AlOx/PEN barrier layers laminated by ISO as prototypes for frontsheet encapsulation (see Figure 2.1). The structure of the laminated frontsheet sample is: Anti-weathering layer/ adhesive/ AlOx barrier/PEN.

Figure 2.4 illustrates the improvement in quality of 40 nm thick single barrier layers that resulted from the optimisation of batch reactor conditioning and sample handling. The WVTR was routinely $<5x10^{-4}$ $g/m^2/day$, i.e. below the Aquatran 1 detection limit. In the method, the test gas with a controlled RH is introduced into the outside chamber of the diffusion cell. The water molecules diffusing through the film to the inside chamber are carried to the sensor by N_2 carrier gas.

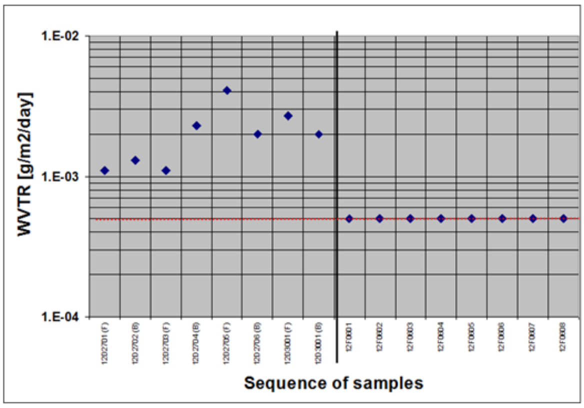
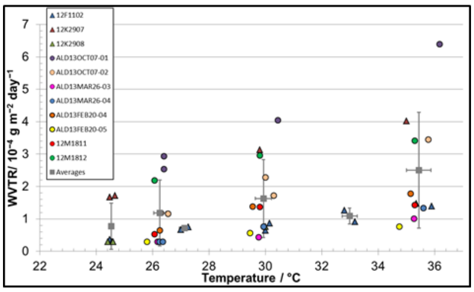


Figure 2.4 – 40nm barriers: pre-clean improvement

Figure 2.5 Mocon NPL CRDS



Due to the lower detection limit of the AQUATRAN 1 system the NPL cavity ring-down spectroscopy (CRDS) method, (to be reported later) was used to measure accurate WVTR values for single ALD barrier layers on planarised PEN. The lower detection limit for CRDS is $3x10^{-5}$ g/m^2/day.

Figure 2.5 shows WVTR for 40 nm ALD barriers at different temperatures between 24-36 °C, and nominally 90 %RH. **Two of the samples had WVTR <$1x10^{-4}$ g/m^2/day at 35 °C / 90 %RH, demonstrating that single ALD barrier layers were able to achieve the target WVTR for flexible frontsheet encapsulation for flexible PV modules.** At 35 °C, there is a cluster of WVTR values between 1-$2x10^{-4}$ g/m^2/day, and some samples with significantly higher values. Higher values of WVTR indicated a higher density of active barrier defects on these samples. Higher values of WVTR indicate a higher density of active barrier defects on these samples. NPL also measured the WVTR of AlOx coated PEN films that were laminated by Isovoltaic into a front-sheet structure. These samples had a WVTR of ~2.5 $5x10^{-4}$ g/m^2/day, the same as the average value of the other NanoMend samples, showing that there was no degradation of the front-barrier by the lamination process.

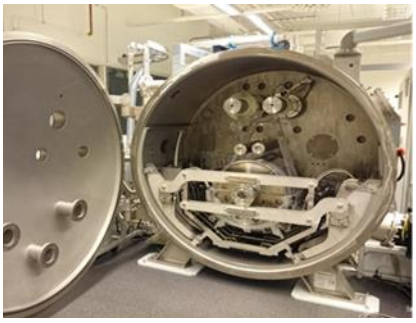
2.4 R2R ALD coatings for packaging applications.

The depositions for large area samples have been made with WCS 500 roll-to-roll ALD reactor (see Figure 2.6 & 2.6). This tool will also be used in the demonstration part of the project. The process uses TMA and water precursors and the tuned process temperature is 105 °C. Water vapour transmission rate (WVTR) tests were made with MOCON Aquatran Model 1G according to DIN 53122:2. The measuring conditions used were 23 °C, 50 %RH. Oxygen transmission rate (O2TR) tests were made with MOCON Ox-Tran Model 2/21 according to ASTM D 3985. The measuring conditions were 23 °C, 0 %RH. In this method, pure (99.9%) oxygen is introduced into the outside chamber of the diffusion cell. The oxygen molecules diffusing through the film to the inside chamber are carried to the sensor by N_2 carrier gas.

The amount of materials with extrusion coated fibre substrates were:

Basis weight of fibre	Coating weight of polymer	Thickness of ALD layer:
Paper 80 g/m^2 /	LDPE 35 g/m^2 /	Al_2O_3 45 nm (550 cycles)
Paperboard 195 g/m^2 /	PLA 24 g/m^2 /	Al_2O_3 45 nm (550 cycles)

The results for ALD coating are shown in table 2.1 and figure 2.7 and it is clear that the application of ALD coating improved substrate properties significantly. The most detrimental effects were caused by the major mechanical contacts (e.g. contacts at the rollers during a winding process) on the deposited ALD layer. In addition, the substrate contamination before the ALD coating was found to be detrimental. The effect of these factors needs to be prevented, or more likely minimised. It is evident that for paper and paperboard substrates, the ALD coating process will always be compromised from an ideal case. The application of a polymer coating (LDPE/PLA) gives a continuous base for the ALD coating enabling the improved barrier performance. It was evident that obtaining sufficient barrier properties is dependent on minimising the harmful effects of contamination and substrate roughness, rather than preventing them. The WVTR level of 0.4 g/m^2/d has been achieved for paperboard/PLA/ALD-Al_2O_3 structure. This was below the target value set in the NanoMend project (<1 g/m^2/d). The good WVTR value has been achieved by applying clean room facilities in substrate adjustments and by avoiding contacts on the coated surface. Further improvement is still possible. E.g., by controlling further the substrate contamination in prior to ALD deposition. The role of detection and cleaning systems in this is highly important.



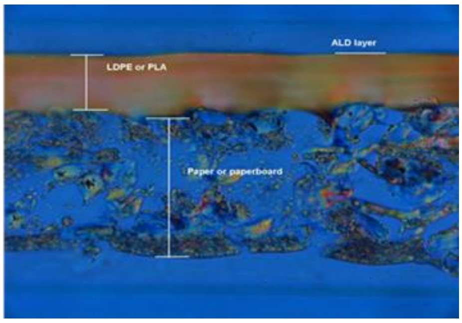
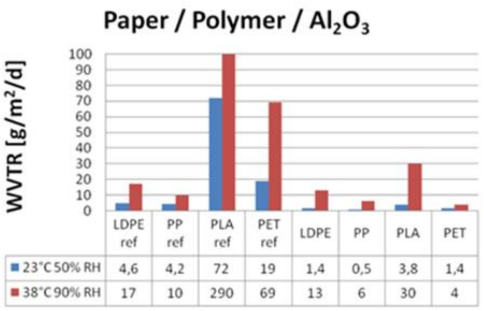


Figure 2.6 Beneq WCS 500 roll-to-roll ALD reactor at LUT Cross profile from fibre/polymer/ALD structure

Table 2.1 WVTR and OTR values pre and post ALD coating. Note WVTR tested at (23 °C, 50 %RH) and OTR tested at 23 °C, 0 %RH)

Substrate	WVTR pre ALD $g/m^2/d$	WVTR post ALD $g/m^2/d$	OTR pre ALD $cm^3/m^2/d$	OTR post ALD $cm^3/m^2/d$	
				Rolled sample	"no touch"
paper+LDPE:	0.4	0.005	10 000	600	150
paperboard+PLA	>50	0.4	1000	20	
BOPP +	0.2	0,03	1100	150	20

Figure 2.7 Improvement in WVTR for polymer substrates with ALD coating



In conclusion In the PV strand, two of the samples had WVTR <1x10^{-4} g/m^2/day at 35 °C / 90 %RH, demonstrating that single ALD barrier layers were able to achieve the target WVTR for flexible frontsheet encapsulation for flexible PV modules. In addition to this, NPL measured the WVTR of AlOx coated PEN films that were laminated by Isovoltaic into a front-sheet structure. These samples had a WVTR of ~2.5 5x10^{-4} g/m^2/day, the same as the average value of the other NanoMend samples, showing that there was no degradation of the front-barrier by the lamination process. In the Paper strand, the WVTR level of 0.4 g/m^2/d was achieved for paperboard/PLA/ALD-Al_2O_3 structure. This is below the target value set in the NanoMend project (<1 g/m^2/d). The good WVTR values were achieved by using clean room facilities for substrate handling and by avoiding contacts on the coated surface. Further improvement is still possible, e.g. by controlling the substrate contamination in prior to ALD deposition and this was the purpose of the cleaning module applied to the paper demonstrator.

3.0 Defect Characterisation

3.1 Introduction

Core to understanding the implementation of ALD coating into the manufacturing of large area substrates in flexible photovoltaics and polymer coated paper products, is the detection cleaning and repair of defects present on the substrate surfaces. Before technologies could be developed as part of NanoMend there was a need to catalogue typical defects present during the substrate manufacture. Initial cataloguing of defects was necessary in order to be able to specify and design in line defect detection techniques and cleaning strategies. The following sections review typical defects for both types of substrate and where possible modelling of the functional effects of the defects on the substrate performance was carried out.

Laboratory based characterisation technologies were applied to analyse defects present on a range of typical substrates supplied by the end users substrates (CPI, SE,I SO, FLI); optical interferometry (HUD) high resolution cameras (ISRA), SEM (TUT, HUD,FRAUN,TNO) and confocal microscopy (HUD). Following the measurement work a generic defect classification system was adopted.

Dedicated functional testing of ALD coated paper and ALD coated barrier films for PV applications (CPI TUT, NPL) were carried out and a correlation of defect density with WVTR and ORT was investigated. The results seemed to indicate that for barrier properties, it is the presence of small numbers of large defects that dominate WVTR and OTR through the barriers. For the PV substrates a theoretical model was devolved which correlated well with experimental values for WVTR.

3.2 Defect classification

Chapter 1 of this report described the various defect types encountered on the substrates across the two technology strands of NanoMend. However, a classification system was needed to allow for proper description and further classification of defects prior to the design of detection and cleaning systems. Within the NanoMend project, two distinct types of substrate were considered, flexible PV layers and polymer coated paper. To this end, it was decided to develop a defect classification system which would allow generic defect classification within the project and across the large area substrate sector in general. No such system exists, however, very recently a system for defect classification in the die polishing industry has been proposed[1]. This system was adopted for the NanoMend project and allows a unified classification of defect to be implemented.

The off line laboratory measurement work (HUD, TUT, FRAUN TNO) allowed consortium partners extract defect information relevant to the end users. This provided information such as type, size, density and position which was used to develop targeted defect detection and cleaning systems. The off line measurement exercise also facilitated the proposal of a defect classification system based on breaking the defect types down into four main groupings and symbols. The defect types encountered by **all end users** were catalogued this way and information stored on the project database (HUD, FRAUN). Figure 3.1a and 3.2b show application of the classification system to the CPI AlOx barrier layer and the SE polymer coated paper.

[1] S Rebeggiani “On Polishability of Tool Steels” PhD Thesis Chalmers University of Technology Sweden (2013)

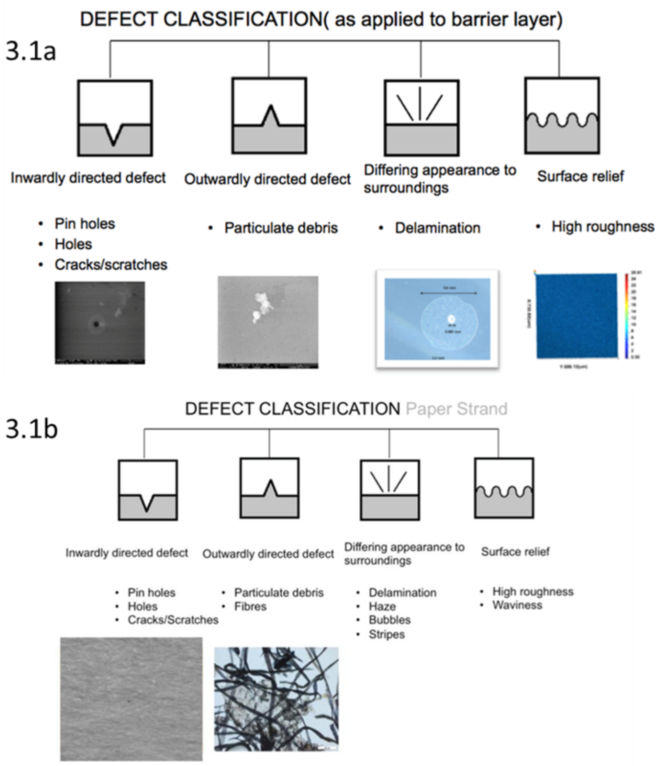


Figure 3.1 Defect classification system a) for barrier layers (CPI) b) Polymer coated paper (TUT, SE)

Both the user needs survey and the following correlation studies informed the development of the demonstrators and the proof of concept systems and resulted in basic detection instrument specifications.

3.3 Correlation for PV barriers substrates.

Following classification it was important to establish where possible the effect of defects on the end user application of the substrates. The logic behind this exercise was, to understand which were the most cost effective defects, to attempt to measure catalogue and clean.

For the PV strand, the single layer AlOx barriers, were investigated in detail due to their inherent high cost (figure 3.2). Several series of barriers substrates were manufactured under different protocols and analysis was carried out to determine the surface defect morphology across the substrates. All surfaces were measured using a combination of laboratory based coherence correlation interferometry, SEM and AFM. Following measurement the WVTR properties were quantified using AQUATRAN and CRDS instruments. An example of one of the test set results is shown in Table 3.1.

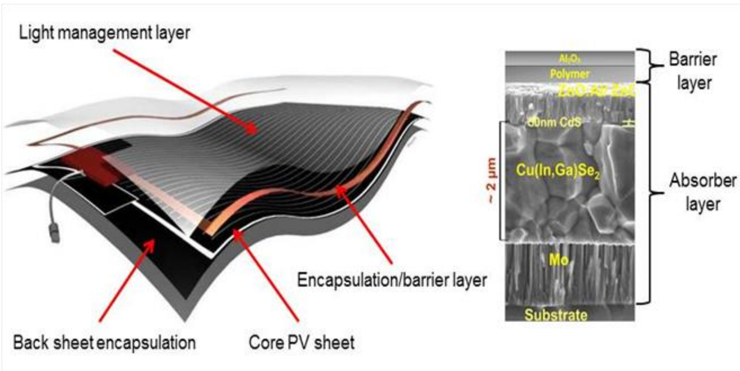


Figure 3.2 Function layers in flexible PV substrates (courtesy Flisom)

Table 3.1 WVTR for substrates prepared with differing levels of cleanliness.

Sample	Manufacturing Conditions	AlO_x thickness	WVTR (g/m^2/24 hrs.) Detection limit $5x10^{-4}$
1	Polymer surface unprotected before loading for ALD (practice 1).	40 nm	$5x10^{-4}$
2		40 nm	$< 5x10^{-4}$
3	Polymer surface protected to the last moment before loading into ALD coater. Some visible scratches were reported on S3 (Practice 2).	40 nm	$1x10^{-3}$
4		40 nm	$< 5x10^{-4}$
5	Contact cleaning of the polymer before ALD (Practice 3).	40 nm	$6x10^{-4}$
6		40 nm	$<5x10^{-4}$

3.4 Surface topography analysis and modeling

Segmentation analysis refined in NanoMend [2] was carried out on the surface data in order to extract and count the number of significant defects present on all the substrates, using a series of mathematical and thresholding techniques designed to extract defects with a lateral dimension greater than 3um and a height greater than 3 x the general roughness[3] as shown in figure (3.3 a & b). As with all the test results the analysis figure 3.3 indicated that there was evidence of correlation between the number of large defects and the WVTR value, figure 3.3c. The high WVTR specimen had a larger density of significant defects as compared to the better performing substrates.

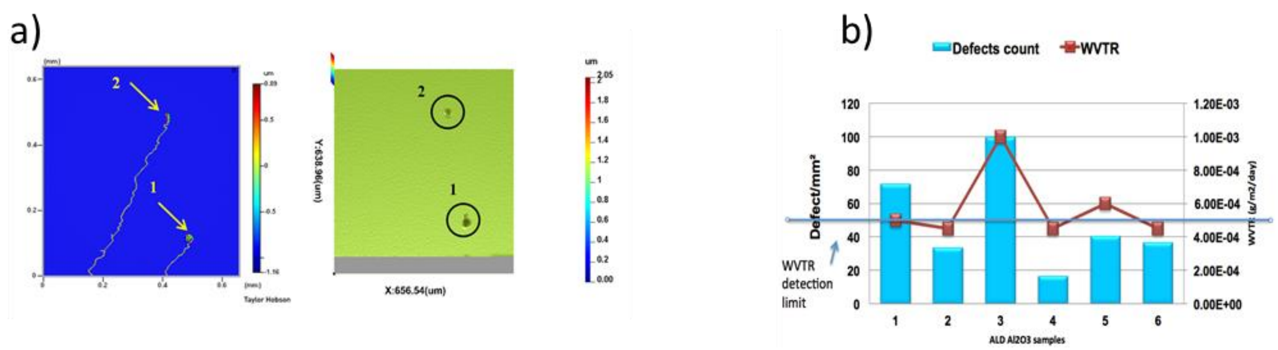


Figure 3.3a) 2 segmented defects extracted from surface measurement data b) and significant defect values density versus WVTR value

To further understand the correlation between barrier defects and WVTR a theoretical model was developed to try to understand the WVTR values and inform future detection systems. The model assumed the water vapour is primarily transmitted through defects and the total substrate WVTR is the

[2] M. Elrawemi, L. Blunt, L. Fleming, and F. Sweeney, "Further development of surface metrology methods for predicting the functional performance of flexible photovoltaic barrier films," *Surface Topography: Metrology and Properties,* vol. 1, p. 015006, 2013.

[3] X. Jiang, K. Wang, F. Gao, and H. Muhamedsalih, "Fast surface measurement using wavelength scanning interferometry with compensation of environmental noise," *Applied optics,* vol. 49, pp. 2903-2909, 2010.

sum of the water vapour transmission through all the defects.

$$WVTR = \frac{Q}{A} \quad (g/m^2/day)\ldots\ldots\ldots\ldots (1)$$

Where; Q is the amount of the water vapour passing through a film of thickness of 40nm and total area A during time t driven by a partial pressure differential across the film. In order to express water vapour permeation through a barrier coating containing several defects (holes), the equation can be modified for (N) pinholes in the sample area:

$$WVTR = \sum_0^N \frac{Q}{A} N \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Further experiment showed good agreement between experimental WVTR results and that predicted by the model thus showing that defects over 3um lateral dimension dominate the substrate WVTR, figure 3.4, and should be the minimum target for any defect defection system.

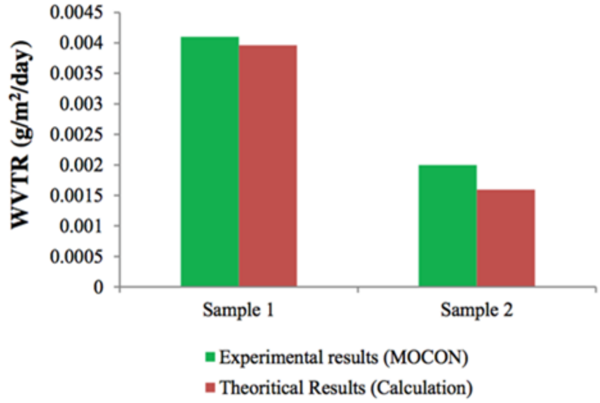


Figure 3.4 Comparison between the theoretical at (3µm lateral cut-off) and experimental WVTR results for two tested samples

3.5 Paper correlations

Detailed surface analysis at (TUT) using SEM optical microscopy and confocal microscopy failed to consistently reveal the presence of pin hole defects which would affect the WVTR and OTR through ALD coated polymer based paper packaging. In order to facilitate correlation studies laser drilling was used (FRAUN) to produce a series well controlled pinhole defects (figure 3.5). Following the laser drilling the substrates were tested for both OTR CO_2Rand WVTR levels.

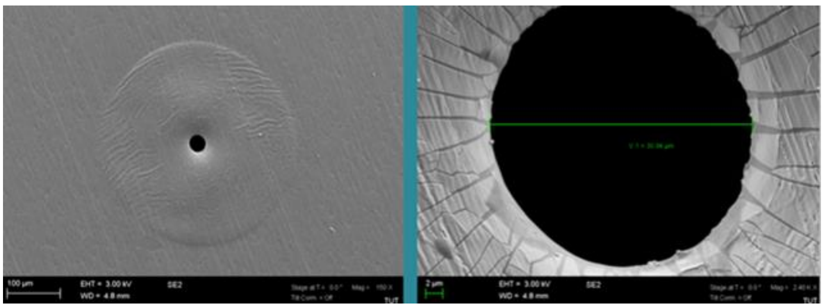


Figure 3.5 Laser drilled pin hole defects in Paper/LDPE/ALD substrate

General, Al_2O_3 ALD layers improved barriers with all polymer coatings figure 3.6. The studies focused on the obtaining WVTR target levels below 1g/m^2/day for a paperboard and ALD coatings with levels of 0.4 g/m^2/day were obtained for defect free samples. Correlation tests showed that pinholes clearly affect the barrier properties of extrusion coated materials. There was a clear correlation between pinholes and OTR. Even the presence of 1 pinhole destroyed both the CO_2 and OTR barrier of the paper-polymer-ALD structures. WVTR results showed that values for laser-pinholed samples are within the std deviation of a pinhole-free sample. Tests also indicated that size and amount of the pinholes affect barrier properties. These tests indicated that with LDPE+ALD structure, there was an excellent WV-barrier, ~1-10 pinholes do not affect WVTR value. However when the amount of pinholes was increased to 30-100 pinholes, AQUATRA was not able to measure the excessive WVTR, table 3.2

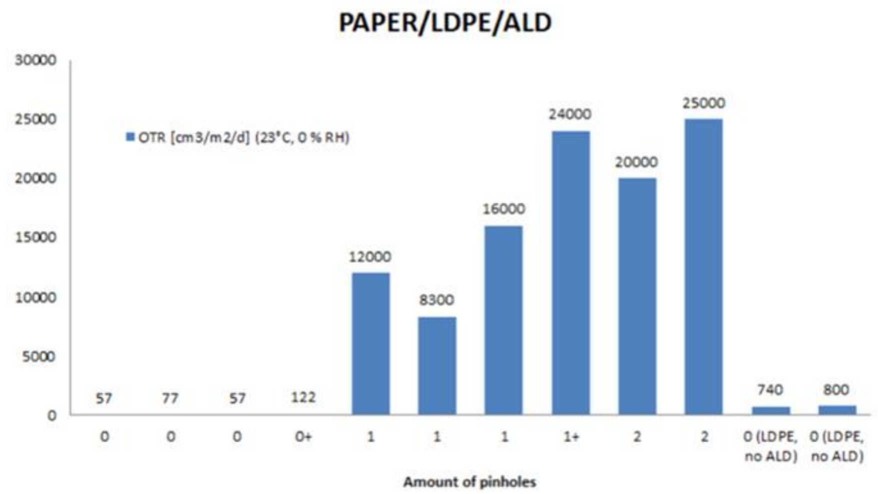


Figure 3.6 OTR levels through simulated defects in Paper/LDPE/ALD substrate

Table 3.2 WVTR value versus pin hole density

First pinhole and then ALD

SAMPLE ID	mg / (m²-day)		
	A	B	AVG
0 = 0 pinhole	834	966	900
1 = 1 pinhole	1480	1117	1298
2= 3 pinholes	130	1070	600
3 = 10 pinholes	670	2417	1544
4 = 30 pinholes			0
5 = 100 pinholes			0
6 = ref, no ALD	8071	7130	7600

First ALD and then pinhole

SAMPLE ID	mg / (m²-day)		
	A	B	AVG
0 = 0 pinhole	2004	1662	1833
1 = 1 pinhole			0
2= 3 pinholes			0
3 = 10 pinholes	1449	823	1136
4 = 30 pinholes			0
5 = 100 pinholes			0
6 = ref, no ALD	8071	7130	7600

PAPER/LDPE ~ 7-8 g/m2/24h (90 % RH/38°C)
PAPER/LDPE/ALD ~ 1-2 g/m2/24h (90 % RH/38°C)

3.6 Defect detection instrument specifications

Following the user needs survey and the defect classification study it was decided that four defect detection systems would be commissioned.

- A demonstrator system at FLI to detect scribe defects in the Mo layers 5µm at a lateral resolution of 10um. Measurement speed 1-10m/min

- A hybrid demonstrator system at TUT consisting of a low resolution high speed system to concentrate on pin hole defects in the centre region of the polymer coated paper (Lateral resolution 10µm, measurement speed up to 500m/min) and a high resolution low speed system measuring the edges of the polymer coated paper to detect particles prior to ALD coating at TUT (Lateral resolution 5µm measurement speed 1-10m/min). The edge defect detection system was interfaced with a cleaning system to removed particulate debris.
- A proof of concept system sited at CPI designed to detect defects in the ALD coated barrier layer. The specification being to detect defects down to 3um lateral dimension, measurement speed 1-10m/min.
- A laboratory based system based at NPL designed to measure defects in the holographic structures produced by ISC. The defects in this case were often below the lateral diffraction limit of red light 900nm at 20X for static off line measurement.

4.0 Substrate Cleaning Studies

4.1 Introduction

A key NanoMend project aim was to link in line defect detection to in line localised cleaning and repair for the two types of target substrates. Following the results of the user needs survey, TNO led a significant research including (HUD, FRAUN FLI and TUT) effort to establish the optimum cleaning and repair technologies following laser scribing of Mo layers on the PV substrates. For the extrusion coated paper substrates the goal establish techniques to facilitate the removal of surface debris prior to ALD coating.

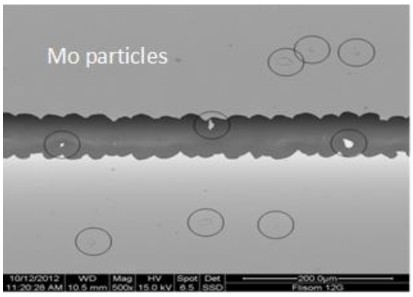
The detailed objectives entailed removal of > 90% of sub-micron particles from polymer substrates and ALD barrier films and fibre-based packaging. All techniques developed needed to be adapted for implementation to roll-to-roll manufacturing at web speeds of 1–10 m/min. A further objective was to investigate repair methods for electrical shunts in the flexible PV modules. Finally integration strategies between detection techniques and cleaning and repair techniques were investigated.

4.2 PV cell material

Flisom supplied samples of polyimide film with a 500 nm Mo back-contact film scribed at various laser scribing conditions. Detailed analysis at TNO and Huddersfield University of the samples (see D3.2) showed that the Mo particles are 500 nm thick Mo film flakes ~5 – 20 µm in size. The particles are erratically distributed along scribes, where highly particle-contaminated areas alternate with entirely particle free areas.

4.3 Paperboard material

Paperboard was supplied by SE and extrusion coated in the pilot line at TUT. In order to facilitate the detection of contamination on the paperboard, a black LPDE coating was applied by TUT. Samples of were then supplied to TNO for the cleaning tests. Stora Enso also supplied cutting debris (i.e. paperboard fibres) collected from their industrial line. The fibres were applied on to the extrusion coated paperboard samples through dipping in a suspension of iso-propanol / dichloromethane followed by drying at room temperature in air.



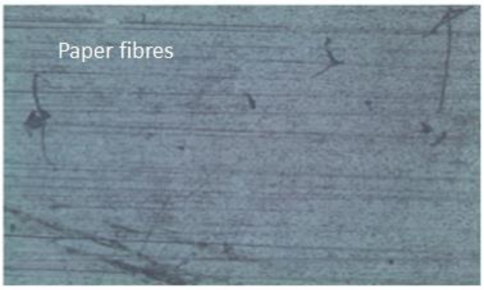


Figure 4.1 PV scribe line Figure 4.2 Polymer coated paper

4.4 Cleaning trials for P1 scribe Mo layer on PV substrates

For Mo scribed substrate laser methods, electrochemical nano bubbles and direct gas cleaning methods were investigated. Laser methods were discounted due to the fact that at high cleaning efficiencies (75%) the laser ablated/damaged the underlying Mo coated substrate. No laser settings allowing effective particle removal without Mo film ablation were found. Electrochemical hydrogen nanobubble cleaning was found to be controlled by the applied potential in combination with the cleaning time and the temperature and a post-cleaning DI water rinse was very beneficial for achieving a high particle removal efficiency (xx%). However, a wet-chemical method was not preferred because after P1 Mo scribing, the subsequent CIGS layer deposition is a vacuum process. Evaporation of solvent, in this case water, taken up by the PI foil extends the time needed to reach the appropriate vacuum for CIGS deposition.

Direct gas cleaning was investigated using localised nozzles to deliver gas to small regions of the substrates. Cleaning using CO_2 snow (derived form adiabatic cooling of high pressure gas) gave > 90% Mo particle removal efficiency on Mo film model systems and then was transferred to a lab-scale Roll-to-Roll pilot line at TNO.

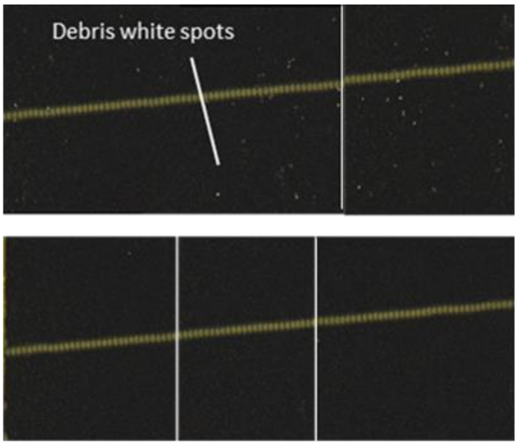


Figure 4.3 Optical microscope images of scribed Mo film with redeposited Mo particles before and after (1 l min^{-1} N_2 gas jet cleaning at a nozzle – substrate angle of 45° , a distance of 2 cm and a web speed 2 m/min.

Table 4.1 Particle removal efficiency determined from scribed Mo film with redeposited Mo particles before and after 1 l min^{-1} N_2 gas jet cleaning at a nozzle – substrate angle of 45° and distance of 2 cm and 6 cm min^{-1} web speed up to 2m/min

Picture #	Before N_2 cleaning	After N_2 cleaning	Mo particle removal efficiency
1	15	0	100%
2	33	7	79%
3	37	4	89%
4	47	3	94%
5	45	4	91%
6	35	7	80%
7	63	8	87%
8	74	10	86%
9	60	6	90%
10	54	2	96%
11	46	3	93%
12	58	4	93%
13	40	1	98%
14	44	2	95%
15	28	2	93%
16	48	7	85%
17	40	1	98%
18	53	1	98%
19	32	4	88%
Overall	852	76	91 ± 6%

It was found that without substrate heating, CO_2 snow cleaning was not effective in removing redeposited Mo particles from the Mo film on foil. Freezing and ice formation prevented Mo particle removal and resulted in severe Mo film surface staining. However when N_2 gas was substituted the jet enabled removal of > 90% of the Mo particles without the need for substrate heating. It was found that the particle removal efficiency was little affected by the variation in the N_2 process conditions. The particle removal efficiency varied between 85% and 95% up to web speeds of 2 m/min. It was noticed that a small fraction a of Mo particle stick to the Mo film and were not removed by N_2 gas jet cleaning.

4.5 Extrusion coated paperboard cleaning

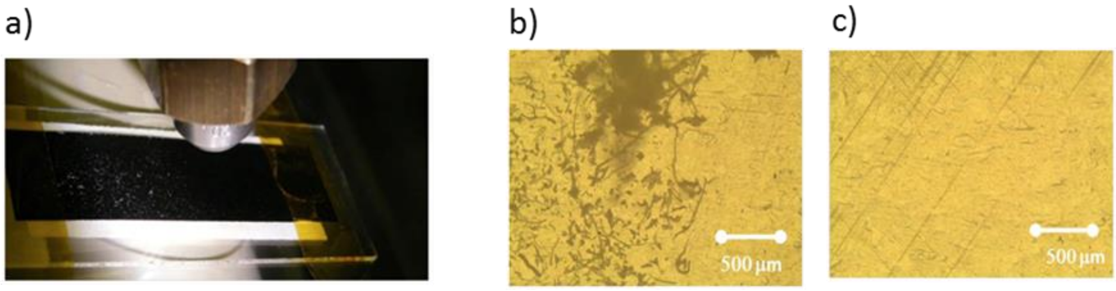


Figure 4.4 a) N_2 gas nozzle on R2R line at TNO b) coated paper pre-cleaning c) post-cleaning

Both CO_2 snow cleaning and N_2 gas jet cleaning were highly effective in removing fibres figure 4.4, i.e. cutting edge debris, from extrusion coated paperboard. In contrast to scribed Mo film cleaning, cooling during CO_2 snow cleaning did not affect the particle removal efficiency. However, because of the ease of operation in an industrial environment, N_2 gas jet cleaning is preferred. A 95% reduction in debris surface area coverage was achieved thus achieving the project target whilst there was no significant effect of substrate temperature and gas on time. An oxygen transmission rate of 250 ± 130 $cm^3\ m^{-2}\ day^{-1}$ was determined at TUT on extrusion coated paperboard R2R cleaned with the N_2 gas jet with Al_2O_3 ALD barrier layer applied after cleaning at LUT. This represented a forty-fold improvement on the oxygen transmission rate of the extrusion coated paperboard without an ALD barrier coating. Within experimental variation, the oxygen transmission rate was the same for cleaned paperboard deliberately contaminated with fibres and only cleaned and non-treated paperboard showing the high particle removal efficiency of N_2 gas jet cleaning.

4.6 Repair techniques for electrical shunts in PV modules

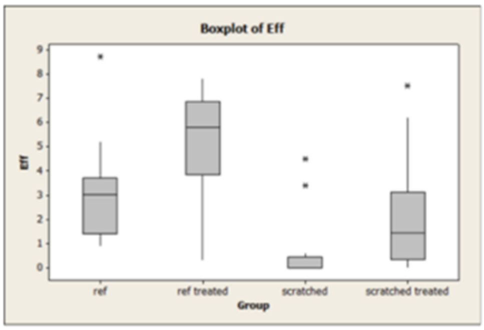


Figure 4.5 Box plot of efficiency of repaired poor quality cell compared to reference cell

An electroless Mo etching method developed for shunt repair was evaluated on glass based CIGS cells prepared at TNO. Pieces of 10x10 cm^2 CIGS cells up to the CdS buffer layer were treated in the Mo etching solutions and finished into 0.5 x 1 cm^2 cells for cell performance analysis. The conversion efficiency of low quality, shunted cells increases from 3% to 6% after shunt repair with simultaneous increase in other cell performance parameters figure 4.5. On the contrary, shunt repair seems to limit the performance of higher quality cells by a decrease in conversion efficiency from 12.5% to 11.5%. However, it cannot be excluded that the difference in cell performance is due to the no-uniformity of the 10x10 cm^2 CIGS cell. Nevertheless, cell performance is more uniform over of the 10x10 cm^2 CIGS cell after electroless Mo etching. Although the feasibility of shunt repair was demonstrated it was not considered feasible or economic within the project timescale to introduce a fluid based cleaning system to the R2R pilot line at FLI.

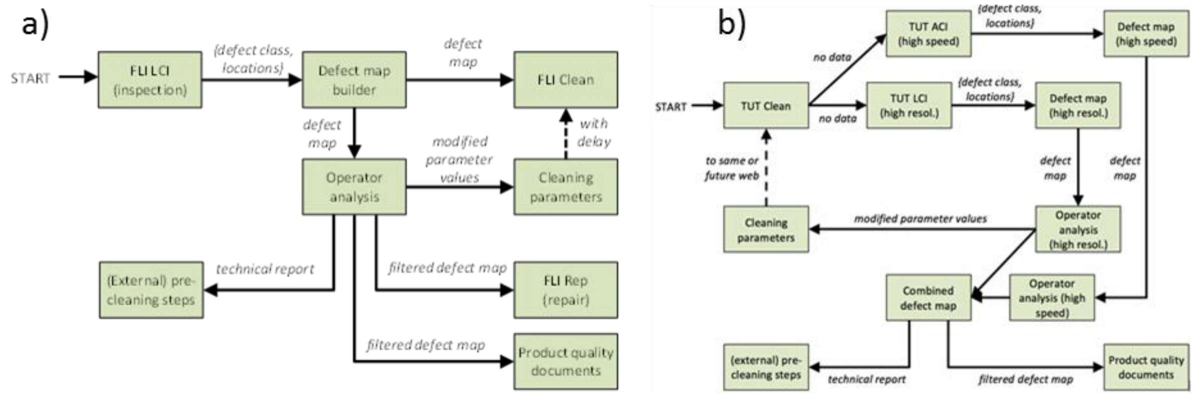


Figure 4.6 interaction strategies for PV demonstrator a) and paper demonstrator b)

4.7 Interaction strategies.

The two primary demonstrator systems within the NanoMend project combined both detection systems with cleaning systems. For the demonstrator at Flisom (FLI) detecting Mo particles the primary interaction strategy was the camera based inspection system (ISRA) detected surface defects and a running defect map was generated. Following the classification of the defects and cataloguing of their position those defined as Mo particles triggered a response from the array of N_2 cleaning nozzles placed across the central 450mm of the web. Operators can change the P1 scribe laser production parameters or produce relevant quality documents, figure 4.6, use the information from the running defect map.

The TUT demonstrator constituted a novel hybrid system i) a low resolution high speed camera based inspection system where the central portion of the R2R substrate is inspected and a running defect map generated. Information from this running defect map is used by operators to change production parameters or produce relevant quality documents ii) a high resolution low speed camera based inspection system inspecting the outer 10cm of the substrate edges for cutting debris. With this system a running defect map is generated and the operators can change the production parameters or produce relevant quality documents. Due to the fact that the density of defects was relatively high the N_2 cleaning is manually activated during edge inspection and run constantly during inspection figure 4.6.

4.8 Conclusion

- Roll-to-Roll N_2 gas jet cleaning removes > 90% of Mo particles redeposited on scribed Mo film on polymer foil at web speeds > 1 m min^{-1}
- Roll-to-Roll removal of fibre contamination by N_2 gas jet cleaning, with efficiencies at 95%, enables ALD barrier coatings that reduce the oxygen transmission rate of extrusion coated paperboard by a factor of forty to 250 ± 130 cm3 m^{-2} day^{-1}.
- The electroless Mo etching process is able to repair shunts in highly shunted cells and reduce the variation in cell performance over a 10x10 cm^2 CIGS cell.

In the demonstrator phase on NanoMend N_2 gas jet cleaning was fully integrated with the pilot facilities at Flisom (PV) and TUT (Paperboard).

5.0 Measurement Technologies Developed in NanoMend

5.1 High Sensitivity Water Vapour Transmission Rate (WVTR) testing of ultra-barrier films

Many of the materials used in the production of electronic products such as photovoltaic modules and flexible displays are particularly sensitive to water vapour ingress. NPL in collaboration with CPI and FRAUN developed a novel system for providing traceable measurements of WVTR with a limit of detection significantly below 5 x 10^{-5} $g.m^{-2}.day^{-1}$. The system utilised a new approach to measuring WVTR directly, based on cavity ring-down infra-red spectroscopy (CRDS) and represents a significant advance beyond existing methods. Measurements can be performed over a broad range of temperature and relative humidity. A relative expanded uncertainty of ±2 % was been achieved for measurements above 1 x 10^{-2} $g/m^2/d$. Measurements with state of the art barrier layers prepared at CPI helped develop and validate the NPL facility. This work has provided a new infrastructure for disseminating traceability to support the development of high performance barrier layers required by the rapidly developing field of organic electronics.

A schematic of the system is shown in figure 5.1. The system is designed to be symmetrical around a single "dry" chamber separated from two "wet" chambers by two samples of the barrier material under test. When the structure is assembled and clamped, two seal rings sit either side of the perimeter of each two barrier layer samples and form a "guard" chamber. The symmetrical design with two pieces of sample material, allows for improved measurement sensitivity by increasing the area through which water vapour can permeate. Ultra-high purity nitrogen is supplied to the "dry" chamber. Following the blue arrows in figure 5.1, dry nitrogen first enters the guard chamber ensuring that the seal around each barrier film perimeter is purged continuously. This novel design minimises leakage through the seal and hence eliminates water ingress to the dry chamber. Any water permeating through the film is collected by the stream of dry nitrogen in the dry chamber and passed to a CRDS with a detection limit of 0.2 nmol/mol. The spectrometer is calibrated with trace water vapour standards between 5 and 2000 nmol/mol (expanded uncertainty of ±2 %), generated using a unique capability at NPL. The CRDS analyser detects water vapour by tuning a laser source to an absorption line of water. By measuring the time it takes light to "ring-down" in a highly-reflecting cavity, it is possible to calculate the absorbance. Conversion of the decay time of the cavity, with and without target gas, enables the concentration of the target gas to be calculated. The temperature of the wet and dry chambers and the bubbler is controlled and can be set from ambient temperature up to a maximum of 40 °C ±0.2 °C.

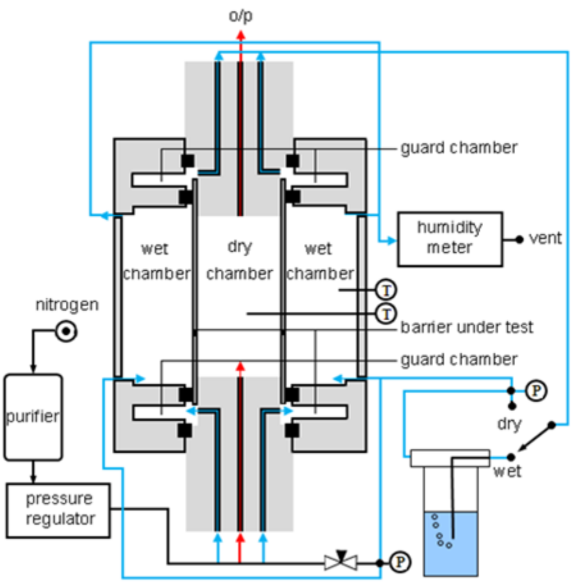


Figure 5.1 Schematic of the system. The flow path of nitrogen through the guard and wet chambers is shown with grey solid arrows. The flow path through the dry chamber to the CRDS is shown with grey dotted arrows

The WVTR is calculated using:

$$W_R = \frac{(x_w - x_z) \times M_w \times Q_A}{V_m \times A}$$

Where x_w is the amount fraction of water measured through the dry chamber (mol/mol), M_w is the molecular weight of water, V_m is the molar volume of an ideal gas (at STP), x_z is the amount fraction of water in the dry nitrogen (mol/mol), A is the area of the barrier film exposed to water vapour (m^2) and Q_A is the flow through the dry chamber (l/day). The system specification is given in Table 5.1

Table 5.1 WVTR CRDS system specification

Properties		Test Method	Unit	Value	C.O.A.
WVTR		NPL (RH;90% T;35ºC)	$g/m^2/d$	$\leq 10^{-4}$	x
Thickness		Internal method	mm	0.125±10%	x
Mass /unit area		Internal method	g/m^2	177±10%	x
Tensile strength	MD	DIN 53455/ASTM D 882	N/mm^2	≥155	x
	TD	DIN 53455/ASTM D 882	N/mm^2	≥155	x
Elongation at break	MD	DIN 53455/ASTM D 882	%	≥70	x
	TD	DIN 53455/ASTM D 882	%	≥70	x
Shrinkage (30min @ 150ºC	MD	Internal method	%	≤0.2%	x
	TD	Internal method	%	≤0.15%	x
Transmission @450-800nm				>80%	x
UV (3000h) and DH (1000h) Resistance (yellowing index /L-a-b values)				<5	-

5.2 In line ultra-precision 3D surface metrology for roll to roll thin film processing utilising Wavelength Scanning Interferometry (WSI)

HUD in collaboration with IBS, CPI and NPL developed a new optical interferometry system for fast in line areal surface measurement of defects on barrier substrates. The WSI system has been implemented at CPI as a proof of concept sensor for the detection of defects in polymer film coated with an Al_2O_3 vapour barrier layers. The WSI technology is protected by pending patents derived from PCT/GB2010/050063 also published as US2012026508 (A1).

The measurement principle of the WSI is based on determining the phase shift of a reflected optical signal while the wavelength of the illuminating light is changed. The light wavelength is scanned through a range by filtering white light from a halogen source using an acousto-optic tuneable filter (AOTF). The system comprises two interferometers that share a common optical path. The interferometer using a filtered white light source (the WSI) is used for measuring surface topography. A second common path interferometer using a super-luminescent diode (SLED) is used to monitor for surface movement due to environmental vibration and an active servo control then keeps the optical path constant by moving the reference arm mirror with a piezo-electric translator (PZT), figure 5.2

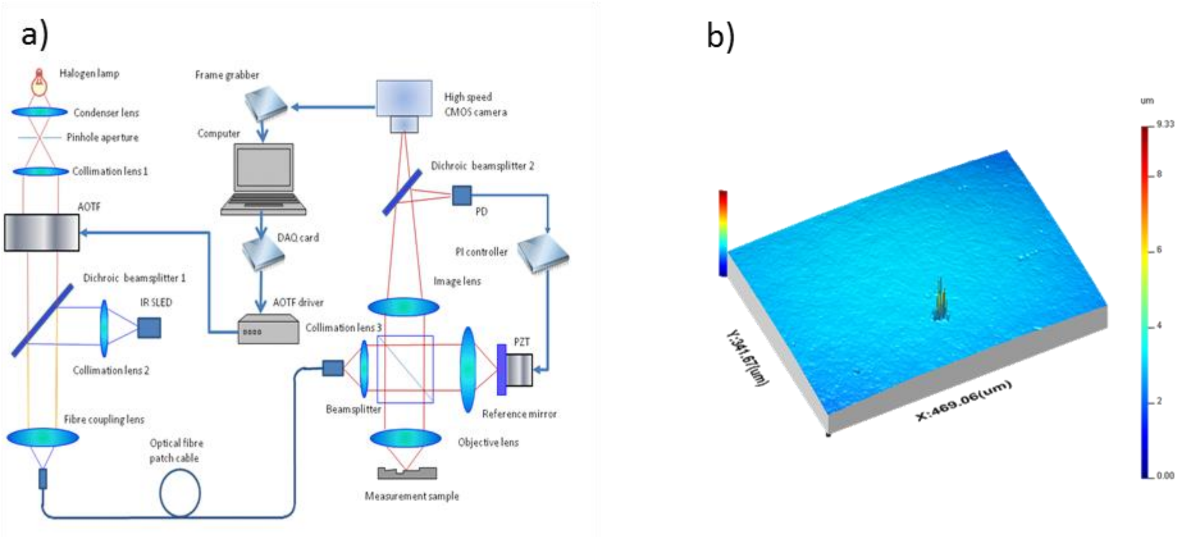


Figure 5.2 a) schematic of WSI system and b) surface measurement taken of barrier surface

Table 5.2 Main specifications of the WSI system

WSI Specification	Value	Unit
Vertical Range	96(2x lens)	µm
Vertical Resolution	6	nm
Lateral Range	2.8 x 2.8	µm
Lateral Resolution	290	nm
Measurement Time	<1	sec
Stabilisation bandwidth	<500	Hz

The wavelength scanning captures, 64-256 interferograms using a CCD camera. The number of interferograms taken depends on specific requirements for precision and range. Isolating a single pixel (which corresponds to a specific point on the sample) from the interferogram set, a sinusoidal changes of intensity with wavelength is apparent. The overall phase shift across the wavelength scan range can obtained from the intensity signal using Fourier transforms. The height of the point represented by the pixel can then be calculated by:

$$h(x,y) = \frac{\Delta\varphi(x,y)}{4\pi\left[\frac{1}{\lambda_{max}} - \frac{1}{\lambda_{min}}\right]}$$

where $h(x,y)$ is the height of the specific pixel, and $\Delta\varphi(x,y)$ the calculated phase shift over the scan range. λ_{max} and λ_{min} are the upper and lower wavelengths of the scan range respectively. The WSI system, developed within the NanoMend project is a critical tool for the evaluation of surface topography where measurement speed is critical factor and the system must work within a vibrationally noisy environment. The initial implementation of the system takes measurements on the substrate at rest and as implemented takes strip images across the while substrate width. The system specification is shown in Table 5.2.

5.3 Fourier imaging systems for the in-line inspection of structured surfaces

The scattering of light from periodic holographic micro-structures on the surface of plastic films is the basis of the optical appearance found in, for example, premium gift-wrap and anti-counterfeit film on high-value toiletries as produced by ISC. These optical grating are often below the diffraction limit of light with the structures typically produced in high volume using roll to roll processes such as thermomechanical embossing.

Adaptable, high-speed and quantitative verification of such optical grating structures over large regions is currently not possible. Currently, a sparsely sampled global inspection 'by eye' is employed, which is highly subjective and suffers from poor repeatability. To address this gap NPL and FRAUN have developed Fourier imaging techniques for the off line affordable inspection of these optical gratings. Fourier imaging systems enable rapid quality mapping of optical grating structures that are fast and repeatable.

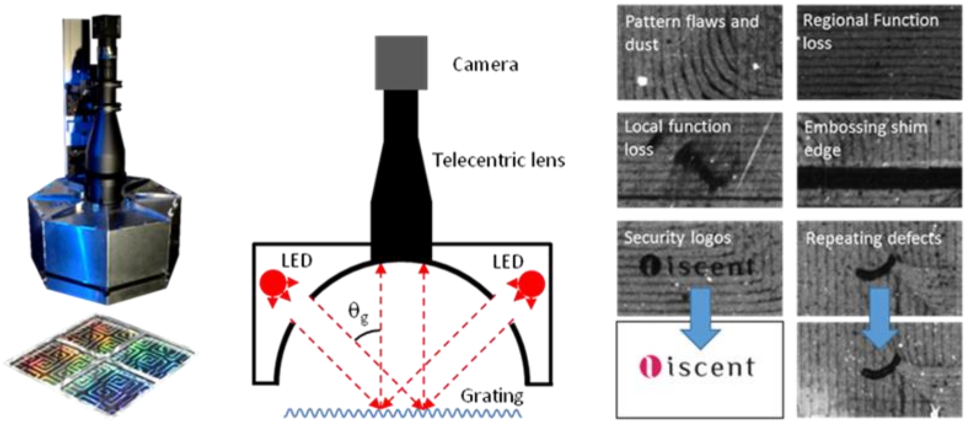


Figure 5.3 Implementation of the Fourier filtered imaging system (left). Schema of the system (centre). Examples of features and defects that can be resolved by image contrast.

The Fourier filtered imaging system is a full field-of-view mapping system that interrogates application specific spatial frequencies in a single-shot global measurement. Using *a priori* knowledge of the desired periodic structure, the light source is configured using a mask to illuminate the sample with k-vectors (angles) matching the desired spatial frequencies in the diffractive structure of the sample. If the structure contains only a homogeneous distribution of the desired spatial frequencies, a certain amount of light will be scattered normal to the surface and be collected by the telecentric camera system, producing a homogeneous image of a particular intensity. Strong image contrast is obtained for functionally critical defects (e.g. pitch and amplitude variations; dust; or scratches) and designed security logo features since they do not scatter the incident light directly in to the low numerical aperture of the telecentric optics with the same intensity. For the ISC samples, bright and dark regions in the resulting images represented regions of high and low diffractive function, respectively (see 5.3). The system is made robust against small misalignments of the sample with respect to the sensor by illuminating the structure with a small range of k-vectors through the use of a weak diffuser between the source and the sample. The Fourier imaging systems developed in NanoMend can be tailored toward specific performance, cost and compatibility requirements, by the substitution of key components. The systems are scalable for monitoring larger substrates in-situ, via parallelisation or cross-web scanning.

5.4 High-speed high-resolution surface inspection

ISRA has cooperated with TUT, FLI NPL to develop in-line surface inspection techniques for high-speed high-resolution roll-to-roll applications. The technologies used line scan cameras to capture data, as the surface is moving and a novel computer architecture to manage date capture and extraction of surface defect data. The systems have three main features:

- Data processing performance of more than 640MB/s image data in one channel. ISRA has further developed the processing speed to 1.2 GB/s.
- Advanced multi-modal lighting techniques.
- Very high resolution down to 3µm for large surfaces at speeds up to 10m/s

Two basic systems were developed a high speed inspection system detecting Mo particulate debris f following P1 scribing in the PV line at FLI and a hybrid system, figure 5.4 combining high speed inspection with high resolution inspection situated at TUT. The high speed inspection elements at TUT were the same as those adopted at system at FLI.

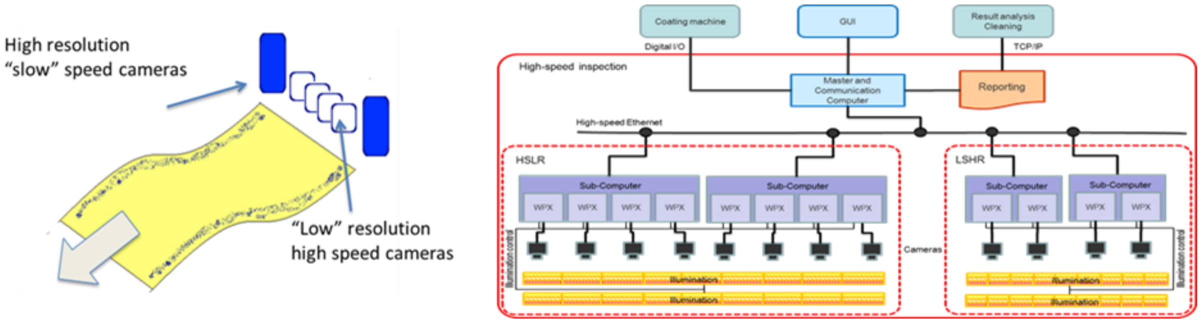


Figure 5.4 a) Schematic setup of the hybrid system at TUT b) Computer hierarchy adopted to deal with high data rates

Table 5.3 Specifications inspection

Specification	Value	Unit
Processing performance for image data	>650	Mb/s
Lateral Resolution	≥3	µm
Illumination modes	≤5	

For the high speed inspection covering the centre portion of the substrate the requirement was a FOV 300 mm with a max substrate 800 m/min and a detection resolution of 10 µm/pixel. Based upon these requirements and camera housing size restrictions 12Kpix-line scan cameras (640 MHz, 66 kHz max. line rate) were used for the inspection system. As the camera housing was larger than the FOV, the cameras were mounted in 2 lines. Dark field illumination was used to capture stray light effects for the detection of particles and contaminations as well as scratches and cracks. Alternatively bright field illumination Provides best conditions for changes in surface reflectivity/roughness and topological defects. The illuminations are flashed and synchronized to a single camera. The High resolution system has FOV 100 mm at each edge at substrate speeds up to 10 m/min with a resolution of ~3 µm/pixel The lighting concept for the high resolution inspection was based on a darkfield set-up High-power LEDs were be used with their light will be focused on the line of inspection. Camera calibration used NPL gratings.

6.0 Inspection and Cleaning Systems Deployment in NanoMend

During the NanoMend two demonstrator systems and one proof on concept system were deployed towards the end of the project. The deployed demonstrator systems combined both defect detection and cleaning technologies. The proof of concept system was a measurement system only.

6.1 Paper pilot line Hybrid System (TUT)

The combined high speed inspection, high resolution inspection and a cleaning system was deployed on the extrusion coating paper pilot production line at TUT.

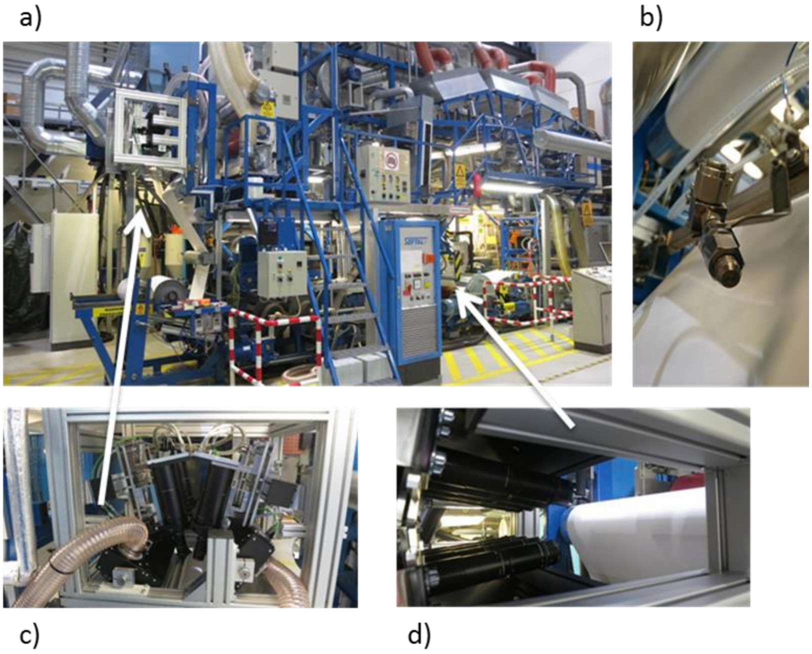


Figure 6.1 a) Pilot production line at TUT b) N2/pressurised air cleaning nozzle c) centre zone substrate inspection system d) edge zone inspection system

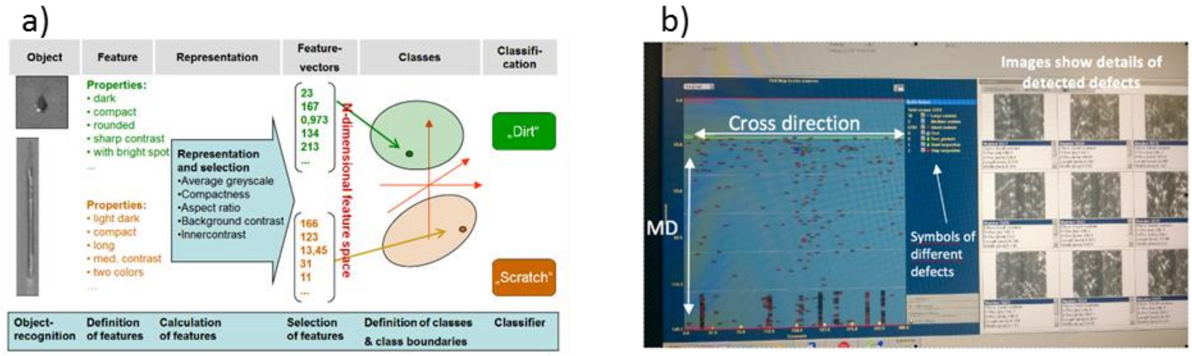
The installation was planned to demonstrate the capabilities of inspection covering two regimes i) High speed inspection of the centre portion of the substrate, to detect the presence of pinhole defects and particulate defects with a resolution of 10um where the substrate speed can be up to 800m/min ii) An edge detection system running at low speed (up to 10m/min) to detect particulate debris and which is then interfaced with the cleaning system which removes surface of debris prior to ALD coating.

Installations were planned so that extrusion coating and high speed (center) inspection could be achieved on the same run. Edge-cutting-cleaning-and edge inspection could be accomplished on the same run but separate from the high speed processing. Pilot line was modified to accommodate the equipment installations and this included the creation of new web paths, installation of new rolls, new electrical and network connections and encoders to monitor the line speed of pilot line. Trials with both detection systems for end-user materials were implemented in co-operation with, LUT, SE, ISC and ISRA. The main focus is in inspection of pinholes for LDPE-coated paperboard and inspection of contaminants (dust) on web edges for ALD. Testing of effects of edge cutting and cleaning prior to ALD will be evaluated.

Efficient deployment of the detection system requires the system to be “trained/optimised” to recognize critical defects (figure 5.2a). To facilitate this a remote access was created for ISRA. This way ISRA could establish a remote connection to the systems and solve possible problems. This remote access was used in the trials in order to optimize the cameras and to create defect categories. The remote access also allows ISRA to download data from the systems for further analysis and vice versa.

The main target with **centre cameras** was to detect possible pinholes on-line during following extrusion coating (figure 5.2b). LDPE-coated paperboard was tested in order to create the defect categories. This was important because of the massive data flow that detection systems are creating. After creation of the correct defect categories, the detection was retested on-line with extrusion coating. The target for the centre inspection is that if pinholes area detected, the operator can change coating parameters, for example extrusion temperatures, and this way optimise the coating process immediately.

Edge cutting (or slitting) process generates particulate/fibre contaminants on industrial lines. At the TUT pilot line the target was to test the effect of cleaning on the quality of extrusion coated material and for that, cleaning process is located was after edge cutting. With **edge cameras** monitoring the outer 10cm of the substrate the success of the pressurized air/N_2 cleaning was confirmed. Cleaning is critical for material prior to ALD-coated. ALD coating is highly sensitive to defects and this emphasizes the importance of cleanliness. Figure 5.2c) shows the ability of the edge cameras to detect additional cutting debris on the right hand edge of the substrate.



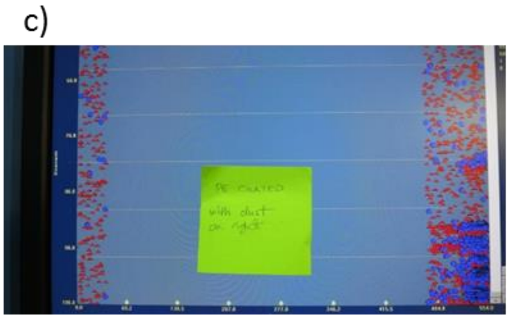


Figure 6.2 a) Processing scheme of defect classification (ISRA) b) Running defect map output from centre cameras c) Running defect map output from edge cameras showing increased debris load on right edge of substrate

For this demonstration system a modular cleaning unit based on N_2/pressurised air was installed and demonstrated with polymeric surfaces and fibre-based materials at varying line speeds. This method can be used to remove loose micron-sized particles from the surface of the R2R material. For final industrial use, the cleaning should be implemented globally across the whole width of the substrate in order to ensure as clean a material as possible for further processes such as ALD.

6.2 PV pilot Production Line System (FLI)

The inspection system implemented at FLI was essentially the same system specifications as the edge inspection of the paper application i.e. the substrate speed was up to 10m/min and the target resolution was 3um. For both systems a similar camera and illumination protocol was utilized. The significant difference for the PV inspection system was that the cleaning interface was linked to the inspection system in such a way as the cleaning nozzles were switched to active on the detection of a specified defect. The cleaning system required an extra interface to communicate between the inspection and cleaning systems (IBSPE).

Several inspection trials were evaluated at 1m/min substrate these comprised i) inspection of bare polyimide film; ii) Inspection of the back contact iii) CIGS layers iv) Complete Stack and v) Back contact P1 Scribe; In this case the system was investigated for its ability to detect Mo particles redeposited on the back contact surface and Mo debris in the Mo scribe lines. To date particles and dust with sizes down to 0.05 mm^2 could be detected reliably on Mo and CIGS. More detailed work to identify smaller relevant defects ("system teaching") and significantly more statistics is needed.

Figure 6.3c&d shows the inspection of P1 scribed web. The scribe lines are clearly visible in defect mapping as well as in the detail information of single defects. The system was designed to identify a complete laser scribe in the cross web direction within the complete field of view. Due to the high reflectivity of the molybdenum surface and the contrast to the laser pattern the scribe was detected with a width of 0.14 mm reliably. Each defect which is detected by the inspection system is allocated exact coordinates. The mappings of defects are shown figure 6.3c&d. An additional dynamometer was been installed to determine the positional coordinates in down web direction as well as the web speed. The cross web positions are obtained by the camera positions. Figure 6.3c&d shows the inspection of P1 scribed web. The scribe lines are clearly visible in defect mapping as well as in the detail information of single defects.

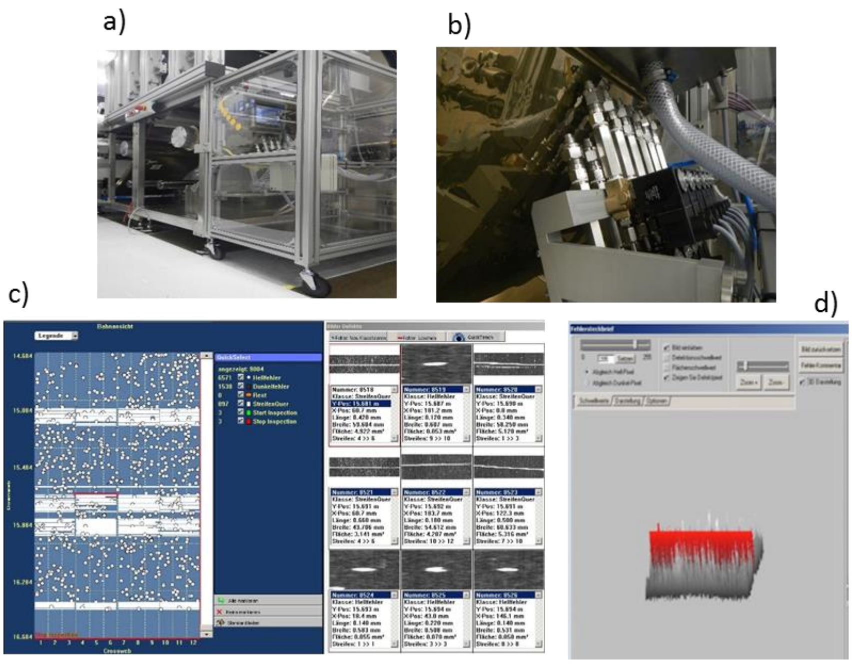


Figure 6.3 a) cleaning system location c) cleaning nozzle configuration c) Running defect map on P1 scribe surface d) detected P1 scribe line

These position coordinates are then communicated to the cleaning system and the respective nozzles, figure 6.3b, are activated at the moment when the respective particle is in front of the nozzles. The communication between the two systems is ensured via an interface which allows the control of the cleaning unit through the software of the inspection system. To assess the cleaning system single defects points were marked on the web and visually assessed to ensure that the nozzle was activated at the moment when the marked defect is at the right position. Results showed that effective activation of the correct nozzle figure 6.3b. The cleaning system showed that in principle it works and can remove particles and dust from the surface, however further optimisation of the air flow and exhaust is needed to avoid redeposition at another position on the foil.

In conclusion the complete the system showed promising results and enabled FLI to understand the subtleties of the inspection system features. More work and time is needed to assess the full potential and impact of this system on solar module manufacturing. FLI is continuing evaluate and start the acquisition of an inspection tool for quality control.

6.3 High precision barrier measurement system

The most cost critical layer in flexible PV is the barrier layer, hence it was decided in the NanoMend project that a proof of concept barrier defect detection system would be developed and deployed as an in process system at CPI. Based on earlier work the system specification was to detect and identify surface defects such as pinholes and particles down to a lateral size of 3 µm with a vertical resolution of 10 nm over a 500 mm width of 40nm thick Al_2O_3 ALD coated barrier film

The difficulties in performing high fidelity surface measurements during R2R manufacturing process are directly related to the ‘noisy’ working environment, speed of production throughput and the large area that needs to be covered. Interferometric techniques have the potential to be used for on-line surface measurement but they are susceptible to environmental disturbances and subject to limited field of view (FOV) especially if high objective lenses are considered in the optical setup. The system implemented by HUD IBSPE and CPI was based on wavelength scanning interferometry (WSI) combined with a built-in stabilisation element to compensate for environmental disturbances (CH4). The WSI was also integrated with a traverse stage (to allow full surface measurement over the substrate widths of 0.5 m) and a vertical auto-focus stage (to position the WSI focus plane on the top layer of the film). The opto-mechanical system was embedded within a film re-winder stand using a metrology frame and kinematic stages, resulting allowing the WSI to align with the barrier substrate surface. One of the measurement challenges was to guarantee the flatness of the film at a fixed height across the substrate width. A porous air-bearing conveyor was used to achieve this and hold the film within the focal depth of the objective lens of the WSI.

The auto-focus was necessary to bring the objective lens to the optimum position to detect surface interference. The method is based on tracking the peak of the coherence envelope of the reference interferometer sourced by the SLED, see Figure 3, where the WSI head is moved normal to the web to scan the focal plane of the WSI objective lens using a stepper motor [2]. Simultaneously the intensity response is monitored by the reference interferometer, with the maximum intensity (coherence envelope peak) being found to be the point of focus.

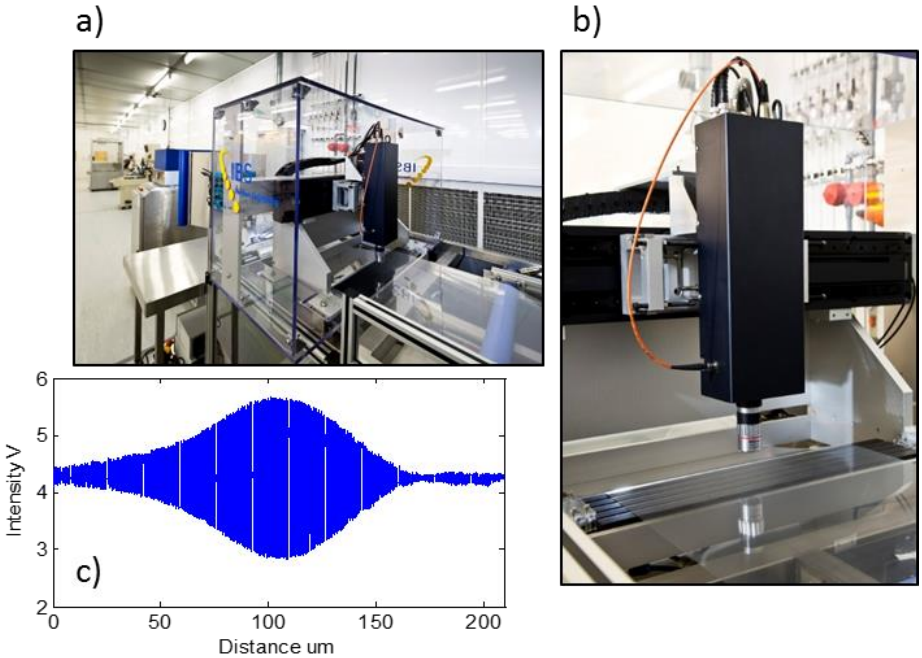


Figure 6.3 a) Opto-mechanical system on film re-winder stand b) Coherence envelope of SLED c) Air bearing system supporting barrier substrate

The film handling for roll to roll process demands non-contact solution that supports the film at a fixed height and maximises the flatness of the web relative to the measurement plane. An air bearing conveyor was used to supply uniform clean dry air (CDA) pressure, through a porous medium with a thin air gap, resulting in a more consistent flying height and better flatness across the full width of the flexible foil web < 5um.

Many measurement files (typically 1000 measurement files per substrate width with overall data size larger than 300 M byte) are produced over large area substrates with a limited field-of-view (FOV=

0.5mm x0.7 mm for 5x objective lens). To access these files automatically, a computerised solution was developed based on monitoring surface topography parameters and extracting only functionally significant defects significant defects have a direct impact on the global surface roughness of the measured data set. Consequently the Sq parameter is chosen as a monitoring function to distinguish between data sets with significant and non-significant/free defects.

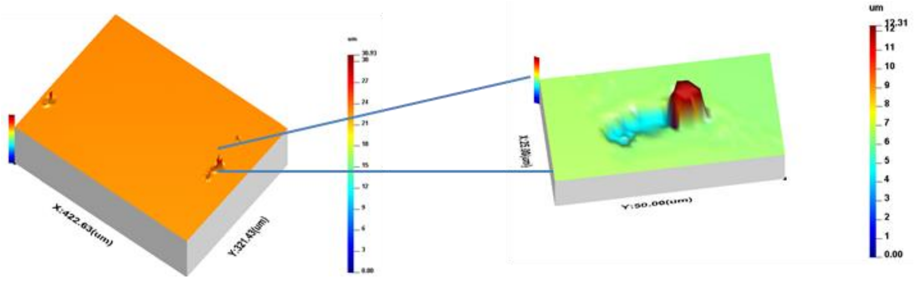


Figure 6.4 Measured surface containing significant defect exploded defect view. In situ coated film measurement, inset image 50 x 25um

In conclusion the opto-mechanical system can be considered as a solution for R2R process as combined to traverse and autofocus stages and air bearing conveyor. The data handling model can effectively distinguish significant defects from non-significant defects without interaction from the inspector.

7.0 Impact

The outcome of the NanoMend project has provided new opportunities to consortium members as well as the wider European metrology companies, automation industry and manufacturing entities to incorporate new in line technologies for detection, cleaning and possibly repair. Integrated into production of large area photovoltaics, packaging, displays, sensors, medical devices, lighting etc., NanoMend technologies will enable benefits including production control, improved yield, reduced costs, reduced scrap, leading to further end-user benefits. Specifically, within the project, NanoMend has demonstrated significant benefits in the two chosen exemplar value chains:

Photovoltaic value chain:
- Reduction in overall PV system costs
- Anticipated increased yield of CIGS PV modules on polyimide
- Comparable solar module efficiencies
- Anticipated increased longevity (> 20 year life) for flexible CIGS (BIPV)
- Significant environmental benefits in terms of use of renewable energy and use of less raw materials

Fibre based packaging value chain:
- Anticipated reduced scrap levels during production
- Increased yield and costs savings via inspection and process feedback
- Source reduction and hence significant environmental benefits

7.1 Strategic Impact

Recent developments in roll-to-roll processing of large area substrates, novel materials development (organic, inorganic and composite) and integration of functional intelligence into flexible substrates such as plastic and paper are paving the way for printed and potentially printable electronics to take main stage with a potential to impact existing markets and create new ones, e.g. displays, lighting, photovoltaics, retail packaging and sensing systems. Several benefits including lower cost, superior performance, robustness and flexibility, thinness, environmental benefits and fault tolerance are expected from these new technologies and processes[1]. Europe now has an opportunity to lead in the development and manufacturing of a wide range of more durable, high value products such as building integrated photovoltaics, large area lighting panels, conformable, rollable OLED displays and fibre based packaging amongst others.

Thin film photovoltaics are forecast to grow to €14 billion by 2019 and € 50 billion by 2029 while OLED displays are forecast to grow to €12 billion by 2019 and €68 billion by 2029. As an example, in the printed and thin film photovoltaic development, Europe is in a leading position with energy conscious governments and politicians driving development through large subsidies for both manufacturing and installation. Correspondingly, the Implementation Plan for the Strategic Research Agenda of the European Photovoltaic Technology Platform[4] names high yield and in-line quality control and tools as important topics in improving the manufacturability of thin film photovoltaic's.

Europe also plays a key role in the global paper & packaging industry with leading players including Stora Enso (Finland) based in Europe. Global sales revenue from top 100 companies accounted for over € 221 billion in 2009[5] and some of the key challenges facing the industry include source reduction and sustainability and addressing market in Asia for non-refrigerated food packaging. The role of packaging is seen to be growing in importance for the following reasons[6]: (a) Preserve and protect the product b) communicate brand image (c) convey information and (d) offer convenience. For example, food waste in the supply chain is 2 % in Europe, although it is significantly lower than 40-50 % in developing countries where there is a lack of sophisticated packaging solutions

7.2 Key challenges addressed in NanoMend

In progressing towards large volume production of products for applications stated above, clearly, there are significant challenges that need to be addressed in ensuring low cost production, high yield, high operating efficiencies and longevity. Contamination and defects at the micro- and nano- scale during production lead to product degradation, increased scrap and increased production costs. Current metrology techniques face the challenge of speed, resolution and the need to be in process. Current global cleaning and repair techniques do not sufficiently address the required levels for micro- and nano-scale defects. Longevity is severely affected by degradation caused by water vapour and O_2/CO_2 vapour passing through the packaging. Defect identification and where appropriate repair usually lags the development of a novel technology. As a consequence, device yields of the novel technology are initially quite low, until efficient metrology cleaning and repair processes are demonstrated and established. For nano-coated or nano-structured surfaces, in-line surface-inspection is not yet commercially available.

Impact from the two NanoMend exemplar applications; flexible photovoltaic module production and fibre-based packaging production, within the wider European manufacturing sector is provided below:

7.3 Photovoltaic value chain: Demonstration of higher yield, reduced costs, higher efficiencies and increased longevity.

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[4] J. Kuusipalo, Paper and Paperboard Converting, 2nd Ed. Finnish Paper Engineers' Association, 2008

[5] Global Forest, Paper & Packaging Industry Survey, 2010 edition published by Price Water House Coopers

[6] Sustainable Packaging: threat or opportunity published by Price Water House Coopers

The European Directive on the 'Promotion of Use of Energy from Renewable Sources', which came into force in June 2009[7], aims to reduce Europe's green-house gas emissions by 20% by 2020. The PV market has grown by an average 30% p.a. over the last 20 years. Annual PV installations were 7.3GW in 2009 and forecast installations were 15.4- 37GW for 2014[8]. Nevertheless, solar PV is not yet commercially competitive as a global energy source and significant further cost reductions are needed if PV is to provide a clean, secure and safe alternative to fossil fuels for large scale electricity generation. Thin film PV technology is improving and offers the best chance for cost reduction to achieve grid parity. This has been described as 'The Terawatt Challenge for Thin Film PV'.

Cu (InGa) Se2 (CIGS) is the only commercialised PV technology that can combine conversion efficiencies that are comparable with conventional Si PV, with the thinness and lightweight achievable with thin film PV. By 2016, the market for conventional rigid CIGS PV is expected to be €2B, with significant additional sales of CIGS modules for building-integrated PV (BIPV) amounting to more than €500M[9]. Flisom (FLI) is aiming for a large share of the emerging market for BIPV systems by developing lower cost roll-to-roll (R2R) manufacture of CIGS PV modules on polymer. NanoMend, through its improved detection of particles and contamination, substrate cleaning and repair of interconnect defects, has developed technologies that can facilitate improved process control and enhance yield and efficiency in R2R manufacture of light weight, long-life CIGS PV modules on flexible substrates, whilst also reducing significantly overall PV system costs.

Reduction in PV System Costs: Manufacture of highly efficient, long-life and light weight thin film PV modules on flexible substrates, rather than on glass, is essential to reduce the installed cost for solar BIPV (Building Integrated PV) systems, significantly below 1€/Wp. For example, the BOS (balance of system) costs for BIPV systems using polymer substrates are estimated to be ~30% lower than for glass[10]. The BOS cost includes transport, installation and maintenance and it varies with the PV application (e.g. BIPV, solar farm). The relative costs for PV systems are usually compared as cost per watt peak generated (Cost/Wp)[11].

Two area-dependent factors must be considered: (i) total system cost and (ii) system output (which directly depends on the efficiency of the active material). High module efficiency increases output per unit area and therefore decreases Cost/Wp.

Cost/ Wp = (System cost/unit area) / (Wp/unit area) System cost = Module cost + Balance of System (BOS) cost

Currently, batch processes using glass encapsulation are used, which produces PV modules that are heavy, rigid, and susceptible to breakage. Module and BOS costs are typically similar in magnitude. NanoMend's contribution to improving the yield and module efficiencies, and at the same time reducing the BOS costs enabled by thin film PV, w will have the potential to reduce overall module costs.

Reduced encapsulation costs: Currently, encapsulation costs are >50% of the solar module costs. NanoMend has delivered high performance barriers (WVTR < $1E^{-4}$ $g/m_2/d$) using R2R ALD in combination with in-line defect detection to enable process control to reduce pinhole phenomena. With improved process control this will increase barrier yield, reducing both scrap and cost. Higher

[7] Directive 2009/28/EC of the European Parliament, http://europa.eu/legislation_summaries/energy/renewable_energy/en0009_en.htm,

[8] Solarbuzz, www.solarbuzz.com

[9] Nanomarkets report on CIGS market (Feb. 2011)

[10] K Zweibel NREL Tech Report NERL/TP-520-38350 (2005).

[11] K Zweibel NREL Tech Report NERL/TP-520-38350 (2005).

performance encapsulation with stable and very low WVTR over very long time (10-25 years) will maintain the efficiency of the PV module over its life, by preventing degradation. NanoMend, via its solution for the detection of and improved barrier quality has delivered tools to enable significantly improved encapsulation and reduce encapsulation costs of the PV module costs. It has been shown that an ALD-AlOx based ultra-barrier material for PV cells with a fluorine-free frontsheet is viable, and the cost of these materials has been reduced to less than half during the project. This material is then cost-competitive with materials currently available in the market place, however due to the early stage of market development it is unknown if the alternative manufacturer's materials are realistically priced or are high or low compared to their production costs.

Increased PV efficiency: For thin-film PV, highest efficiencies have been demonstrated for CIGS cells with record efficiencies of 20.3% achieved at lab scale on glass[12] and 17.6% on polyimide[13]. Flisom's research partner EMPA has been developing record-breaking photovoltaic devices for over 12 years. FLI is transferring EMPA's processes to industrial settings with R2R industry-rated equipment. NanoMend has enabled the production of higher quality films using defect detection and localised cleaning, thus leading to the potential for further increase in efficiencies.

Increased PV yield: NanoMend technologies, integrated in production of PV modules have the potential to enhance module yield due to faster and more effective detection mapping of particles and scribing faults at different stages of processing, improved efficiency of particle removal by targeted local application of directional gas based cleaning methods and due to future integration of shunt repair methods.

The inspection technologies developed in NanoMend can increase the efficiency of the solar modules by identifying processes that lead to dead areas of the cells (defects that cause a loss of energy conversion due to allowing recombination rather than 'fatal' defects that prevent an entire cell from working). For a 10 MW installation produced by the same factory costing € 5,000,000, we can estimate the increase in profit margin were the efficiency of the cells to increase from 14% to 15%. If we assume that all other costs remain the same and there is a 10% profit margin on the 14% efficiency cells, then there would be a reduction in area of cells required to supply the same power, this would reduce the cost to the manufacturer. Therefore, assuming that on the € 5,000,000 installation that there is € 4,500,000 of costs and € 500,000 of profit, then the production cost of solar modules to the manufacturer would fall to € 4,200,000, enabling a € 800,000 profit, or 16% rather than the 10%; or a reduction of selling price to € 4,800,000 without profit loss

Increased longevity of PV modules: Once PV solar modules are manufactured, they have to be encapsulated in order to protect them from environmental effects, especially from humidity and oxygen. Current approaches to improving barrier performance using multi-layer sputtered or evaporated inorganic coatings with organic inter- layers are expensive and their performance degrades over time as the structure saturates with water vapour. NanoMend, through use of high-quality barrier ALD layers will a very low water vapour transmission rate ($<1x10^{-4}$ g/m^2/day at 35 °C / 90 %RH) and offers a significantly enhanced longevity.

Environmental benefits: The demonstration activities proposed within NanoMend and subsequent penetration into production will enable greater utilisation of Renewable Energy Sources (RES) as part of the drive to meet the EC initiates on renewable energy sources (52,53) and low-carbon economy.

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[12] P. Jackson et al., (2011) New world record efficiency for Cu(In,Ga)Se2 thin-film solar cells beyond 20%. *Progress in Photovoltaics: Research and Applications*, n/a. doi: 10.1002/pip.1078.

[13] A. Chirila et al., (2010) "Optimization of composition grading in Cu(In,Ga)Se2 for flexible solar cells and modules", in *Proc. 35th IEEE Photovoltaics Specialists Conference*, Hawaii, p.656-660.

7.4 Fibre-based packaging value chain: Demonstrate better functional integration, scrap reduction and significant environmental benefits:

Modern fibre-based packaging is based on raw materials which come from renewable sources. This requires, amongst others, the use of biodegradable extrusion-coated polymers in the structure. Improved fibre-based packaging has a potential to reduce the use of synthetic polymer, thus enabling fibre-based materials to take market share from wholly polymer-based material further saving non-renewable resources. The role of the fibre material in the structure is mainly to provide mechanical properties (strength, temperature resistance) for the structure, e.g., the rigidity of the material is used for liquid packaging.

The market for extrusion-coated polymers as functional and barrier coatings on paper and board was valued at €1.17 billion in 2008. The main product used as a functional or barrier coating on paper/board is polyethylene (PE), which with other extrusion polymers, accounts for some 46% of the market, while aluminium foil accounts for 18% of the market. The main market for these materials is in liquid packaging board (LPB), which is used for fresh and long-life products such as beverage/liquid packaging, liquid dairy, fruit and vegetable juices, non- carbonated soft drinks and soups. This means that many grades of LPB used for this application comprise about 75-80% paperboard, with 20-25% PE coated on both sides of the board. Aseptic board, which is used for long- life products, requires greater barrier properties to ensure the packed product retains its freshness for months or even years. As a result, many grades of aseptic board contain 5-6% aluminium foil as well as PE; other materials, such as Ethylene Vinyl Alcohol (EVOH) are used by some producers due to recycling issues with aluminium foil.

Within food and liquid packaging, barriers to moisture, light, aroma and oxygen are needed. Fresh products do not need the same degree of barrier protection as long-life products. In recent years, pharmaceutical and healthcare markets are growing fastest, where sales of barrier coatings for paper and board are small. This is due to the increased interest in health and well-being and a generally ageing population within the developed world. New coatings are constantly developed to meet the demands of food preservation together with tightening legislation and environmental issues. Future trends steer fibre-based packaging material production towards source reduction, which leads to a use of thinner, denser, more functional barrier coatings on fibre/paper materials.

Due to demands for higher quality together with cost and material reductions, the fibre-based packaging materials of the future will be thinner and hence more sensitive to defect formations in processing. NanoMend has demonstrated the feasibility of novel in-line defect detection and cleaning technologies in the industrial production of polymer-coated papers. It has also found synergies between the defect detection utilizations prior to nano-coating technologies and large-scale paper converting production and functionality. R2R processing is an essential part of all large-scale fibre-based packaging productions and NanoMend has given the packaging industry an opportunity to produce next generation biodegradable, high-barrier-coated paper products for packaging purposes in high volume, reliable roll-to-roll processes through demonstration of inspection cleaning and ALD coating technologies.

The results from the cost-modelling performed in NanoMend show that the bio-degradable PLA/AlOx barrier is potentially a competitive technology to the incumbent foil-lamination packaging materials if a roll-to-roll ALD machine that had the same material consumption rates as LUT and CPI's machines could be built, however the long-term stability of this material is unknown and the ability to convert it into a 3-dimensional carton and for the barrier-layer to survive that process is also unknown, although conversion to a 3-dimensional carton was demonstrated in NanoMend.

The costs of applying an ALD AlOx as an optical–enhancement layer (ISCENT holographic structures) on a 0.5 m wide machine at 1 run per day is was shown to be economical at ≤€6 per m^2, however this could be significantly reduced if the production machines could be run faster, which is Anticipated as optical-enhancements are less demanding of total surface-area coverage than barrier films.

Scrap reduction: A successful implementation of novel defect detection and cleaning processes has highlighted the potential of huge economic benefits in the high-volume production of polymer-coated papers facilitated through a reduced amount of production scrap, increasing yield and quality and avoidance of further cleaning processes. The NanoMend project was in line with EC directives on packaging and packaging waste and the European agenda to maximise the use of renewable energy sources[14].

The typical proportion of production scrap formed in a basic polymer-coated paper production lies between 5-6%. Thus, the basic extrusion coating line with 100 ktons annual production produces 5-6 ktons of scrap every year. Up to 20% of this can be said to be related to defects (1-kton). As the price of the end product is typically 1000 €/t and the average return of scrap of 150 €/t, approximately €850k is lost due to defects every year in one production line. NanoMend has demonstrated a set of tool, which can play a critical part in reductions in scrap and hence cost savings. Furthermore, future production is likely to use less material and thinner coatings due to environmental requirements and hence, coatings of the future will be more sensitive to defect formation and the amount of production scrap is likely to increase. By demonstrating novel defect detection, cleaning and repair systems, NanoMend has met demands improved quality control tool for the future which can address the amount of production scrap.

Increased yield: NanoMend has enabled local cleaning of observed defects in processing, which is not possible in current R2R production, thus leading to increases in overall yield and in particular increased yield for ALD coated polymer layers on paper/board.

Environmental benefit: Fibre-based packaging is based on raw materials which come from a renewable source. Improved packaging using the outputs from the NanoMend project could be implemented to reduce the amount of added polymeric material which must be used in the barriers to get adequate b performance. Improved barrier performance will enable fibre based materials to take market share from wholly polymer based materials thus saving non-renewable resources.

7.5 Economic impact and new opportunities for leading players from the European automation, manufacturing instrumentation industry

The inspection technologies have been key to many developments in the project and have enabled quantitative measurements of production that was previously qualitative. This has enabled the identification of processing issues that once solved have increased the quality of the materials produced.

It is expected that, following commercialisation one-two years after project completion, NanoMend technologies will offer a timely opportunity for European production houses to integrate them into their production lines, incrementally. For example during the project a Patent has been filed for the WSI technology and a Licensing agreement signed between HUD and IBSPE to develop a commercial WSI system. (The WSI technology is protected by pending patents derived from PCT/GB2010/050063

[14] EC directive 94/62/EC and amendments including EC directive 2004/12/EC, Directive 2005/20/EC and regulation EC No.219/2009

also published as US2012026508 (A1)). Industrial partners within the consortium have a thorough understanding of the market place and current technologies, available market solutions and limitations were highlighted in the project DOW. NanoMend has run in parallel with and complementary to a number of European and nationally funded projects (e.g. Clean4Yield) and private initiatives in the area of R2R processing of large area substrates, novel materials development and integration of functional intelligence into flexible substrates for the many new applications has been facilitated.

In addition to the consortium partners, a wider European level supply network involving SMEs and large companies are expected to benefit from NanoMend technologies at different stages of the manufacturing value chain (e.g. providers of materials, components, parts constituting the equipment, service organisations). Expertise within the consortium has been utilised to ensure appropriate traceability and standards are established for wider adoption (NLP; for WVTR and WSI technologies). For example, European manufacturers of lighting and illumination equipment will benefit from the new requirements posed by metrology equipment manufacturers. European camera and related component manufactures can compete for an increased share in the market, which is dominated by players from the Far East.

The consortium's Technology Transfer Panel (TTP) in conjunction with the International Advisory Board (IAB) has worked closely with the consortium and external partners to enable technology transfer and create new opportunities for SMEs across Europe (in process measurement; IBPSE (NL) Renishaw (UK) ISRA (D)). Industrial partners within the consortium are already engaged with a number of SMEs as part of their supply network and NanoMend has provided further opportunities to these SMEs.

Initial demonstrations of NanoMend technologies have focused around pilot production lines (e.g. at CPI FLI and TUT) and can now be integrated into full production at different production houses for specified applications. FLI's unique position within Europe to commercialise CIGS based PV is expected to provide the required drive for initial trial production and subsequent wider adoption, whereas TUT has provided the required impetus for initial trial production at SE and ISC.

Significant economic benefits are expected to arise out of NanoMend to all consortium partners involved and more specifically, other industrial and SME partners part of the supply network, involved in the manufacture of flexible substrates, barrier layer production, metrology equipment (IBSPrecision, Renishaw, Taylor Hobson, ISAR) and makers of electronic products on flexible and rigid substrates, including: (a) Film converter companies (SE, ISC), substrate manufacturers DuPont, barrier provider companies (including CPI and Isovoltaic), OEM suppliers (Beneq) who will be able to supply improved barrier coatings and equipment to a new and rapidly growing market in high volume photovoltaic market and in general to the growing flexible electronics industry. (b) Automation and instrumentation companies (including ISRA Vision and IBS Precision) will be able to supply new integrated detection, cleaning and repair systems to improve yield in R2R manufacture using plastic and polymer-coated paper substrates (c) Thin film PV company and supply chain partner such as FLI will take the lead in producing large area, high efficiency, long life, flexible solar cells at an affordable price that allows grid use of a renewable energy source (d) European paper, packaging and wood products companies would benefit from improved barrier material by allowing it to introduce fibre-based products from renewable sources into packaging applications which are not possible with the current technologies (including Stora Enso and Iscent) (e) Academic and contract research institutes (including Fraunhofer EMFT & IVV, NPL, TNO, HUD, LUT, TUT) will benefit from new knowledge gained and IP developed that could be potentially licensed to the supply network. Thus an economic multiplier effect can be envisaged as the technologies are commercialised.

7.6 Application roadmaps to enhance European manufacturing impact

An application plan has been developed as part of WP7, which has aided both the innovation strategies of the partners and boosted the dissemination activities of the project and hence the potential impact on European product development (services and manufacturing sectors). European Technology Platforms (ETPs) including EPoSS, Photonics, Photovoltaics, Forestry.

In addition to the applications demonstrated within NanoMend, the technologies developed and manufacturing processes within NanoMend can be applied to a wider range of applications including:

(a) Energy industry: Flexible solar modules, BIPV, Transportation-integrated PV, Mobile PV on flexible substrates, wind energy (b) Lighting (low energy lighting using flexible substrates) (c) Displays including indoor and outdoor signage, billboards, TV and computer screens, point-of-sale displays (flexible and rigid substrates) (d) Medical devices (e) Sensors and Integrated systems (flexible substrates) (f) Electronics industry (on glass and flexible substrates) (g) Automotive industry (coated metals and glass) (h) Aerospace industry (functionalized surfaces) (i) Packaging industry (coated packaging material ,embedded sensors, ultra-long life products) (j) Construction industry (coated glass and foils, functionalized surfaces)

A summary of anticipated future impact and industrial involvement, exploitable results and market potential is provided below:

Company	Main Business	Size	Expected Outcomes	Exploitable Results	Market Focus	Market Potential
ISOVOLTAIC	Development and production of back sheet for photovoltaic modules.	Approx. 250 employees; approx. 200 Mio €	- Inline detection, Cleaning and repair system for production line. - Enhanced detection of different defects on-line, facilitating us to identify and repair root causes, ultimately reducing scrap.	- Inline detection of produced products and thus to guarantee the same quality over the whole material width. - Elimination of defect induced scrap would produce a direct saving of ~450T€ in the year 2015 on one production line.	Worldwide	- Opportunity to pass on some of the saving to customers and increase customer satisfaction. - Working with the NanoMend consortium would provide the opportunity to access new markets, with an expected revenue of 14-15 Mio€
STORA ENSO	Integrated paper, packaging and wood products company	26,000 employees, €10.3B sales in 2010	- New know-how in the field of roll-to-roll defect detection, cleaning and repair of fibre-based polymer coated packaging materials.	- Process know-how to improve yield, reduce costs, and reduce scrap. - Process know-how to integrate new barrier coatings	Worldwide	- Transfer into production, any process improvements arising out of detection, cleaning, leading to significant savings of production costs, reduction of production scrap and higher quality products.

ISRA VISION	Machine Vision supplier for high-speed in-line surface inspection and industrial automation	390 emp.; €68m	- High-speed inspection methods ready for industrialisation for surface-defects on nano-scale and factor 10 in speed and resolution compared to current high-end surface inspection systems.	- Highest speed and resolution in-line surface inspection - Inspection system for inspection of barrier layers of flexible PV-foils - Inspection system for nano-coatings of paper in roll-to-roll process	Worldwide	1:150-200M€ 2: 10-20M€ (emerging) 3: 30-50M€
IBSPE	Ultra precision metrology	30 emp. – 5 M€	- High resolution sensor; - Know-how about optical systems; - Know-how PV metrology requirements	- High resolution sensor and system to determine nanometre form errors and detect defects	1st Europe through own subsidiaries – 2nd through IBS network of world-wide agents	5- 10 M€
FLISOM	Manufacturing of flexible solar modules. - R&D of thin-film manuf. methods.	16 emp.	- Improved defect detection - Particle removal - Contingency methods	- Increased manufacturing quality - Faster quality processes - Increased production yield	World	- Flexible solar modules - Building-integrated photovoltaics - Transportation-integrated photovoltaics - Mobile photovoltaics
Iscent	Design, development and production of large area nano- and micro-structured optical light scattering films for packages	Start-Up company – est. Turnover 2013 400 k€	-Integration of optical films for improved replication durability, cleaner surfaces and quality measurement	- Designs, optical films and processes for packaging solutions Additional micro-structured patterns	Worldwide packaging, technical applications	-Direct sales of several million Euros per year

7.7 European dimension

In building the NanoMend consortium, the EU instrumentation and the chosen applications sector has been widely examined and it has been determined that no one member state of the EU has the required breadth and portfolio of skills to successfully deliver the project results. We have therefore built a partnership of organisations from across Europe that collectively possess the skills, knowledge and results required in pursuit of our aspirations to deliver the scientific, economic and societal objectives given above. Within NanoMend, there are participants based in 6 European countries and these partners serve markets and have operations in most other countries in Europe. It can therefore be reasonably estimated that the European impact of this project can be implemented across most of Europe and associated member states. NanoMend also brings together the supply network partners that are not necessarily present in any one country. NanoMend consortium benefits from both long-standing research and commercial collaborations and the creation of new trans-national relationships.

Moreover, the development of a traceability infrastructure will be of benefit to a wide number of industries both inside and outside the consortiums' expertise. For this reason, it is essential that the work be undertaken on a European level to ensure the best take up of the methodologies and their eventual implementation in international standards.

7.8 Steps needed to bring about the impact

In order to achieve the impact on industry and society, actions are foreseen within and after the project. During the project, impact will be realised by integrating the new technologies, processes and equipment in pilot initiatives and chosen demonstrators at Flisom and TUT. The project builds on a solid foundation built by the consortium partners in different areas and as a result, minimises the overall technical risk in general to the project. In order to ensure effective dissemination and communication to wider industry and other stake holders and industry uptake of the new technologies, appropriate measures for dissemination, communication and exploitation will be taken during and after the project, as part of WP07 and are detailed in the section below. Industrial participants within NanoMend Flisom, Iscent and Stora Enso are planning to use the project outcomes within their own production facilities.

7.9 Other national and International activities

A number of consortium partners are already involved in or linked to previously funded European projects that are related to the proposed work e.g. FP7 'PlasmaNice', FP6 'FLEXONICS', FP7 'OLAtronics'. These existing links to other research programmes across Europe will be used as networking opportunities and channels for dissemination, once the project starts. Moreover, Flisom is part of two current projects FP7 HipoCIGS, a project on high efficiency and low cost CIGS solar modules and an Austrian National project 'Flexible PV-Systeme', where Flisom is contributing to lamination and testing with novel encapsulation materials. Synergies between these projects would lead to increased experience in lamination, encapsulation materials and overall increase in solar module efficiency and reliability.