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EMRP
European Metrology Research Programme
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TABLE OF CONTENTS

1 Executive Summary

Introduction

This project has established the validation and traceability of measurements of thin films properties and developed new methods and advanced reference materials to support thin film manufacturing quality control. Aligned with reduced costs and time-to-market of new products, these results will help to maintain European leadership in the multi-billion Euro worldwide sector of thin film optoelectronics.

The Problem

The manufacturing of thin films is of key importance as it underpins a significant number of industries where Europe holds a leadership position. Of strategic importance for the EU are high value thin films used in the optoelectronics industry, such as plastic and printed electronics, displays and lighting, memories and solar cells. The ability to manufacture large areas of thin films is a key competitive advantage of the technology; however it carries significant challenges, such as the need for strict quality control methods able to detect any variations and defects occurring during production. A particular challenge is to disentangle the interdependence of different thin film properties. To support the industry to ensure quality control of thin film manufacturing, the validation and traceability of measurements of thin films properties need to be established and methods for accurate characterisation of film microstructure need to be developed.

The Solution

In response to this problem, this project set out to establish a pan-European metrology capability with the goal of providing validated and/or traceable metrology for thin film materials properties, composition and structure, and for controlling large area homogeneity and consistency of properties.
This project has developed:

- Prototypes of measurement equipment for advanced large area thin film characterisation including crucial combination of new hardware and fast data analysis software.
- Novel advanced microstructure characterisation tools and reference standards for both 2D and 3D characterisation of challenging thin film materials.
- Validated and traceable measurement setups to support quality control of thin film manufacturing that is now available throughout European countries.

Impact

The new calibration samples and methodologies developed in this project are already in use by industry and therefore the traceable measurements are being disseminated across the value chain. Additionally, a number of European companies have already benefited from the new measurement procedures by gaining key insights into how processing/manufacturing steps affect the performance and quality of their thin film products, including advanced barrier layers and photovoltaic devices.

The traceable facilities developed in this project are being commercially exploited to support industrial development of cost-effective thin film devices. Partnerships between project partners and stakeholders have been established to further exploit the project results. Exploitation routes include IP protection and commercialisation of reference samples. The project has also supported wider dissemination and uptake of its outputs via inputs to relevant standardisation bodies.

Additionally, significant advance of scientific knowledge has been generated that will have an impact in terms of multiple method approaches to thin film metrology in Europe. It has allowed integration of research programmes of small and large National Measurement Institutes across Europe, leveraging investment and reducing duplication.

In the longer term, the measurement tools developed in this project will underpin the improvement of quality control in thin film manufacturing. This will reduce production costs and time-to-market for new products and so help reinforce European leadership in this technology. In addition, thin films technology will contribute to European energy strategies and directives by enabling the development of cost-effective renewable technologies (such as solar cells) and energy efficient electronic devices.

2 Project context, rationale and objectives

Improved production quality, aligned with reduced costs and time-to-market of new products, is necessary to maintain European leadership in the multi-billion Euro worldwide sector of thin film optoelectronics. The major challenge is the control of consistency in thin film processing.

The manufacturing of thin films is of key importance since it underpins a significant number of industries where Europe holds a leadership position. Of strategic key importance for the EU are high value thin films used in the optoelectronics industry, such as plastic and printed electronics, displays and lighting, memories and solar cells.

The future market opportunities for these thin film products are vast:

- The market for inorganic thin film photovoltaics is anticipated to rise to $13.1B by 2017[1].
- The market for printed electronics is expected to rise from $57B by 2019 and to $250B by 2025.

Other drivers for these technologies include contributing to European sustainable energy targets:

- Products that are more energy efficient with lower greenhouse gas emission (e.g. organic light emitting diode, OLED);
- Renewable energy sources (e.g. thin film solar cells);
- Reduced transport/handling costs due to lightweight and flexible products.

According to the European commission document "*Europe2020, A European strategy for smart, sustainable and inclusive growth*", 2010, page 13: "Meeting the EU's objective of 20% of renewable sources of energy alone has the potential to create more than 600 000 jobs in the EU. Adding the 20% target on energy efficiency, it is well over 1 million new jobs that are at stake".

Despite the large economic, environmental and societal interest, the market entry for some of these technologies has been disappointingly slow worldwide. Behind this is a lack of relevant measurement methodology and standardisation to allow strict quality control of thin film manufacturing. Difficulties are due to the fact that properties of complex thin films and multilayers used in industry are strongly affected by the production process and cannot be assessed in terms of a single parameter. The measurement of one property often relies on precise measurements of others. Although European National Measurement Institutes (NMIs) have capabilities that can be adapted or used for specific measurements on thin films, there is a great need for a coordinated action in the direction of an integrated methodology for thin film characterisation that is relevant to industry. Furthermore this methodology needs to be based on accurate measurements i.e. traceable to NMIs, to enable consistency over time and across different production processes.

The next generation of thin film optoelectronic devices use non-traditional materials (organic, inorganic and composite) and takes advantage of low-cost, high-volume production such as continuous and roll-to-roll processing which have the potential to markedly reduce production costs and to provide a step change in the energy, sensor, display and lighting sectors. Typically thin film device quality is evaluated at the end of the production process with little information on reliability and variability during processing. As a consequence, films out of specification are produced, leading to waste of production runs and increase of cost. Furthermore, the product lifetime is compromised due to lack of appropriate quality control.

Advanced thin film devices are based on complex structured multilayered architectures, which are strongly influenced by processing history and conditions (layer deposition is often sequential and materials properties are highly dependent on microstructure) and therefore end-of-production quality assessment is not suitable. Furthermore, the combination of inaccurate models and non-traceable measurement methods leads to a wide variation in reported parameters, even when comparing nominally the same material and processing conditions. Therefore, reliable measurement methods and measurement strategies for process quality control for high throughput manufacturing and device performance evaluation are currently lacking, undermining confidence in the area and slowing down market penetration. The lack of these methods leads to limited measurement resolution (e.g. water vapour transmission rate, WVTR, can only be measured down to $5x10^{-4}$ g/m/day) and high uncertainties (e.g. up to 2 orders of magnitude for thermal properties and up to one order

[1] Materials Market for Inorganic Thin-film photovoltaics: 2010 to 2017, NanoMarkets 2009.

of magnitude for charge mobility measurements) that are insufficient to support industry in the quality control of thin film manufacturing.

This project sought to address the complexity of thin film measurement by developing complementary metrology to address the following challenges:

Characterisation of property homogeneity over large areas
The use of large areas is a competitive advantage of thin film technology and maintaining consistent product quality across these areas is a paramount concern. However it carries significant challenges, namely the need for strict quality control methodologies able to detect variations due to process drift or local defects, *e.g*. due to substrate imperfections. Thickness variations of just a few nanometres can cause specifications of final devices to change (e.g. luminance output, solar cell efficiency). The conflicting goals of rapid and reliable measurement over large areas to detect changes in product quality while simultaneously having high lateral resolution to capture local defects illustrate the challenge of bringing appropriate metrology to meet industry needs. This is especially true if the metrology is to take place in-line, where measurement speed is essential. The few available techniques or methodologies capable of measuring large areas with high resolution are often too slow or too expensive to meet industry needs. For example, ellipsometry has been used to measure optical properties and film thickness over large areas. In this case, the ellipsometry head is usually fixed and an optical fibre is used to scan the film surface. However, the movement of the fibre can result in changes of light polarisation, which affects the accuracy of the values measured.

Non-destructive reliable microstructure characterisation
The 3D arrangement of elements (or molecules) in thin films determines film properties, such as electrical and thermal conductivity and ultimately the performance of the final device. A reliable high performance thin film device normally requires optimised microstructure that does not change during post processing or device operation. The lack of accuracy in the measurement of microstructure means that manufacturers of complex thin films rely on trial and error optimisation of the microstructure to achieve high product performance. The characterisation of these microstructure phases within a thin film is very challenging, in particular at buried interfaces (e.g. in 3D). It requires high selectivity (to separate signals from different elements), high sensitivity (to measure even small diffusion of one element into another phase) and high spatial resolution (down to few nanometers). X-ray and Raman spectroscopy can be used to investigate microstructure.

In X-ray characterisation, the analysis and quantification of experimental data often relies on the use of fundamental atomic parameters databases or comparison to reference standards. However, complex novel thin film samples, such as novel photovoltaic active layers (e.g. CIGSe) are very difficult to measure because the standard procedures for quantitative measurements do not allow reliable correlation between features and composition at different phases within a thin film. Depth profiling (ISO TC201/SC 4) of compositional gradients in thin films is a challenge for various characterisation methodologies.

Raman spectroscopy enables fast and non-destructive on-line and in-line monitoring of industrial processes without any further sample pre-treatment. However, Raman measurements of very thin layers and of complex films, can be inaccurate due to the requirement for high lateral resolution and because of a decrease in signal intensity. Furthermore, comparison to standards is not always possible for new material systems due to the lack of appropriate reference materials. Polarisation dependent Raman (p-Raman) has been used to determine molecular orientation of thin organic films, which normally can't be achieved non-destructively using X-ray methods. However the method requires validation.

Validation and traceability of measurements of film properties (e.g. electric charge mobility, thermal conductivity, water vapour transmission rate (WVTR))

With the continued drive towards miniaturisation of thin film electronic and optoelectronics, effective thermal management has become a key issue because it has a direct impact on device performance and reliability. The thermal transport properties of thin layers vary considerably from those of bulk materials due to differing structural and morphological characteristics, which in turn affect the mechanism of thermal transport. It is thus not possible to estimate the thermophysical properties of a thin layer from its parent bulk material. Nowadays, there are very few methodologies able to measure thermal properties of thin multilayered films *in situ* for both

surfaces and interfaces over the required range (exceeding a few hundred degrees). Moreover, existing methods are not validated to the SI.

Another important parameter for thin film electronic and optoelectronics is the charge carrier mobility. The Organic Electronics industry requires materials with higher charge carrier mobility to improve performance. However they are unable to reliably compare different materials because there is no reliable method to measure this parameter. Different methods are used and results can vary by orders of magnitude. A recent survey organized by the Organic Electronics Technical Working Area of the Versailles Project on Advanced Materials and Standards (VAMAS) has indicated the need for i) validated measurements of charge carrier mobility in organic thin films and ii) low-level water vapour transmission rate (WVTR) measurements through barrier layers. Barrier layers are used to protect electronic devices from moisture that can cause early failure. Advanced thin films applications, such as organic light emitting diodes (OLEDs) require barriers with extremely low permeation rate (10^{-5} – 10^{-6} g/m^2/day) to achieve device lifetimes of >10,000 hours. The standard technique used in a variety of industries has a limited detection of only 5 x 10^{-4} g/m^2/day and therefore does not have the required sensitivity to measure state of the art barrier layers.

With the overall objective of underpinning the commercial viability of new high-tech thin film optoelectronic technologies, we set out to develop new and optimise existing metrology to control consistency and uniformity in thin film production. To meet this goal, the specific objectives were targeted:

1. Traceability and validation of measurements of materials and thin film properties (thermal transport properties, charge carrier mobility, atomic fundamental parameters relevant for thin film characterisation);
2. Traceable, accurate measurement of water vapour transmission rate through barrier layers to low levels;
3. Morphology characterisation by non-destructive and contact-less measurements;
4. Characterisation and development of reference materials and transfer standards relevant to production;
5. Development of new techniques for measurement of film thickness and optical/optoelectronic properties over large areas and/or with spatial discrimination for in-production applications;
6. Development of traceable optical measurements for inhomogeneous thin films.

3 Research results

This project has achieved all its objectives and has delivered significant technical and scientific breakthroughs that are already having a direct impact in European industry. Results are presented in relation to the specific objectives of this project.

3.1 Traceability and validation of measurements of materials and thin film properties (thermal transport properties, charge carrier mobility, atomic fundamental parameters relevant for thin film characterisation)

High quality thin film optoelectronic devices are required to have:

- good electrical performance (key parameter: charge mobility);
- performance stability (key parameters: thermal management and microstructure);
- long term durability (key parameters: number of defects and homogeneity of properties).

These properties are interdependent and therefore the accuracy of measuring one material parameter (e.g. charge mobility) relies on low uncertainty of measurements of other properties (e.g. spatially resolved thickness).

New protocol for charge carrier mobility determination with reduced uncertainty

Charge carrier mobility is a figure of merit commonly used to rate thin film semiconducting materials for their suitability in optoelectronic applications such as solid-state lighting or photovoltaics. While for inorganic semiconducting thin films, methodologies for measuring the charge mobility are well established, the same is not true for new organic semiconductor materials. The very low charge mobility of the latter (several orders of magnitude lower that for inorganic materials) poses severe challenges for traditional characterisation methods. Although large variations are found in published mobility values for identical materials, there is little open discussion about the reproducibility of those results.

The project has addressed this issue through an interlaboratory study of mobility measurements using the space-charge limited current method. This method was selected within a list of typical methods used by industry and research laboratories as the most promising method for reproducible measurements. NPL, Imperial College London and INMETRO, in collaboration with TWA36 Organic Electronics of VAMAS, found that charge carrier mobility measured on nominally identical devices could vary by more than one order of magnitude, with the largest sources of variation being poor electrodes and film thickness variation (Figure 1). The accuracy of thin film thickness is therefore a key measurement parameter for these ultrathin films. It was demonstrated that poor choice of measurement parameters can lead to false results, which can have direct impact in providing confidence to device manufactures that rely on this figure of merit to optimise their products. Moreover, we demonstrated that charge mobility values extracted from identical data by different scientists would typically vary by 300%. We proposed a protocol for analysis and reporting that was found to reduce this analysis variation to as little as 20%. We also published general guidelines for improving the reproducibility of benchmark mobility measurements. The analysis protocol, including a semi-automated data analysis worksheet, was made available free of charge to stakeholders[2] and will be kept up-to-date with new advances in the field and with stakeholder input.

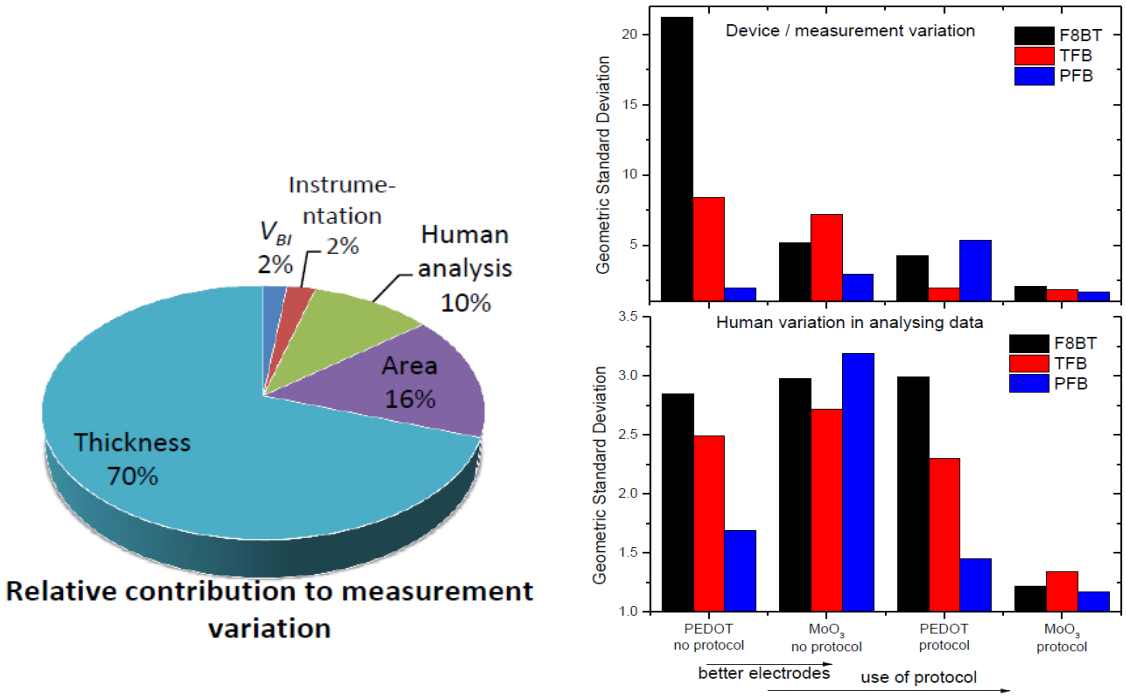

Figure 1: Left: relative contribution of different parameters to the reproducibility of measurements of charge mobility in organic thin films (V_{BI} represents built-in-voltage). Right: Geometric standard deviation of charge mobility values measured for three thin film materials (F8BT, TFB and PFB) using two types of electrodes (PEDOT or MoO_3) and showing the positive effect of using the analysis protocol developed in this project.

[2] The protocol can be downloaded at http://www.npl.co.uk/science-technology/electrochemistry/research/organic-electronics/towards-reliable-charge-mobility-benchmark-measurements-for-organic-semiconductors

New traceable facility for the measurement of the thermal conductivity of thin films

Another challenge for thin film optoelectronic devices is thermal management. Traceable and accurate thermal properties of these materials have to be measured on the thin film because the microstructure and the thickness of the film influence the materials properties, such as thermal conductivity. In fact, some materials have shown variations of over 2 orders of magnitude in thermal properties when measured in bulk relative to thin film format. This project has solved this issue by developing and validating a novel facility for thermal conductivity measurement of thin films up to 1000 °C based on modulated photothermal radiometry (Figure 2). LNE has validated this facility by measuring the thermal conductivity up to 400 °C of chalcogenide thin films ($Ge_2Sb_2Ti_5$) grown on a silicon substrate, provided by a project stakeholder. The obtained results showed that the thermal conductivity of such thin film materials strongly depends on the temperature and microstructure (amorphous or crystalline phases), with value at 420 °C about ten times higher than that measured at 23 °C. Our results were in good agreement with literature data for similar $Ge_2Sb_2Ti_5$. Spatially resolved thermal characterisation was also performed at CMI to investigate homogeneity of these thin films.

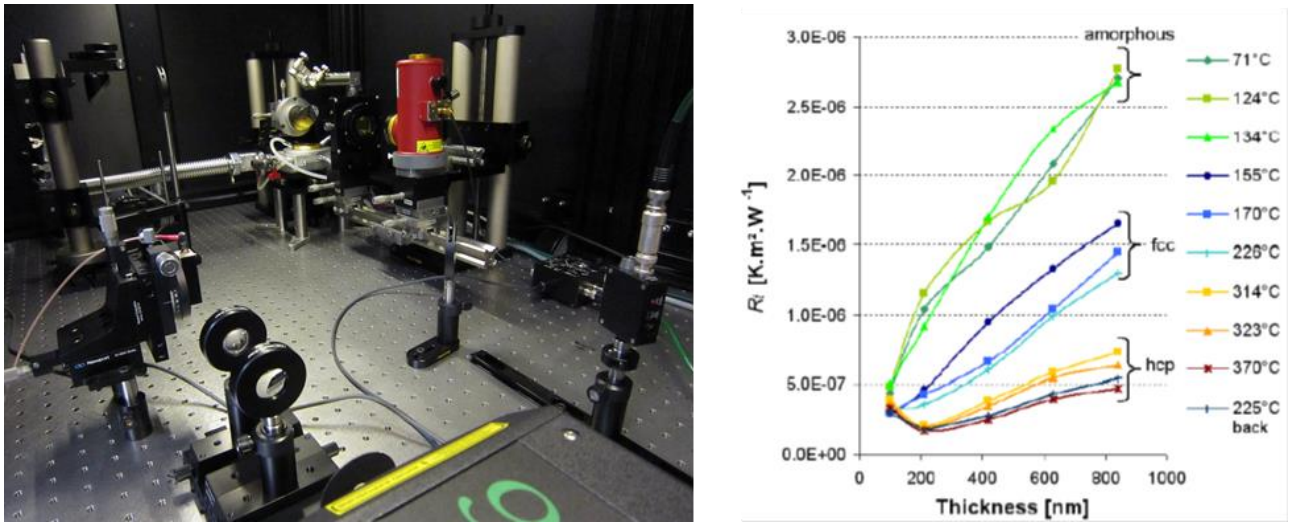

Figure 2: Left: general view of the modulated photothermal radiometry facility of LNE. Right: Thermal resistance (R_t) as a function of thickness and temperature showing the effect of microstructure on thermal conductivity of thin film phase change memories.

Reduced uncertainty of atomic fundamental parameters

Microstructure characterisation often relies on X-ray spectrometry that requires fundamental parameters (such as mass absorption coefficients, fluorescence yields, etc) to quantify materials properties. Therefore, reducing uncertainty in the measurement of these fundamental parameters has a direct impact in the accuracy of measurements of microstructure. High accuracy is particularly relevant for complex thin film samples where small contamination of one element inside another phase can strongly affect performance.

In this project, experiments were performed using the Metrology beamline at SOLEIL synchrotron, France, on the hard X-rays branch and at Bessy, PTB, Germany. The accurate determination of X-ray fundamental parameters has been obtained for a series of key elements in promising thin film photovoltaics (e.g. Cu, Zn, Ni, In). Good agreement has been demonstrated between higher energy (1-20 KeV, at SOLEIL) and lower energy (0.1-10 KeV, at BESSY) measurements with deviations of less than 2 %, especially around the K-edge of Cu. Comparison with other databases such as that published by Elam[3] showed a great improvement of accuracy, especially around the L-edges. Substantial development of X-ray spectrometry (XRS) to characterise elemental composition and impurity concentration of complex thin films has also been achieved. Both the mass deposition and the stoichiometry have been determined successfully. This work provided the underpinning metrology for the X-ray developments described in section 3.3.

[3] W.T. Elam, B.D. Ravel, J.R. Sieber, Rad. Phys. Chem. 63 (2002) 121-128.

3.2 Traceable, accurate measurement of water vapour transmission rate through barrier layers to low levels

To ensure long term durability, thin films are often encapsulated with a barrier material. For advanced applications, such as for organic light emitting diodes and photovoltaics, these barriers require water vapour transmission rates (WVTR) of the order of (10^{-4} - 10^{-6}) g/m^2/day. As a comparison, sensitive food and pharmaceutical products require barriers with WVTR of only (1 - 100) g/m^2/day. The ability to characterise the performance of advanced barrier materials requires the capacity to detect extremely low amount fractions of water, typically a few nmol/mol. During this project, NPL has developed a new facility for the traceable measurement of water vapour transmission rate through barrier layers that provides accuracy and traceability with a detection limit below 5 x 10^{-5} g/m^2/day (Figure 3). The methodology used, based on infrared ring-down spectroscopy combined with NPL's dynamic reference standard generator facility, allows stable and repeatable operation with an estimated relative expanded uncertainty of approximately ± 2 % for measurements above 1 x 10^{-2} g/m^2/day. In collaboration with the Encapsulation Working Group of the Organic Electronics Association, the method was validated in an international Round Robin when compared with typical methods used in industry. It also generated datasets on barrier layers developed by Total S.A. and industrial stakeholders that provided vital information about the effect of manufacturing conditions on the quality of the barrier films.

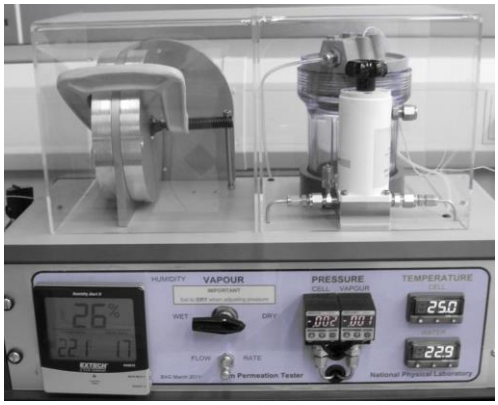

Figure 3: NPL's traceable water vapour transmission rate measurement facility.

However, WVTR measurements do not provide spatial resolution and the measurement is an average property of the thin film barrier. For high performance barriers, most water ingress occurs due to small defects in the film or inhomogeneous thickness. Therefore accurate measurements of such properties on large areas are crucial and will be discussed further in this report.

3.3 Morphology characterisation by non-destructive and contact-less measurements

Thin film microstructure can severely affect the value of thin film figures of merit. For complex samples, often formed of multilayers or composite layers (with two or more elements/molecules) the measurement of the distribution of these elements in 2D and 3D is extremely challenging. For example, measurements of advanced photovoltaic active layers (e.g. CIGSe) using standard quantification schemes do not allow the unambiguous correlation between spatial or compositional properties of the specimen. Depth profiling of compositional gradients in thin films is a challenge for various characterisation methodologies. We tackled this problem by developing novel reference materials and advanced procedures for X-ray and Raman spectroscopy that enable the investigation of complex thin film microstructures.

Different X-ray and Raman spectroscopy methods were used to reliably characterise the microstructure of complex thin films. The tasks covered surface and buried surface characterisation, depth profile traceable measurements and the development of calibrated reference samples with known impurity concentration or elemental depth profiling. In view of establishing traceability, independent characterisation methodologies were

applied and validated by careful assessment of the respective procedures. Here, traceable off-line methodology is intended to support the qualification and calibration of on-line and in-line instruments.

Non-destructive chemical analysis of thin films Si photovoltaics

The combination of polycrystalline silicon (poly-Si) thin films with aluminum doped zinc oxide layers (ZnO:Al) as transparent conductive oxide enables the design of appealing optoelectronic devices at low costs. For a poly-Si/ZnO:Al layer system the knowledge of the interaction between both layers and the interface reactions upon thermal treatments is crucial. PTB, HZB and FhG analysed the influence of thermal treatments on solid phase crystallized poly-Si thin-film solar cells, focusing on chemical interface reactions and modifications of the poly-Si absorber material quality. A reliable depth-resolving analysis of the elemental composition close to the poly-Si/ZnO:Al interface was carried out by Grazing Incidence X-ray Fluorescence spectrometry (GIXRF) (Figure 4).

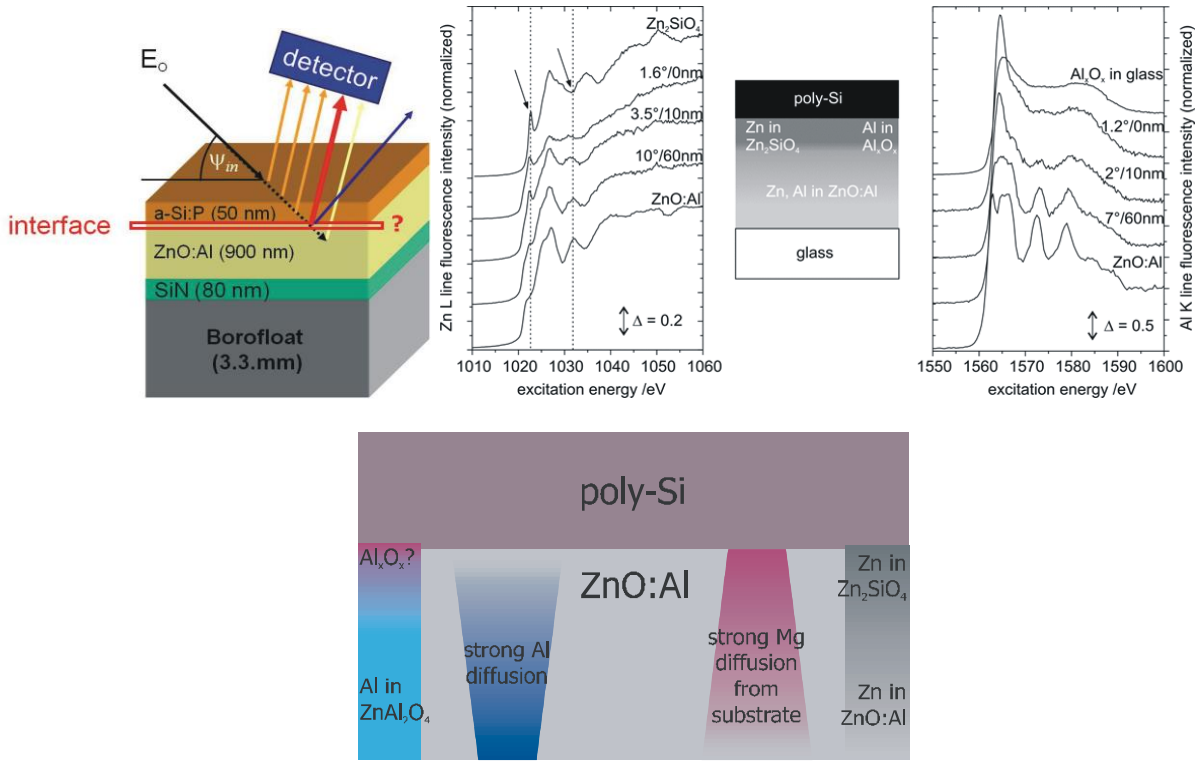

Figure 4: Layout of poly-Si/SiN/ZnO:Al sample and normalized GIXRF-NEXAFS spectra of the Zn L3,2 edges (left) and the Al-K edge (right) of poly-Si(50 nm)/ZnO:Al(800 nm)/glass stacks after rapid thermal processing at 950 °C, measured at various incident angles and penetration depths, respectively, into the ZnO:Al (as indicated). For comparison, the respective spectra of homogeneous ZnO:Al, Zn2SiO4, and Al2O3 in glass are also shown (θ = 2° to 3.5°). Arrows and dashed lines indicate characteristic features in the spectra. For a better clarity, the curves are vertically displaced. The schematic in the middle outlines the preferred chemical bonding state of Zn and Al dependent on the distance from the poly-Si/ZnO:Al interface extracted from the GIXRF-NEXAFS fluorescence spectra. Bottom image summarises depth distribution of elements as derived from experiments.

The investigation of the chemical species of Zn and Al by X-ray fluorescence analysis combined with near edge X-ray absorption fine structure spectroscopy (GIXRF-NEXAFS) involved the following aspects:

- Analysis of the poly-Si/(SiN)/ZnO:Al interface during high temperature treatments;
- Analysis of the interface, the near-interface region and the bulk material;

- Zn-L3,2 NEXAFS: at the interface region zinc silicate (Zn2SiO4) and in bulk ZnO;
- Al-K NEXAFS: at the interface region aluminum oxide (AlxOy) and in bulk comparable to ZnO:Al;
- High temperature annealing, leading to a change of the chemical species at the interface.

We demonstrated that temperatures above 1000 °C promote the formation of new chemical compounds within about 10 nm of interface, such as zinc silicates (Zn_2SiO_4) and aluminum oxide (Al_xO_y). These results give valuable insights about the temperature-limitations of Si/ZnO thin-film solar cell fabrication and the formation of high-mobility ZnO-layers by thermal annealing.

For highly efficient thin film solar cells, optimisation and band gap engineering can be achieved by tuning their elemental composition as a function of depth. However, the lack of appropriate metrology meant that most development was based on trial and error. This project solved this issue by demonstrating that GIXRF analysis using monochromatic synchrotron radiation and well-characterised instrumentation is well suitable for a non-destructive and reference-free analysis of compositional depth profiles in thin films. PTB, PANalytical and HZB demonstrated that variation of the incidence angle provides quantitative access to the in-depth distribution of the elements, which are retrieved from measured fluorescence intensities by modeling parameterised gradients and fitting calculated to measured fluorescence intensities (Figure 5). The results showed that double Ga gradients in $Cu(In_{1-x},Ga_x)Se_2$ can be resolved by GIXRF.

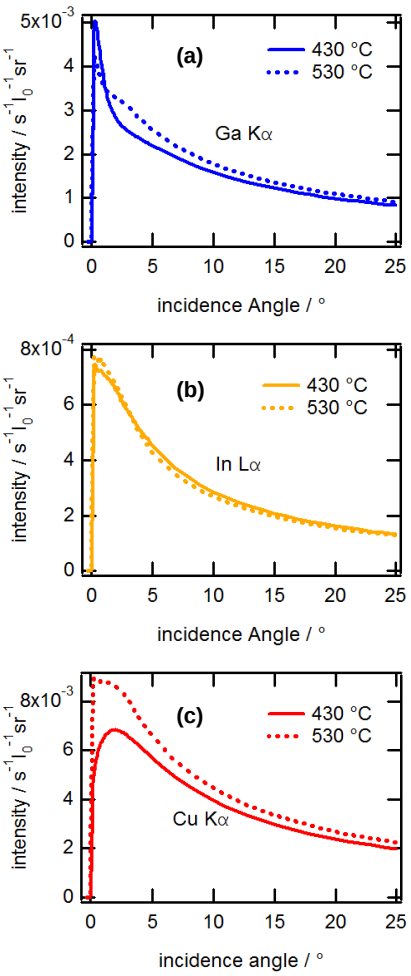

Figure 5: GIXRF intensities for (a) Ga Kα, (b) In Lα and (c) Cu Kα in dependence of the angle of incidence for two different $Cu(In,Ga)Se_2$ films synthesised by three-stage co-evaporation process at 430 °C or 530 °C.

Combined methodology using Raman Spectroscopy, X-Ray Fluorescence and Grazing Incidence X-Ray Diffraction (GIXRD)

A set of optoelectronic materials originating from the Cu(In1-xGax)Se2 production process was analysed with respect to its usage as calibration specimens for in-line or on-line process control by Raman spectroscopy. Spectra of these components were measured under traceable conditions. The Raman mode positions of pure CuInSe2 and CuGaSe2 serve as the basis for a linear correlation between mode position and Ga/(In+Ga)-ratio. In addition, reference-free x-ray fluorescence analysis was employed to reveal the integral elemental composition and therefore the quality of these reference samples. Artificial samples from the production process were mapped, showing Raman peaks not detectable under the white light microscope (Figure 6). A strategy to quantitatively assess the lateral area information from the pictures was presented. While at low processing temperatures the ejection of Cu droplets from the source leads to highly inhomogenous surfaces, higher processing temperatures diminish this complication. Combining Raman spectroscopy and X-ray spectrometry substantially contributes to a more reliable process control for Cu(In1-xGax)Se2 systems. While Raman and GIXRD can identify different chemical phases, GIXRF can detect the elemental distribution of non-Raman active components (Figure 7).

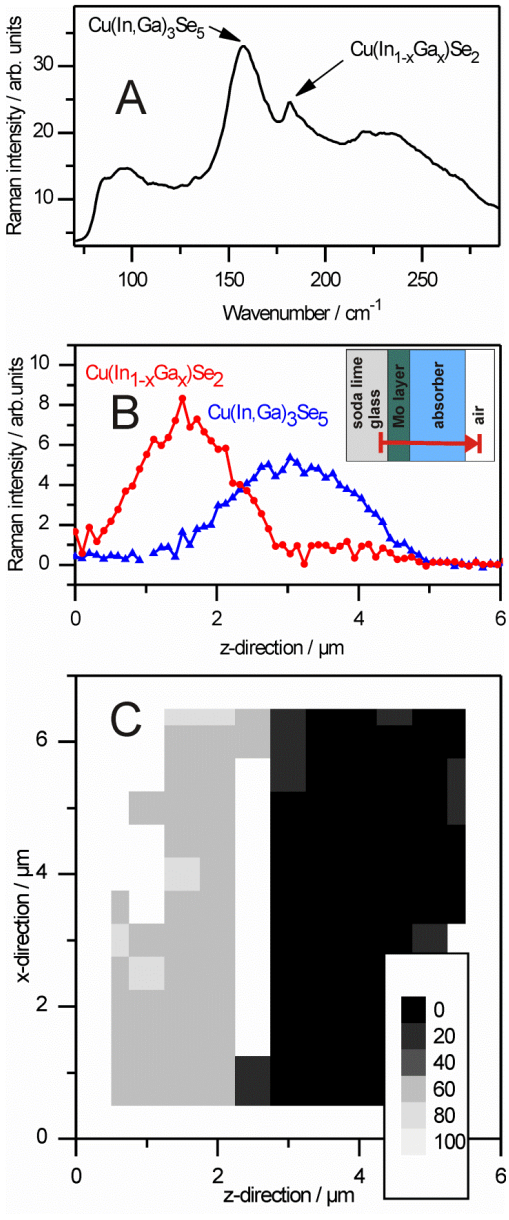

Figure 6: Averaged surface Raman spectrum (top) of the sample completely processed at 430 °C, a sketch of sample orientation and cross-sectional Raman line mapping (middle) acquired with 100 nm step size and the 2D-Raman shift mapping (step size 0.5 µm) of the cross-section (bottom) showing the Ga/(In+Ga) content in % along the edge (x) and in depth (z).

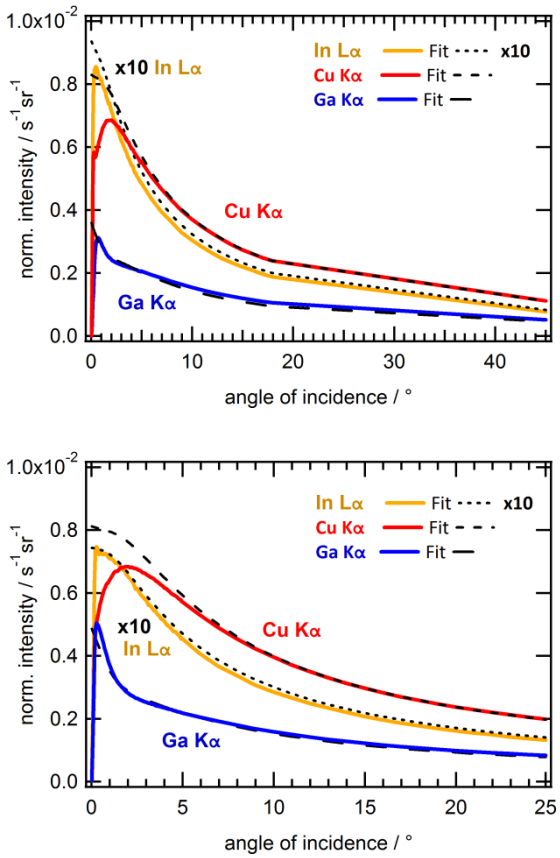

Figure 7: GIXRF intensities of the elements Cu Kα, In Lα and Ga Kα for the 330 °C sample containing NaF (top) and completely processed at 430 °C (bottom).

New ultra high vacuum (UHV) X-ray synchrotron facility available at SOLEIL.

As part of this project, CEA has installed and commissioned a new UHV x-ray facility at SOLEIL. The UHV chamber is based on a versatile PTB instrument that was further developed in collaboration between PTB and TU Berlin. It includes a 7-axis manipulator that allows for an independent alignment of the samples with respect to all degrees of freedom. In addition, a rotational and translational movement of several photodiodes is provided. The instrument enables various analytical techniques based on energy dispersive X-ray detectors such as reference-free X-ray fluorescence analysis (XRF), total-reflection XRF, and GIXRF in addition to optional X-ray reflectometry (XRR) measurements. With this instrument, samples having a size of up to 100 mm x 100 mm can be analysed with respect to: i) mass deposition, ii) elemental or spatial composition, iii) layer composition and thickness, iv) depth profile of matrix elements or implants, v) the species of nanolayers, nanoparticles or buried interfaces.

Measurements of molecular orientation

Molecular orientation in anisotropic thin films has strong influence in thin film parameters, such as charge mobility and extinction coefficient. In this project we compared two different methods to measure molecular orientation: polarisation dependent X-ray absorption fine structure spectroscopy and polarisation dependent Raman spectroscopy.

If a molecular bond has a certain orientation in space its orbital shows an angular dependence on the electric field vector of the incoming radiation. Changing the orientation of the molecule with respect to the electric field vector excites some features of the fine structures differently and an increase or decrease of the respective

resonance intensities is observable. The used undulator radiation of the plane grating monochromator (PGM) beamline in the PTB laboratory at BESSY II provides linearly polarised radiation.

A set of three 6,13-Bis((triethylsilyl)ethynyl)pentacene (TES-PEN) and 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-PEN) samples on silicon substrate has been provided by IC. By means of a top cast preparation technique TES-PEN and TIPS-PEN were deposited at different substrate velocities V_{sub}., which lead to variation in the layer thickness and the crystallinity.

Polarisation dependent X-ray absorption fine structure spectroscopy

As mentioned previously, for the determination of chemical species we employed the combined method of GIXRF and NEXAFS. However, in order to be able to measure the orientation of the deposited organic molecules, we had to change the angle between the electric field vector of the incoming radiation and the orientation of the molecule and analyse the data to extract a preferential orientation (Figure 8). Figure 9 shows polarisation dependent C-K NEXAFS. We observed that the shape of the resonances are kept constant but the peak height significantly changes depending on the relative orientations of the polarisation vector and the probed molecular bond, which allows the determination of a preferential direction and the amplitude of the molecular orbitals signals of the thin films under investigation. The determination of the orientation is possible because π* and σ* orbitals exhibit a spatial orientation, with the direction of the maximum orbital amplitude determining the angular dependency of the K shell spectrum.

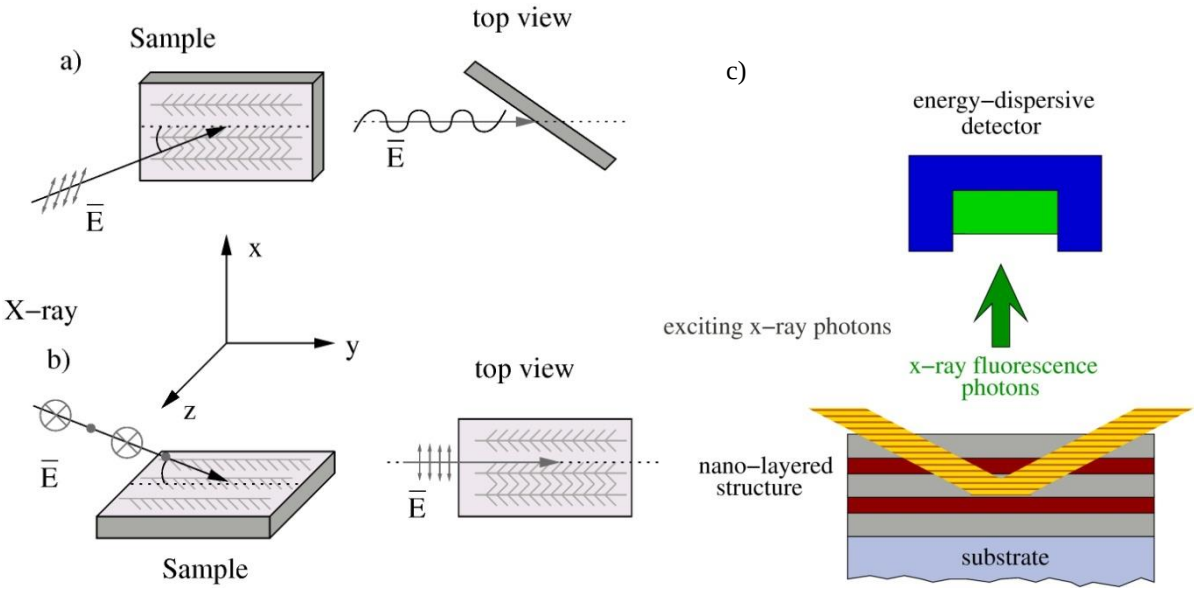

Figure 8: Sketch illustrating the different degrees of freedom for rotary motion and the position of the electric field vector of the incoming radiation with respect to the sample surface and the molecules. a) and b) show the two extreme angles being accessible. From the view of the surface a) exhibits the p polarised and b) the s polarised case. To the right the arrangement of the of the UHV chamber is depicted.

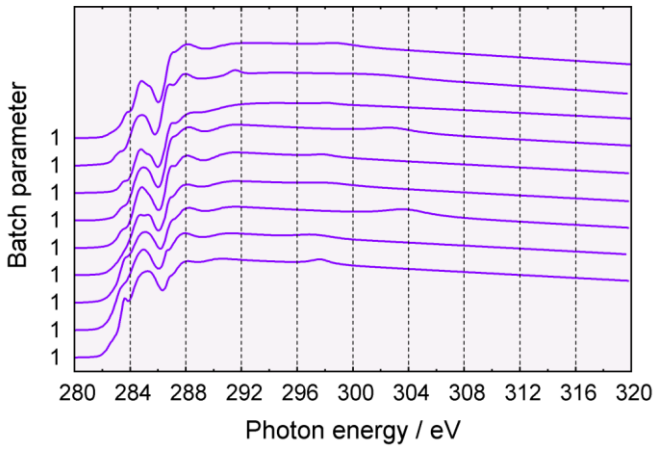

Figure 9: C-K NEXAFS spectra recorded at an incident angle of about 15° when varying the angle χ between the molecular angle and the electric field vector. A variation of this angle χ changes the intensity of π* and σ* resonances.

Polarisation dependent Raman spectroscopy

Another approach to the measurement of molecular orientation is using Raman spectroscopy, where the anisotropy of vibrational modes is used as a probe to the orientation of the molecules in space. When measuring TIPS-PEN thin films clear signatures for the short and the long axis vibrational modes were observed (Figure 10). These features can be used to probe the orientation of the molecule in space when the excitation (or collection) light polarisation is varied (Figure 11).

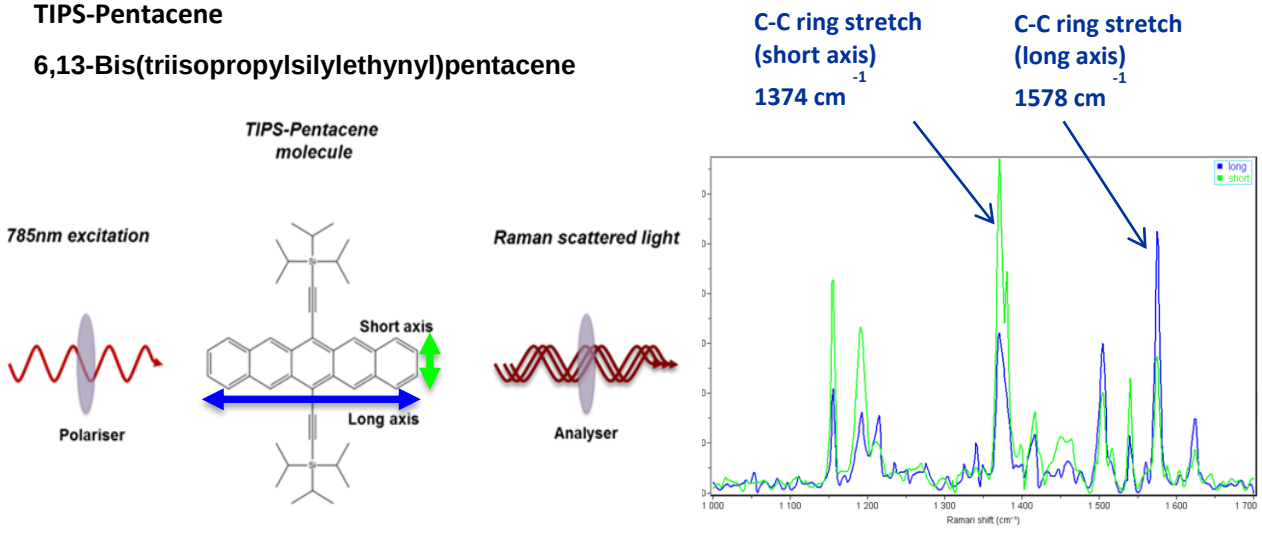

Figure 10: Sketch of TIPS-Pentacene molecule and corresponding Raman spectra taken with light polarized parallel to the short (green) or to the long (blue) axis.

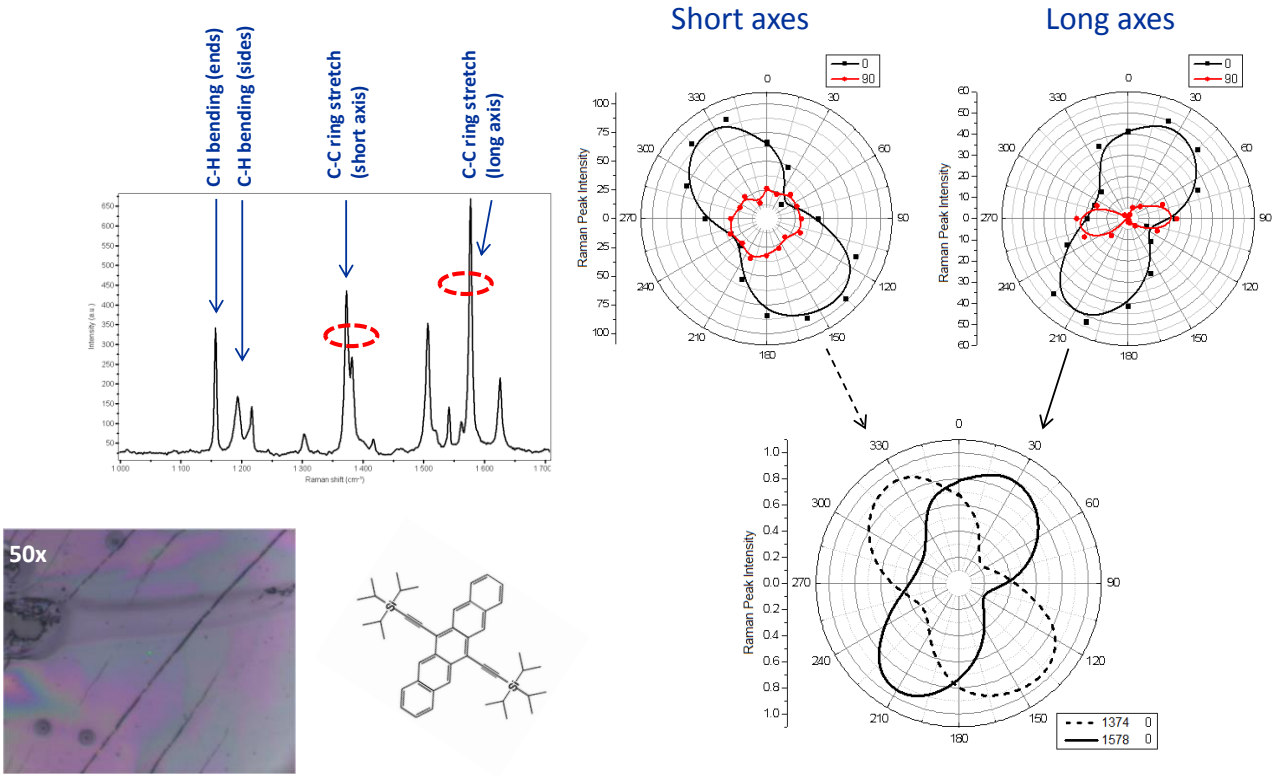

Figure 11: Polarisation dependent Raman measurements of TIPS-PEN thin films. When combining the orientation of the short and long axis we observed that they were not at the expected 90º angle. This indicates that the molecules are oriented out of the plane of the substrate and therefore that this method can provide 3D description of the molecular orientation in space.

3.4 Characterisation and development of reference materials and transfer standards relevant to production

Reference materials and transfer standards are important to ensure that industry can calibrate their equipment to obtain reliable results. The reference materials should to be as close to the materials under test as possible and should be fully characterised, which is challenging when the materials in question are complex thin films. This project has developed novel procedures and qualified advanced complex thin film structures to be used by industry, as will be reported in the next three subsections.

Development of a procedure to qualify multilayered specimen as reference or calibration samples for in-line and on-line calibration

We investigated three multilayers of ZnO/Al2O3/ZnO deposited on Si as possible reference specimen for in-line or on-line calibration (samples M4, M5 and M6) and compared the reliability of different methods to determine the thickness of the layers. Starting with conventional XRF in conjunction with the reference-free approach the total mass deposition of each element could be determined in absolute values (Table 1). In addition, XRF gave information about contaminations and their masses (Figure 12 shows data for sample M4). Angular dependent GIXRF and XRR measurements were used to determine properties such as thickness, elemental depth distribution and layer sequence (Table 3). Their combined use ensured traceability and reliability of the results. In general, XRR leads to reliable results for the determination of layer thickness and sequence provided the thickness is between a few nanometers and half a micron. But for interface structures and contamination analysis the sensitivity of XRR is often not sufficient and GIXRF has proved to be more

sensitive. GIXRF gives a more detailed picture about the elemental distribution in these samples. We demonstrated that the fitting procedure for angular dependent GIXRF data is more stable in contrary to XRR showing a strong sensitivity to the initial values (Figure 13 and Table 2). All these methods together allow for a reliable qualification of reference samples which can be used as calibration standard for process-oriented analytics.

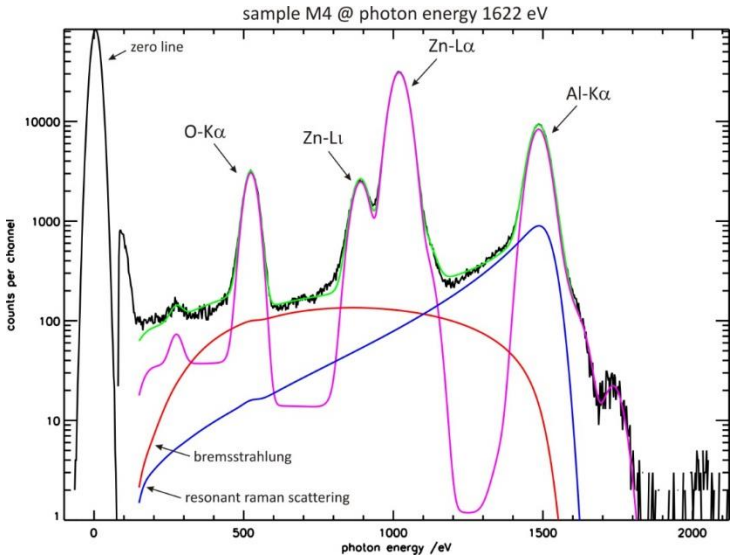

Figure 12: XRF spectrum of sample M4 measured at 1622 eV, which was deconvoluted with experimentally obtained response functions.

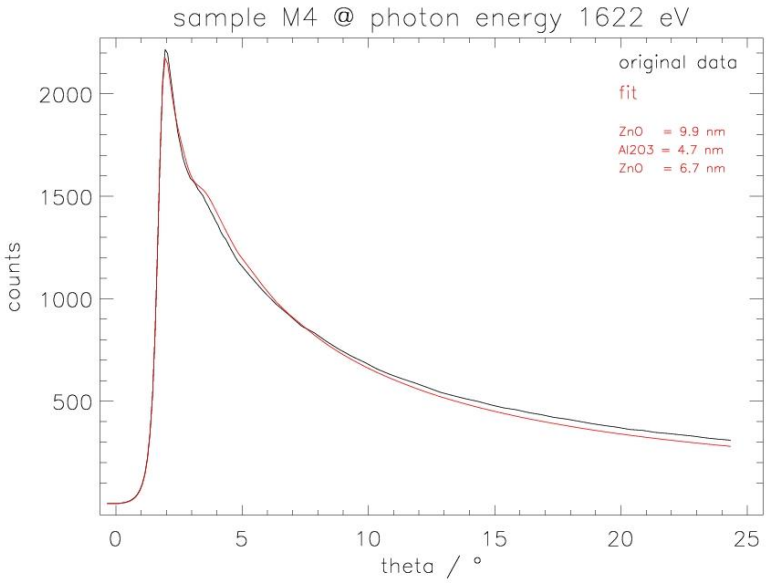

Figure 13: Fluorescence intensity dependence on the grazing incidence angle of the elements Al and the respective fit of sample M4. The exciting photon energy was set to 1622 eV.

Table 1: Overview of the calculated thickness resulting from primary fluorescence (XRF).

Sample	Layer	*Integral thickness / nm*
M4	ZnO	31
	Al_2O_3	13
M5	ZnO	43
	Al_2O_3	22
M6	ZnO	61
	Al_2O_3	31

Table 2: Overview of the calculated thicknesses by fitting the angular dependent Al Kα fluorescence line using GIXRF. The first row contains the most upper layer and the last one the close to the Si substrate.

Sample	d(ZnO) / nm	$d(Al_2O_3)$ / nm	d(ZnO) / nm	$d(Al_2O_3)$ / nm	d(ZnO) / nm
M4	9.9	4.7	6.7	n.a.	n.a.
M5	8.9	4.2	8.2	4.7	5.3

Table 3: Overview of the calculated thicknesses by fitting the reflectance measured with XRR. The first row contains the most upper layer and the last one the close to the Si substrate.

Sample	ZnO		Al_2O_3		ZnO	
d / nm	7.9		7.4		8.5	
n and k	0.999257	0.000222692	0.99945	0.000675246	0.999456	0.000467497

Development of novel 2D-mappings reference sample for traceable micro Raman measurements

When using laterally resolved micro Raman measurements in quantitative analysis, reference samples are needed for the assessment of calibration factors and measurement uncertainty associated to the x- and y-axes. As a basic requirement these microscopic structures should have their dimensions traced back to the International System of Unites (SI) and cause an appropriate Raman signal. Additionally, a good all-in-one Raman reference should present the following features:

- high Raman contrast
- periodic flat structure
- long range calibration up to 200 µm in each direction
- large pitch of 4 µm to provide calibration of long ranges with step size of 1 to 2 µm according to the Nyquist theorem
- small pitch of 0.8 µm to provide high resolution calibration for smaller ranges
- two dimensional orthogonal pattern: both axes can be calibrated simultaneously and structure does not need to be rotated
- squared pattern to allow easy assessment of the data in spite of line-by-line displacement
- certified pitches
- structures that allow the determination of the detected area size (point sources, edges)

- structures that allow validation of the optical resolution (point grids, 1D grids)

PTB has designed, fabricated and tested a novel new all-in-one Raman reference. Raman contrast was achieved by covering a silicon wafer with a 15 nm chessboard coating of gold alloy. A Raman line mapping of the chessboard has been revealed. Traceability to the meter was ensured via scanning force microscopy (SFM). A patent application has been submitted and industrial stakeholders have been interested in commercialising such reference material.

Development of micron-thick SiO2 reference samples for traceable ellipsometry measurements

The accurate measurement of optical properties in the range of few microns is very challenging because the thickness and the dielectric constant cannot be independently obtained. Furthermore, there is a lack of reference samples that could help companies to validate measurements and calibrate their equipment. This project has developed SiO2 reference samples with thicknesses between 2µm and 10 µm. Due to the challenge in characterising these samples the project has developed a multi-method approach combining ellipsometry at BAM as the main technique, X-ray- fluorescence (XRF) at PTB and reflectometry at Aalto to validate the determination of thickness. This multi-method approach enabled the determination of thickness and optical constants (Figure 14) with accuracy much higher than the sample inhomogeneity (of ~1%).

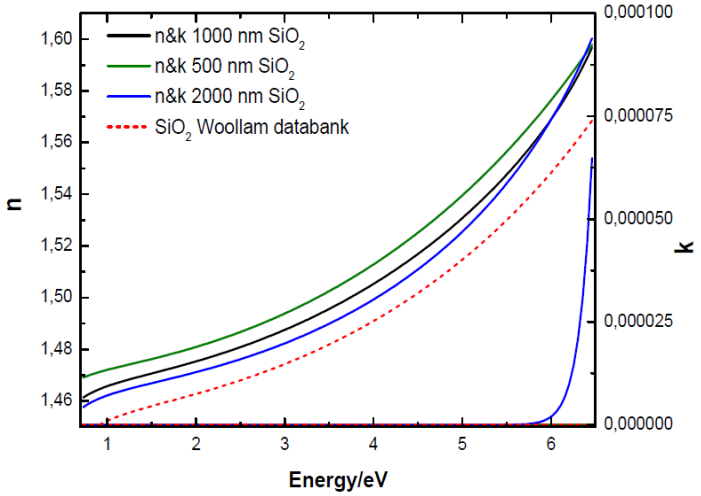

Figure 14: Optical constants (refractive index (n) and extinction coefficient (k)) of SiO2 layers on Ti-covered Si with different thicknesses obtained by traceable ellipsometry measurements.

The reference thin film and methodology developed in this project are already in use by a measurement equipment manufacturer that is now disseminating traceability to their customers.

3.5 Development of new techniques for measurement of film thickness and optical/optoelectronic properties over large areas and/or with spatial discrimination for in-production applications

As mentioned in the previous sections, the homogeneity of thin film properties is a crucial parameter in determining the figures of merit for thin films. In the project we tackled this issue by developing metrology tools and methods to support the industrial production of thin films materials over large areas. We specifically focused on:

- The development of techniques able to link the performance of devices on the macroscopic scale and microscopic properties of the thin film or multilayer structures;
- The development of optical inspection techniques for large area metrology capabilities.

New method for opto-electrochemical mapping and new procedure for reliable photocurrent mapping

NPL developed a technique to relate the macroscopic properties of thin film with their microscopic structure, by realizing a multi-electrode probe (Figure 15) for electrochemical imaging of dye-sensitized solar cells in collaboration with Solar Print. NPL has also worked with stakeholders to develop a reliable and simplified measurement procedure for photo-electrochemical mapping using a two-electrode approach to simulate the effective behaviour of the thin films devices. The advantage of such approach is to reduce the instrumentation requirements to simple source-meters. The effects of different measurement parameters have been investigated and published in a peer-reviewed paper.

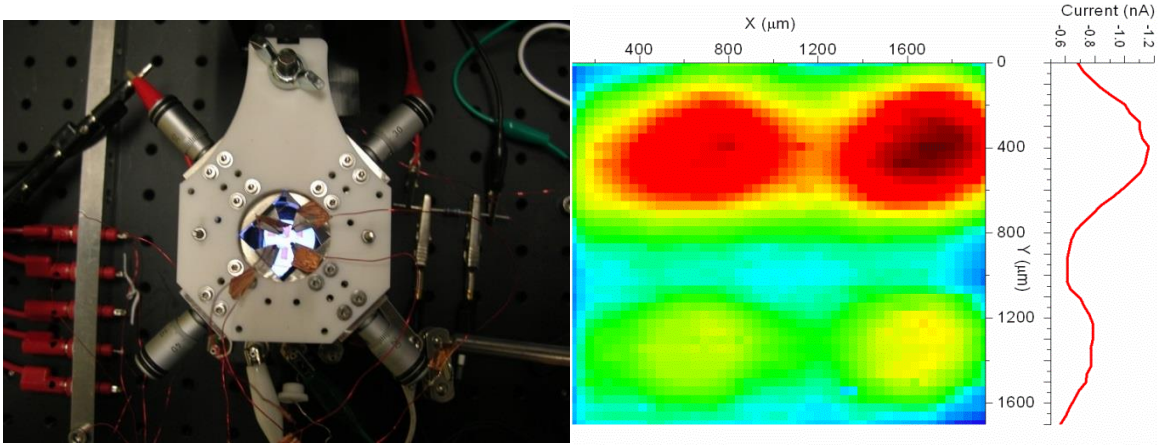

Figure 15: Left: Picture of the multielectrode probe prototype during photo-electrochemical mapping measurement at NPL. Photo-electrochemical map of photocurrent generation of a TiO2 surface locally sensitised with different dyes.

In addition, we have also developed a procedure for photocurrent mapping of new generation thin film solar cells with slow response time. Our results demonstrated the need for tight control of laser power stability, particularly for cells with non-linear dependency of photocurrent on light intensity, as this cannot be easily corrected by data processing. Remarkably we demonstrated that for solar cells with slow response time, measurements performed using typical light intensities (1 Sun and below) are very unreliable and that for accurate photocurrent maps, much higher laser powers can be used, as long as they don't induce degradation/change of the device performance. This was related to an increased cell response time and is likely to have the same effect on other photovoltaic technologies that suffer form charge trapping or that can benefit from light soaking.

Finally, we demonstrated the need for a validated measurement procedure for photocurrent mapping of solar cell to ensure accurate results. Improper choice of measurement parameters can lead to incorrect images (Figure 16) that can hide the existence of even large defects in the solar cell, potentially leading to reduced device performance and early device failure.

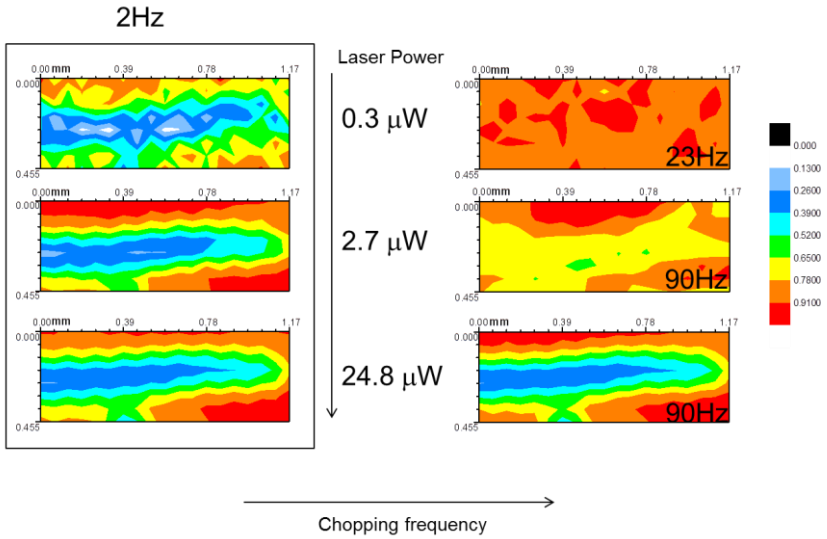

Figure 16: Photocurrent maps of dye sensitised solar cell with long defect. Accuracy of photocurrent map measurement requires much higher excitation laser power than conventionally used.

Optical characterisation of thin films and devices with spatial discrimination

BAM has investigated the limits of lateral resolution of imaging ellipsometry and used ellipsometry and nulling imaging ellipsometry to identify issues linked with the manufacture of thin films. For that purpose, a set of microstructure thin films using materials relevant to photovoltaic applications was provided by a materials developer stakeholder. The substrate used for all the samples was a thick gold layer deposited on a glass slide and a 3 nm thick Cr layer was used as an adhesion layer. The layers were functionalised by a self-assembled monolayer of octadecanethiol. Structured PCBM (phenyl-C61-butyric acid methyl ester) and cyanine dye layers as well as spin coating blends of PCBM and cyanine dyes were prepared and investigated by imaging ellipsometry and spectroscopic ellipsometry from the near IR to far UV spectral range .

The structured cyanine dye layer on Au covered glass was chosen as an example. The image of the investigated area with a dimension of 450x450 µm^2 is presented on the left side of Figure 17 and was obtained at 546 nm. Defects like interruptions in the cyanine stripes and contamination of the surface (likely due to residual solvent and/or local poor organisation of the molecules) can be observed. These defects were very clearly identified in the measured Ψ and Δ maps (see Figure 18), but identifying these imperfections in the calculated thickness map obtained using null imaging ellipsometry was significantly more challenging.

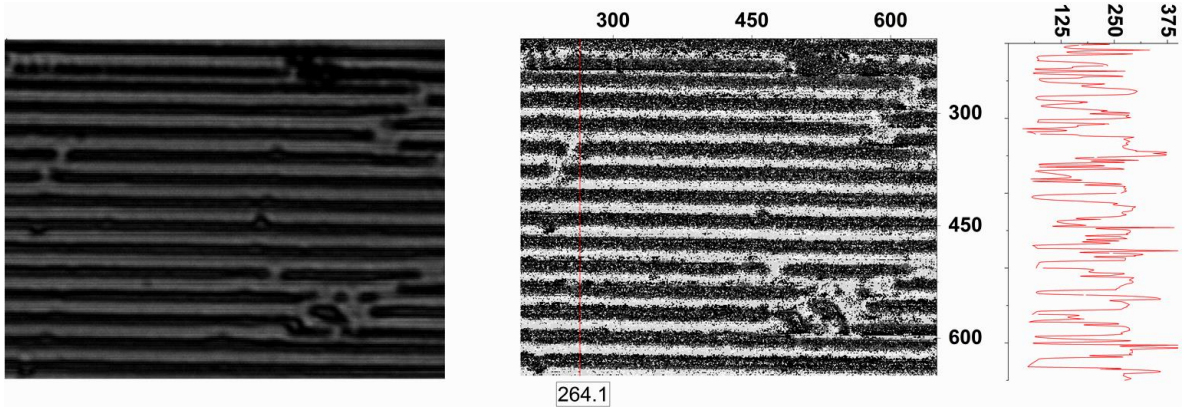

Figure 17: left: image to be mapped presenting micro-structured cyanine film, taken at λ= 546 nm using nulling imaging ellipsometry; right: calculated thickness map of the investigated area.

Ellipsometric Ψ and Δ contrast images were recorded at different wavelength in the visible range and by employing a theoretical model, the thickness of the cyanine across the sample was calculated. An example of Ψ and Δ maps taken at 546 nm wavelength is presented in the Figure 18 with the calculated thickness shown on the right side of the images.

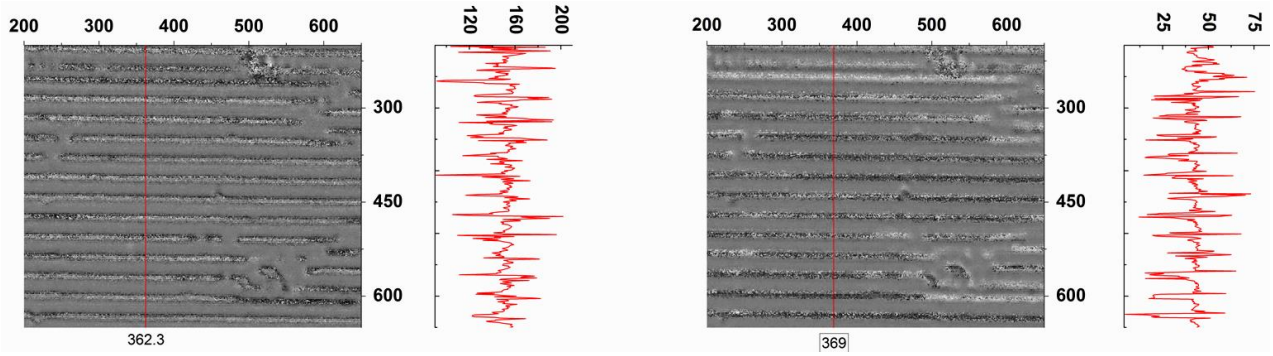

Figure 18: Measured Ψ and Δ maps using the EP^3-SE nulling imaging ellipsometer; λ=546 nm.

This is a very successful qualitative result considering that the structures formed by the cyanine dye are at the resolution limit of the experimental set-up. While the dimension of the cyanine stripes was not entirely resolved, the position of the defects was correctly identified.

Development of new equipment for large area optical characterisation and inspection

In order to develop new optical inspection tools for large area metrology of thin films, VSL and CMI have designed and realised a large-area (tens of cm to m scale) polarisation-encoded ellipsometer and a large area digital reflectometer, respectively. These devices combine advanced optical inspection methods with large scale metrology capabilities.

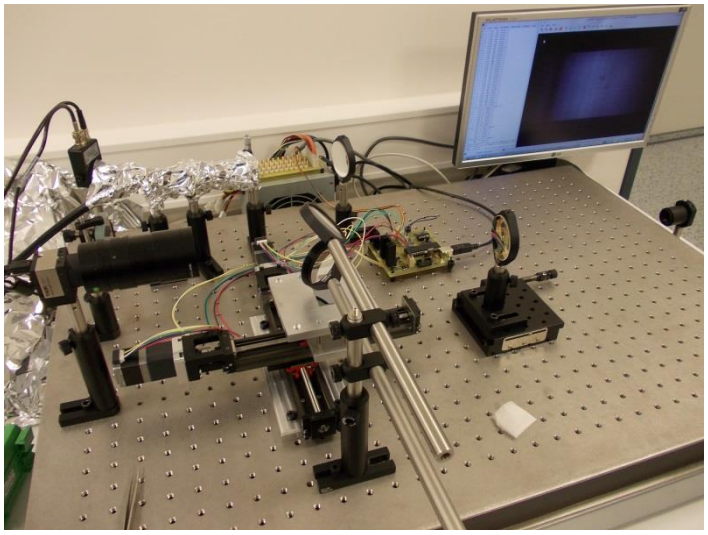

Figure 19: Photography of the digital reflectometer built at CMI.

CMI built a large area digital reflectometer that can evaluate thin film thickness with areas up to 113 x 136 mm in size, with theoretical lateral resolution of 18 microns (Figure 19). The performance of the new device was tested on STEP-WAFER standard sample obtained from Ocean Optics (Figure 20). The apparatus has also been used to map the thickness distribution of a SiNx thin film deposited on a 6” Si wafer and the results were

in a good agreement with the results obtained by BAM. CMI also developed software tools that are able to effectively process acquired data.

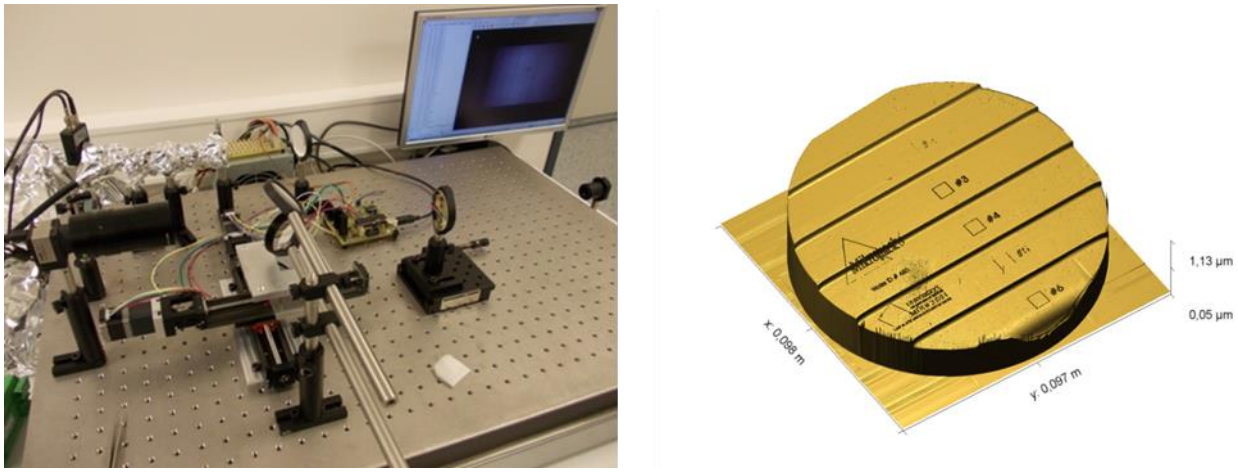

Figure 20: Left: photography the digital reflectometer. Right: Digital reflectometer evaluated map of SiO2 thin film thickness of the STEP-WAFER standard sample.

VSL has designed and realised a compact ellipsometer module that can be attached to a translation mechanism to expand the lateral measurement range order to implement a traceable metrology tool for film thickness and refractive index measurements on large surfaces. Simulations of the expected measured intensity at different angles were used to support the design phase of the work (Figure 22). The large scale measurement setup uses a 3D coordinate measuring machine (3D CMM) as a positioning device for the ellipsometer measurement head (Figure 21). In the current configuration this allows a lateral range of 1 m x 0.5 m. The control of the 3D CMM poses a boundary condition on the maximum weight that can be handled for the measurement module, which is about 0.6 kg. This constraint was taken into account during the design of the ellipsometer head by removing as much mass of the construction elements as possible without compromising the structural integrity and stability. Conventional ellipsometers usually use rotating polarisation optics or phase plates to scan the polarisation as well as rotating input and output arms to acquire angle dependent information. In our design, the moving components have been restricted to only the input and output arms and a custom made fixed polarisation encoder has been used to enable the generation of various polarisation states. This approach eliminated the need for rotating optics thus minimising the total mass, simplifying the design and reducing additional causes of mechanical instabilities. Measurements of samples provided by Total S.A. were used to validate the setup.

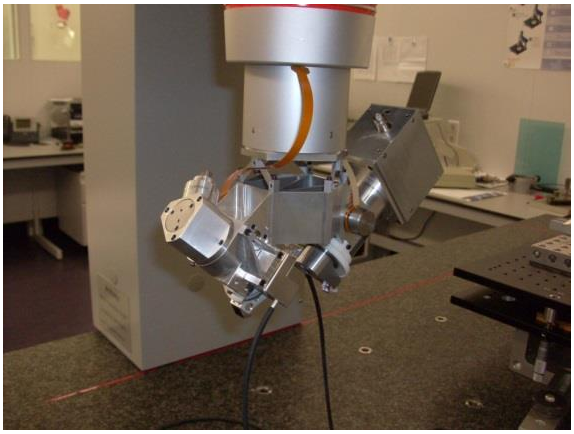

Figure 21: The ellipsometer head developed by VSL attached to a 3D CMM.

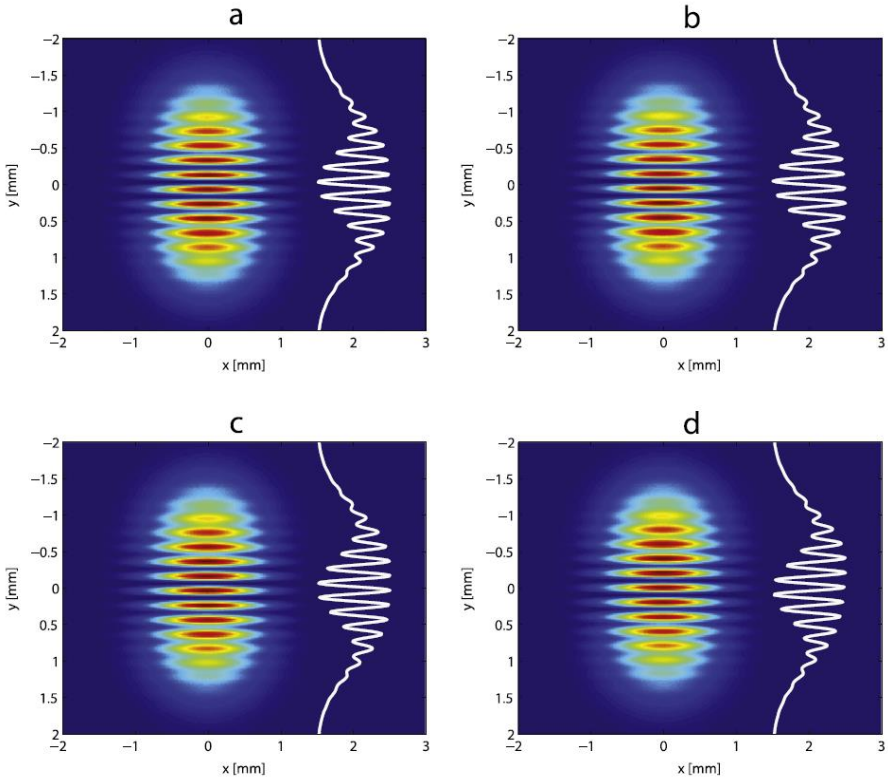

Figure 22: Simulations showing the typical structure of the measured intensity for four different incident angles, 30° (panel a), 45° (panel b), 60 °(panel c), 80 ° (panel d). The two beams emerging from the polarisation encoder are still recognizable in the interference pattern. Along with the 2D intensity distributions, in each plot the 1D intensity distribution, taken at x=0, is also shown. The interference fringes carry information on the phase shift between s and p polarisations.

The project also addressed the challenging problem of having fast, precise and accurate measurements of thin films on large areas. The development of these facilities was supported by BAM, who has provided reference measurements of large samples by spectroscopic ellipsometry. The goal was to analyse large areas using non-destructive and contact-less investigation methods. A set of 4 SiN_x layer with a dimension of ~ 10x10 cm^2 were prepared by PECVD in a square pattern on Si substrates and investigated using spectroscopic ellipsometry from far UV to mid IR (Figure 23). The thickness of the coatings in the centre of the samples was determined to be ~ 90±2.5 nm. The accuracy of the determined parameters (thickness and optical constants of the SiN_x layers) was ensured using a multi-sample analysis. Furthermore, the stoichiometry of the layers was analysed. The decrease in the refractive index and the strong contribution of the N-H band in the mid IR spectral range indicated an excess of N.

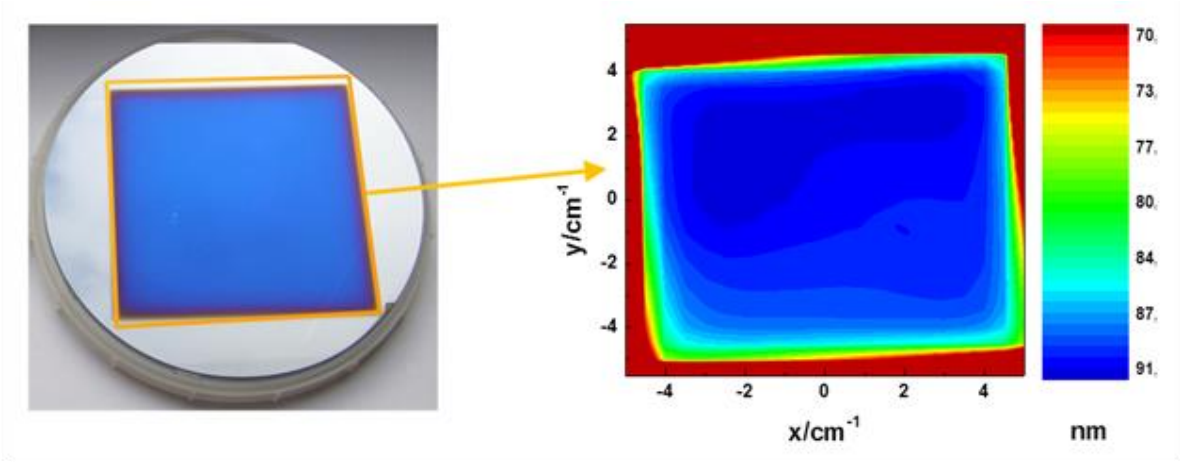

Figure 23: Photo of a representative SiN_x layer vs the thickness map obtained using mapping ellipsometry.

As deviations to stoichiometry often induce inhomogeneity effects, the quality of the samples was studied by means of mapping ellipsometry in the visible range. For that purpose, 483 points arranged in a square scan pattern were measured on the covered region. The calculated thickness map of one of the four samples is presented in Figure 23. As can be seen, the thickness variation in the centre of the sample is minor, so the sample can be considered mostly homogeneous.

An additional sample with a diameter of ~ 15 cm and exhibiting more inhomogeneity than the previously presented samples was provided by BAM. A SiO2 layer was deposited on a Si(111) substrate by means of PCVD. Using mapping ellipsometry (1008 measurement spots arranged in a circular scan pattern), the inhomogeneity of the SiO2 layer was investigated. The thickness map was calculated by considering an optical model and presented in Figure 24. A maximum thickness variation of 21.5 nm (which translates to a thickness inhomogeneity of ~22%) was observed.

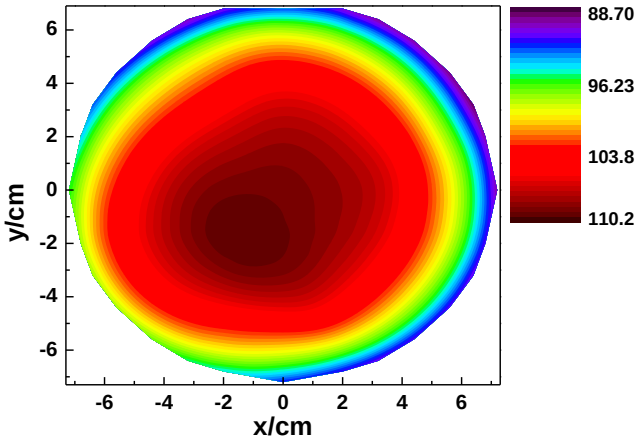

Figure 24: Calculated thickness map for SiO_2 layer deposited on a 6" wafer of Si(111).

3.6 Development of traceable optical measurements for inhomogeneous thin films

Most optical measurements consider that the material under investigation is uniform (or homogeneous) within the measurement area. However, as mentioned previously this is often not the case for complex thin films, such as some advanced thin film photovoltaic materials. It is also not true for patterned thin films, especially as patterning features become so small that each feature can no longer be resolved individually by optical methods. In this project we have developed measurement methodologies and data analysis methods to perform accurate optical measurements on highly inhomogeneous thin films, such as complex photovoltaic materials and patterned thin films.

Combined ellipsometry and reflectometry method

The measurement of optical properties of inhomogeneous thin films is very challenging because the optical parameters for the material are not well defined. To tackle this challenge, the project has developed a multi-method approach combining ellipsometry and reflectometry methodologies at BAM and Aalto. Aalto and BAM determined the refractive index and thickness of thermally grown and evaporated SiO2 on top of silicon substrates. Oxide layer thickness non-uniformities were also spatially mapped for layers up to 6000 nm thick. Other characterised thin film materials include photoresist coated silicon wafers. The refractive index and thickness were determined simultaneously within the wavelength range of 400-700nm with variable angle spectrophotometry and the results were compared with ellipsometry measurements. Angular resolved reflectometry data agreed well with ellipsometry and was used to improve the reliability of the determination of the optical parameters.

Imaging and mapping ellipsometry were used by BAM to determine the properties of non-ideal and patterned thin films. For that purpose, patterned SiO_2 and photoresist layers were deposited on single-crystalline silicon (100)-oriented wafers with diameters of 150 mm provided by the Fraunhofer Institute in Erlangen. Two different patterns with different lateral resolutions were written on Si wafers by means of photolithography.

The optical properties and layer thicknesses were determined by spectroscopic ellipsometry from far UV to near IR range. Large scale and small scale homogeneity were additionally studied by means of mapping and imaging null ellipsometry.

Using mapping ellipsometry, the thickness of the silicon oxide layer has been calculated, showing its homogeneity across the two SiO_2 patterned layers. A maximum of 1.3%, which translates to ~4 nm inhomogeneity across the sample, was calculated.

In contrast to the SiO_2 films, the photoresist layers proved to be more inhomogeneous. A large scale inhomogeneity of ~ 6% (~93 nm) was determined over the photoresist coating. Figure 25 shows the thickness profile determined for one of the studied photoresist patterned samples.

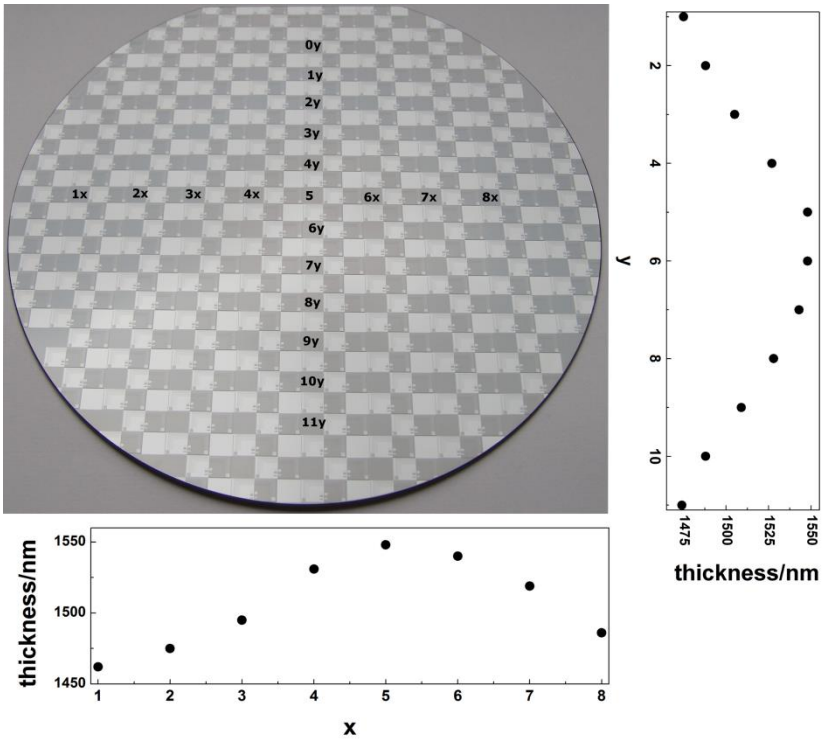

Figure 25: Photoresist coating with repetitive pattern. The numbers indicate the measurements sites of the ellipsometric measurements.

Important results were obtained by analysing the microstructures present for the four patterned layers by using imaging null ellipsometry. As can be seen in Figure 26, structures with a lateral resolution of ~ 5µm were very well resolved. The blue spectrum indicates the distance between the two rectangular uncoated regions to be around 5 µm in agreement with the nominal thickness indicated. The imaging ellipsometer also proved to be a valuable investigation technique in the detection of micro-defects present in the uncoated regions of the substrate (see red spectrum).

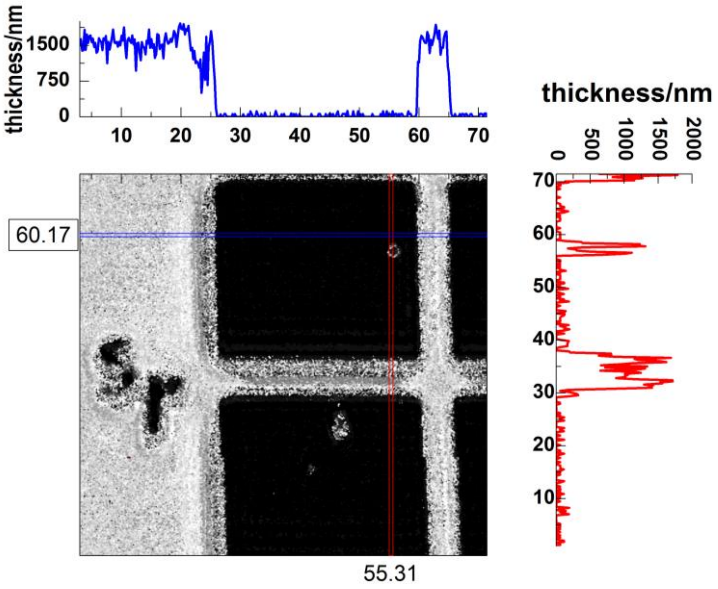

Figure 26: Thickness map of a 76x76 µm^2 area on the photoresist layer obtained by imaging ellipsometry.

These were very important quantitative results for the present task and for the optical characterisation with spatial discrimination described in section 3.5.

The small scale inhomogeneity was particularly investigated close to the patterns created in the coating layers. One of the studied regions, a 76x76 µm^2 area, is shown in Figure 27. A thickness variation of the layer of ~ 1000 nm was observable.

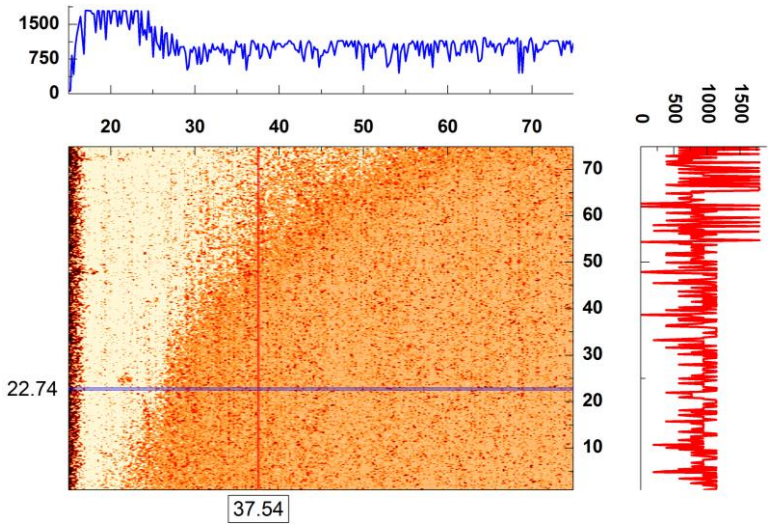

Figure 27: Thickness map of a photoresist covered area in the vicinity of a pattern.

In this project, we proved the successful use of ellipsometry in the detection of precise thickness and optical constants of the investigated layers, and the capability of the method to i) indicate the presence of microscopic defects, ii) small and large scale inhomogeneity and iii) resolve structures with dimensions down to 5 µm.

Procedure for traceable 2D micro Raman measurement of inhomogeneous thin films

As mentioned previously, complex thin films often present composition and morphology variations that can strongly affect their performance. For instance, for Cu(In1-xGax)Se2 thin-film solar cell production the traceability of the measurement of dimensions and composition is very important and very challenging. Progress in depth-profile determination of microstructure has been presented in section 3.3. In this section, we demonstrate the development of a procedure for traceable 2D micro-Raman mapping of these inhomogeneous thin films. We developed a procedure for traceable Raman measurements and determined the traceable reference spectra for Cu(In1-xGax)Se2 thin-film solar cells. To support this work, elemental surface composition and integral elemental composition of the samples were characterised by reference-free x-ray fluorescence analysis under variation of the incidence angle. With these results, a quantitative area assessment of lateral Raman mappings was presented together with a complete uncertainty budget. The strategy has been based on histogram analysis of chemical distribution images from individual components. Sample surface features that cannot be recognised in optical microscopy, were identified and quantified by Raman. Furthermore, the Raman method was adapted to obtain cross-sectional mappings in order to identify in-depth phase distributions and composition gradients (Figure 28). Raman and X-ray spectrometry were proven as complementary non-destructive methods combining surface sensitivity and in-depth information on elemental and species distribution for reliable quality control of Cu(In1-xGax)Se2 absorbers and Cu(In1-xGax)3Se5 surface layer formation.

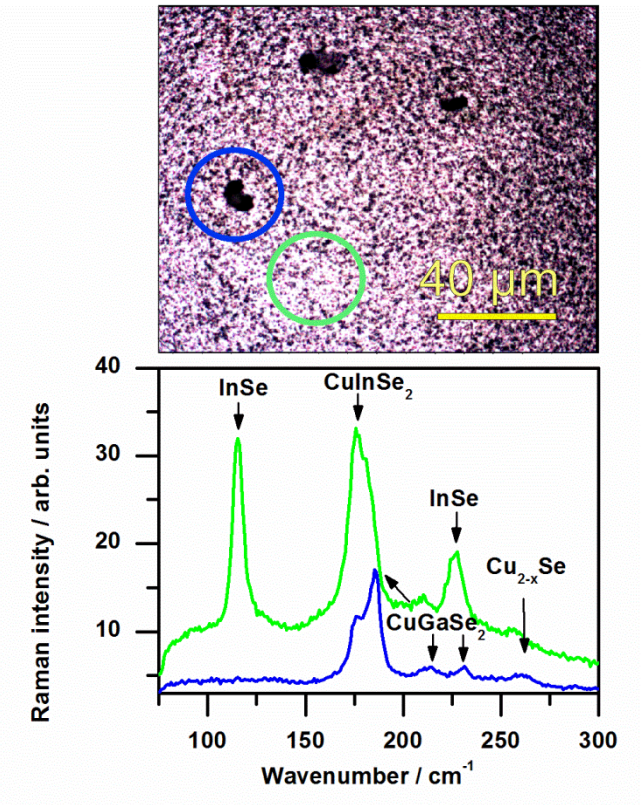

Figure 28: Bright field microscope picture of an inhomogenous sample prepared at 330°C (top) and averaged Raman spectra from different areas together with compound assignment (bottom).

4 Actual and potential impact

Dissemination activities and engagement with stakeholders

Scientific publications and presentations

This project adopted a strong industrial dissemination strategy using different formats and media to target a broad audience. Effective knowledge transfer mechanisms have led to 18 high quality scientific articles published or submitted for publication in peer-reviewed journals and over 60 conference contributions (46 presentations and 18 posters), many of which were invited talks.

Training activities (workshops and tutorials)

This project organised and delivered numerous workshops and tutorials. As a key highlight, in the final year of the project we also organised a 5-day symposium on '*Analytical Techniques for Precise Characterization of Nanomaterials*' (ALTECH) which attracted over 160 participants. The symposium was organised as part of the European Materials Research Society (EMRS) 2014 Spring Meeting (http://www.emrs-strasbourg.com/index.php?option=com_content&task=view&Itemid=1619&id=700) that attracts over 3000 scientists and engineers from industry and academia every year. To maximise the impact of the activity, the symposium included presentations on the project outputs and tutorial sections.

The following workshops were organised:

- Highly precise characterisation of materials for nano and bio technologies within EMRS Fall Meeting, 17-21 September 2102, Warsaw Poland;
- Fundamental Atomic Parameters, Berlin, Germany, February 2013;
- Traceable Optical Thin Film Characterisation, Berlin, Germany, September 2013;
- Reliable characterisation methodologies for advanced materials, within the International Congress of Metrology, Paris, France, October 2013;
- Workshop on Fundamental Parameters, Paris, France, March 2014;
- Analytical Techniques for Precise Characterization of Nanomaterials, within EMRS Spring Meeting, 26-30 May 2014 Lille, France.

Additionally, training/tutorials were delivered on:

- Sentech Seminar on Thin Films Measurements, Germany June 2013;
- Accurate determination of film thicknesses and optical constants with ellipsometry, Paris, October 2013
- New methods in thin films metrology for microelectronic applications by means of mapping and imaging ellipsometry, Berlin, Germany, June 2014;
- Imaging and advanced measurement of molecular electronic materials, London, UK, March 2014;
- Metrology for quantitative Raman mapping evaluation, Lille, France, May 2014;
- Quantitative X-ray fluorescence analysis under grazing incidence condition for stratified materials based on X-ray Standing Wave field calculations, Lille, France, May 2014;
- Metrology for thin films and nanotechnology: New applications for optical surface measurements, Göttingen, Germany, July 2014.

The early meetings were designed to keep the direction of the project aligned with stakeholder needs, while the later events were focused on the dissemination of the outputs to ensure that impact would last beyond the life of the project.

The workshops have successfully brought the attention of different stakeholder communities (e.g. optical, X-ray, Raman spectroscopy) to the multi-method approach to thin film analysis being used in this project. Some

of the stakeholders became project collaborators and were the first to utilise results from the project to improve their competitiveness.

Other dissemination

We created a mailing list of companies and institutes that were regularly updated on the progress of the project through targeted newsletters. Other means of disseminating the work to a broader audience included the project website, technical online network news (e.g. LinkedIn, Research Gate) and online news on technical websites. As an example, a short story about the project has been published in the online technical website *Solid State Technology – Insights for electronics manufacturing* (http://www.electroiq.com/content/eiq-2/en/articles/sst/2012/03/metrology-project-launches-in-europe-for-thin-films.html).

Impact on standardisation

Innovative thin film technology is currently lacking standardisation which is, in part, due to the fact that some of these technologies are not yet fully established in industry. Therefore this project has focused on the ground work to underpin future standardisation: ensuring traceability of methodologies, validating techniques currently used, developing standard samples for in-site measurements and developing best practice guides. This ground work was disseminated to the following standardisation working groups:

In the metrology community:

- BIPM CCQM SAWG (Bureau International des Poids et Mesures (BIPM), Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology, (CCQM) Working Group on Surface Analysis (SAWG))

The involvement of the consortium in BIPM CCQM SAWG led to the participation in the pilot study P-140 that addressed the characterisation of CIGS solar cell thin film with matrix element depth profiles which was one of the key systems of interest in this project.

- Versailles Project on Advanced Materials and Standards (VAMAS), Technical Working Area (TWA) 36: Organic Electronics

The charge mobility interlaboratory study performed as part of this project has been proposed and accepted as a project of the TWA36 of VAMAS. The results of that study led to the development of a new measurement protocol that reduced uncertainty of data analysis from 300% to 20%. The protocol has been made available free of charge and will be the basis for future standardisation activity.

NPL has been appointed as chair of the technical working area TWA36 and will continue leading work in this area towards international agreed procedures.

- BIPM Consultative Committee for Thermometry (CCT) – Working Group (WG) 9

LNE presented results of the development of the new traceable facility for thermal measurements of thin films.

Impact on the industrial community:

- Working Group “Encapsulation” of the Organic and Printed Electronics Association

This project provided input to the Working Group Encapsulation of the Organic and Printed Electronics Association. One activity carried out as part of the group was an international intercomparison of water vapour transmission rate (WVTR) measurements: the preliminary performance of the NPL system was compared to other methods based on different principles and operated by five other laboratories. A multi-layer reference barrier was sent to each participating laboratory and each participant made a series of repeat measurements of WVTR at 20 ^{o}C and 50 % relative humidity. Results validate the traceability of NPL’s WVTR facility.

- International Standards Organisation (ISO), Technical Committee (TC) 201: Surface chemical Analysis / Working Group (WG) 3 X-ray Reflectivity and total reflection X-ray fluorescence spectroscopy

PTB established links with this working group and provided feedback on draft documents. This technical working group is developing international standards for reliable X-Ray spectroscopy characterisation of a range of materials systems including thin films. The high quality of data obtained in this project, combined with the expertise developed on X-ray methodologies for thin films characterisation has attracted interest from the

TC201 working group which requested PTB for feedback on draft documents, which are not publically available. Through this interaction, the work from this project will directly impact the development of new standards that the thin film industry uses to ensure good data quality.

Industrial uptake and early impact

A manufacturer of measuring equipment has already started using the thick SiO_2 film reference sample and the developed calibration procedure developed in this project to disseminate traceability across the value chain. These results were only possible by the demonstration of a multiple technique approach to the reliable characterisation of such complex thin films.

Industrial stakeholders have also benefited from high quality data to support the development of their thin film materials. Examples include:

- A thin film manufacturer in the UK made use of the new NMI capabilities developed in the project for traceable measurements of water vapour transmission rate to obtain valuable insight into how different fabrication processes affect the performance of their thin film barriers layers.
- A manufacturer of thin film solar cells identified issues in the manufacturing process after using the novel protocol for photocurrent mapping developed in this project. This will enable them to improve the quality of their products.
- A thin film manufacturer learned valuable insights into the temperature-limitations of Si/ZnO thin film solar cells through high resolution measurements of speciation (where temperatures above 1000 °C were shown to promote the formation of new chemical compounds within about 10 nm of the interface).
- A manufacturer of reflectometry thin film measurement devices is already using a reference material for unusually thick layers of dielectrics (SiO2) developed by this project. Examples for the targeted community of this technology are test laboratories measuring critical thicknesses of barrier layers, varnishes, protective layers for the semiconductor and the PV industry.

A number of the techniques and reference materials developed during the project have the potential for further exploitation:

- *New capabilities available at NMIs/DIs that will support industry*
  - The traceable water vapour transmission rate facility developed in this project is being commercially exploited by NPL to support industrial development of cost-effective barrier layers typically used to ensure long durability of thin films devices, such as organic light emitting diodes (OLEDs). Given the trade-off between price and performance of these barriers, the precise characterisation of the required minimum level of performance will allow significant cost savings for industry, reducing product price and opening new addressable markets.
  - The novel compact ellipsometry head designed and built during this project, together with faster and accurate data analysis is expected to be jointly exploited by VSL and TU Delft through collaboration with commercial partners.
  - NPL has developed and validated a new protocol for accurate photocurrent mapping of solar cells demonstrating that poor choice of measurement parameters can lead to false results, which can have direct impact in R&D costs when scaling up solar cell production. This result has attracted interest from an industrial-academic consortium stakeholder and discussions about collaboration beyond this project are being held.
  - A novel facility for traceable measurement of thermal conductivity in thin films for temperatures up to 1000 °C based on modulated photothermal radiometry is now available at LNE to support the thin films microelectronics industry. Measurements of temperature dependent conductivity have already benefited a thin film manufacturer by providing insight into the development of thin film phase change memory devices.
  - A new digital reflectometry and new analysis software setup is now available at CMI to support the thin film optics industry.

- *Further exploitation activities*
  - PTB has filed a patent application for a novel 2D sub-micron calibration sample for spatially resolved Raman measurements with dimensions traceable to the metre that was designed, produced and validated at PTB. This was developed in response to the lack of appropriate calibration samples and allowed successful µ-Raman measurements on samples with known size below 400 nm. A number of companies have requested access to the prototype calibration samples and discussions about commercial exploitation are ongoing.
  - A procedure was developed by PTB and HZB to produce industrially relevant reference samples for in-line monitoring for quality control of complex multicomponent thin films, using Raman Spectroscopy. The use of these samples allows monitoring of relative concentrations or different elemental compositions, which is crucial to reliable thin film photovoltaic performance and will be exploited by HZB to improve the efficiency of their solar cells.
  - A great improvement in accuracy of determination of fundamental x-ray parameters has been achieved for elements of interest for advanced thin film applications, when compared with data bases such as that published by Elam. For example, good agreement has been demonstrated between higher energy (1-20 KeV) measurements at CEA and lower energy (0.1-10 KeV) measurements at PTB with deviations of less than 2%, especially around the K-edge of Cu. Cu is an important element for new photovoltaic technologies. Reduction of the uncertainty of atomic fundamental parameters will have an immediate positive impact in the accuracy of all X-Ray based measurements and will be quickly disseminated through PTB's collaboration with the International Atomic Energy Agency.
  - New collaboration between NPL and the University of Edinburgh has started to push the development of multiple electrode systems for electrochemical imaging of thin films a step closer to industrialisation.
  - Aalto University is in discussion with a company interested in using the design of an in-situ reflectometry method developed in this project to build their new thin film deposition chambers.
  - A procedure for thin film element gradient control and a method for characterisation of elemental gradient will be further developed by TU Berlin and PTB towards commercial exploitation.

The examples listed above show how this project was a good example of the implementation of the EMRP, which intends to support the development of smaller European National Measurement Institutes and streamline research across Europe, leveraging investment, reducing duplication and increasing impact.

In addition to the exploitable R&D mentioned, significant advance of scientific knowledge has been generated, as described in section 3 (Research Results), that will impact the scientific and technical community by going beyond the previous state of the art.

Wider Social / Economic / environmental impact

The measurement tools developed by this project will underpin the improvement of thin film manufacturing quality control for the necessary technologies that will enable Europe to meet the directive targets. Through reduction of time-to-market and production costs, the project will help reinforcing the leadership position of Europe in the creation of thin film and flexible or printable electronics tailored to meet key societal and economic needs.

Thin film devices use fewer raw materials and their manufacturing methods often make use of lower temperature and/or shorter time processes. This trend will reduce energy usage for production and will reduce impact in raw elements reserves. In the longer term, this project will help save energy and reduce greenhouse gas emission by ensuring commercial viability and underpinning production of energy efficient thin film devices, such as organic light emitting diodes (OLEDs) and solar cells. This will potentially impact Directive 2010/31/EU on energy performance of buildings and Directive 208/28/EC on the use of energy from renewable sources. New solid-state lighting (e.g. OLED) is expected to outperform almost all other light sources in terms of efficiency and thus provide a saving potential of about 50% of electrical energy, "which would make possible low consumption lighting and a major potential reduction in global electricity consumption by 2025. High tech

materials are increasingly at the basis of innovative “green techs”, associated with renewable energy (i.e. Cu-Indium- Gallium-Selenium or CIGS photovoltaic "thin-film" technology for solar cells) and with minimizing greenhouse gas emissions.” (Page 17, COM(2008) 699, The raw materials initiative — meeting our critical needs for growth and jobs in Europe.)

Thin film device technologies supported by this project will allow flexible and large area electronics. This will provide a step change in how people deal with optoelectronic devices, underpinning the Internet of Things. These novel devices will seed a multitude of applications that will force the establishment of new industries directly creating new jobs. According to the European commission document “Europe2020, A European strategy for smart, sustainable and inclusive growth”, 2010, page 13): “Over a million new jobs are expected to be created just by meeting the EU’s objective of 20% renewable energy and 20% target on energy efficiency.”

5 Website address and contact details

We set up a website for the project and have maintained it since. The project website will stay online to further the dissemination of the project results. The website address is:

http://projects.npl.co.uk/optoelectronic_films/

The project coordinator will continue to be available for requests under the following e-mail address:

fernando.castro@npl.co.uk.

The impact team can be reached under: andreas.hertwig@bam.de and thin-films@bam.de.

6 List of publications

The project has released a large number of publications. These are listed here in categories.

Research articles in peer-reviewed journals:

1. P. J. Brewer, B. Goody, Y. Kumar, M. J. T. Milton, “Accurate measurements of water vapor transmission through high-performance barrier layers“, Rev. Sci. Instrum. 83, 075118 (2012).
2. P. Petrik, B. Pollakowski, S. Zakel, T. Gumprecht, B. Beckhoff, M. Lemberger, Z. Labadi, Z. Baji, M. Jank, and A. Nutsch, “Characterization of ZnO structures by optical and X-ray methods”, Applied Surface Science, 281, 123 (2013)
3. P. Petrik, T. Gumprecht, A. Nutsch, G. Roeder, M. Lemberger, G. Juhasz, O. Polgar, C. Major, P. Kozma, M. Janosov, B. Fodor, E. Agocs, M. Fried, “Comparative measurements on atomic layer deposited Al_2O_3 thin films using ex situ table top and mapping ellipsometry, as well as X-ray and VUV reflectometry”, Thin Solid Films 541, 131 (2013).
4. P. Petrik, “Optical thin film metrology for optoelectronics“, Journal of Physics, Conference series, 398, 012002 (2012).
5. T. Gumprecht, P. Petrik, G. Roeder, M. Schellenberger, L. Pfitzner, B. Pollakowski and B. Beckhoff (2013). “Characterization of Thin ZnO Films by Vacuum Ultra-Violet Reflectometry”. MRS Proceedings, 1494, pp 65-70. doi:10.1557/opl.2012.1677.
6. C. Becker, M. Pagels, C. Zachäus, B. Pollakowski, B. Beckhoff, B. Kanngießer, and B. Rech, ”Chemical speciation at buried interfaces in high-temperature processed polycrystalline silicon thin-film solar cells on ZnO:Al”, J. Appl. Phys. 113, 1089 (2013).
7. D. Rosu, P. Petrik, G. Rattmann, M. Schellenberger, U. Beck, A. Hertwig, “Optical characterisation of patterned thin films”, Thin Solid Films, in press, DOI: 10.1016/j.tsf.2013.11.052.
8. C. Streeck, S. Brunken, M. Gerlach, C. Herzog, P. Hönicke, C.A. Kaufmann, C. Becker, J. Lubeck, B. Pollakowski, R. Unterumsberger, A. Weber, B. Beckhoff, B. Kanngießer, H.-W. Schock, and R. Mainz, ”Grazing-incidence x-ray fluorescence analysis for non-destructive determination of In and Ga depth profiles in Cu(In,Ga)Se_2 absorber films”, Appl. Phys. Lett. 11, 113904 (2013).

9. A. Cappella, J.-L. Battaglia, V. Schick, A. Kusiak, A. Lamperti, C. Wiemer and B. Hay, “High temperature thermal conductivity of amorphous Al_2O_3 thin films grown by low temperature ALD”, Advanced Engineering Materials, 15,1046 (2013).
10. S. Wood, J. S. Kim, D. T. James, W. C. Tsoi, C. E. Murphy, and J.-S. Kim, “Understanding the relationship between molecular order and charge transport properties in conjugated polymer based organic blend photovoltaic devices”, The Journal of Chemical Physics, 139, 064901 (2013).
11. O. E. Gawhary, A. J. L. Adam, and H. P. Urbach, “Nonexistence of pure s- and p-polarized surface waves at the interface between a perfect dielectric and a real metal”, Phys. Rev. A, 89, 023834 (2014).
12. I. Juric, E. Tutis, “Traps and transients: dark injection spectroscopy in organics and the tail of density of states”, Organic Electronics, 15, 23901 (2013).
13. N. Fleurence, B. Hay, G. Davée, A. Cappella and E. Foulon, “Thermal conductivity measurements of thin films at high temperature by modulated photothermal radiometry at LNE”, Physica Status Solidi (c), submitted.
14. S. Pourjamal, H. Mäntynen, P. Jaanson, D.M. Rosu, A. Hertwig, F. Manoocheri and E. Ikonen, “Characterization of thin film thickness”, Metrologia, 51 S302 (2014).
15. R. Koops, P. Sonin, M. v. Veghel, O. El Gawhary, “A compact new-concept ellipsometer for accurate large scale thin films measurements”, Journal of Optics 16 (2014) 065701.
16. J. C. Blakesley, F.A. Castro, W. Kylberg, G.F.A. Dibb, C. Silva, J.S. Kim, “Towards reliable charge-mobility benchmark measurements for organic semiconductors”, Organic Electronics, 15, 1263 (2014).
17. S. Zakel, B. Pollakowski, C. Streeck, S. Wundrack, A. Weber, S.Brunken, R. Mainz, B. Beckhoff and R. Stosch, Quantitative Raman spectrometry and x-ray fluorescence analysis as non-destructive methods for spatially resolved chemical characterization of Cu(In,Ga)Se2 absorber films, accepted in Applied Spectroscopy.
18. Y. Ménesguen, M. Gerlach, B. Pollakowski, R. Unterumsberger and M.-C. Lépy, High accuracy experimental determination of copper and zinc mass attenuation coefficients for photons in the 100 eV to 30 keV energy range, submitted to Physical Review A.

Project newsletters sent by e-mail to the stakeholder community and published in the website

1. Newsletter No. 1 with a general introduction to the project and its participants: published 2012-08.
2. Newsletter No. 2 with a feature on the transmission of water through barrier layers (NPL): published 2013-07.
3. Newsletter No. 3 with a feature on optical thin film characterization (IISB), and on Raman spectroscopy (Imperial College): published 2013-09.
4. Newsletter No. 4 with a feature on X-ray spectroscopy and mass-attenuation coefficients (CEA): published 2014-01.
5. Newsletter No. 5 with a feature on the large area mapping ellipsometer device (VSL): published 2014-04.
6. Newsletter No. 6 which features the highlights of the project: published 2014-07.

Further publications, Web announcements, and announcements in social networks

1. Regular announcements and updates have been released through the web page.
2. Online news have been published in the social network LinkedIn in the groups for printed electronics, scanning probe methods, plastic electronics, thin films network, and technological thin films.