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1 Executive Summary

Introduction

EU targets for the use of renewable energy and energy efficient devices are driving rapid growth in the global market for low-carbon goods and services, resulting in increasing demand for advanced materials and related technologies. Thin films, with a thickness from a fraction of a nanometre to several micrometres, are key components in numerous energy applications such as solar cells, LEDs, energy efficient windows and solid state power electronics which are used to control the flow of electricity from the grid. The lack of reliable measurement protocols and calibration procedures for thin films has hampered the development of these technologies. A key challenge is that thin film materials typically have complex structures, requiring multiple characterisation techniques to analyse them adequately. This project developed a measurement framework for reliably characterising thin films, and has delivered new instrumentation, industrial consultancy, calibration services, standards documents, new solar cell technology, and a spin out company.

The Problem

Energy technologies require manufacturing of devices, such as solar cells and LEDs, in high volumes. Prior to this project, the uptake of advanced thin film materials used in such devices was slow due to the challenges in demonstrating the required performance and reliability. Additionally, more batches than expected were rejected during quality control after manufacture, partly due to the lack of clarity about which of the multiple measurement parameters were the most important to optimise for best performance.

Multiple energy technologies are required to ensure Europe's shift to a low carbon economy and support energy security. Devices such as power electronics, solid state lighting, solar energy and energy efficient windows are based on complex thin film materials which often have non-uniform composition and are notoriously difficult to measure. That means that key measurement challenges are common to multiple energy technologies and if solved can have significant impact in the field. Innovative measurement methods and modelling are needed to enhance device functionalities and improve competitiveness. Measurements are needed to characterise the structure of thin films and their novel electronic and thermal properties, and models are needed to help interpret the measurements and relate them to product performance.

The Solution

This project set out to develop complementary metrology tools for reliable characterisation of complex thin films used in energy applications. This required the development of models for interpretation of advanced measurements and correlation to product performance as well as development and validation of novel measurement facilities in close collaboration with stakeholders.

Impact

This project developed an innovative and ambitious multi-faceted metrology framework for reliable characterision of thin films in energy applications. Close engagement with a wide range of stakeholders resulted in the direct uptake of the technology and knowhow developed, including: (a) new traceable measurement facilities that allow correlation of the effect of temperature and irradiation on parameters of thin films energy materials; (b) increased solar cell efficiency demonstrated in an EU production line when compared against current technology by applying the passivated Si high efficient solar cells developed in this project; (c) a patent application for high efficiency Si thin film technology and based on this the spin-off company ElFys Inc. has been established and started operating; (d) new instrumentation has been made available to end users via license agreements; (e) several NMIs are providing consultancy and other services to large EU companies using know-how developed in this project, this will help with increase competitiveness. (f) a new Calibration and Measurement Capability (CMC) for the quantification of thin film CIGS layers was registered with and approved by BIPM, the highest international authority in metrology; (g) Part 1 of draft standard (DN 50989-1) on data analysis in spectroscopic ellipsometry was published with significant input from this project and is now available online; (h) 4 Good Practice Guides that will help companies make best use of their equipment.

The know-how, new facilities and instrumentation developed in this project will facilitate the development of new technologies and increase competitiveness of European energy technologies. By extending Europe's leadership in energy technology and innovation, this project has helped to support economic growth and an energy efficient future for Europe.

2 Project context, rationale and objectives

EU targets for the use of renewable energy and energy efficient devices are driving rapid growth in the global market for low-carbon goods and services, resulting in increasing demand for advanced materials and related technologies. Energy technologies require manufacturing of devices, such as solar cells and LEDs, in high volumes. Prior to this project, the uptake of advanced thin film materials used in such devices was slow due to the challenges in demonstrating the required performance and reliability. Traditionally these devices were first manufactured and their different characteristics subsequently separately measured, meaning that adjustments to the manufacturing process had to take place after manufacture, which was an expensive and time consuming process. In addition, more batches were rejected during this quality control process than expected, partly due to the lack of clarity about which of the multiple measurement parameters were the most important to optimise for best performance. In order to accelerate innovation in energy technologies, provide confidence in the adoption of advanced thin film materials and reduce costs in manufacturing, it is critical to understand (i) which parameters need to be measured, (ii) which parameters correlate with device performance and reliability, (iii) what the accuracy of that measurement needs to be, (iv) which measurements should be done during the manufacturing process and (v) which can be performed after manufacture.

A single technology will not be sufficient to ensure Europe's shift to a low carbon economy. This requires a wide range of technologies, including power electronics (based on multilayers of thin film semiconductors), solid state lighting, solar energy and energy efficient windows. This project builds on some of the outputs of EMRP project *IND07 Metrology for the manufacturing of thin films* to develop new traceable measurement methods for these devices.

Multiple energy technologies are required to ensure Europe's shift to a low carbon economy and support energy security. Devices such as power electronics, solid state lighting, solar energy and energy efficient windows are based on complex thin film materials which often have non-uniform composition and are notoriously difficult to measure. That means that key measurement challenges are common to multiple energy technologies and if solved can have significant impact in the field. Such technical challenges include maximising performance, durability and cost-effective manufacturing. Innovative measurement methods and modelling are also needed to enhance device functionalities and improve competitiveness. Measurements are needed to characterise the structure of thin films and their novel electronic and thermal properties, and models are needed to help interpret the measurements and relate them to product performance. The complexity of these thin films and the associated measurement challenges requires a coordinated multi-method approach that cannot be achieved by a single institution alone.

The specific measurements needed for the different devices include:

- Power electronics, based on multilayers of thin film semiconductors: wavelength dependent dielectric function (how a material responds to an electric field), structure
- Photovoltaics, used for the production of solar energy and thin film coated: relationship between structure and performance, product quality control, electrical and optical properties
- Solid state lighting, based on layers of thin films: material performance of large area devices
- Energy efficient windows, coated with low emissivity thin films to ensure high transmittance in the visible part of the spectrum, and low heat transmittance: optical characteristics and thermal parameters
- Thermal solar energy absorbers, coated with thin films: dielectric characterisation, thin film refractive index, effect of temperature stress on thin film performance (temperatures become very high when the transfer fluid is not circulating)

Scientific and technical objectives

The goal of this project was to develop complementary metrology tools for thin film characterisation, and included the following objectives:

1. Development of models for the interpretation of advanced materials measurements and their correlation to product performance.

2. Traceable determination of the correlation between material composition and electronic structure over a broad spectral range. This should include the production of reference standards, calibration samples and reference measurement techniques.
3. Validation of measurement techniques for elemental depth, selectivity and sensitivity for thin film energy materials such as novel compound materials with matrix elemental depth gradients, organic/inorganic hybrids, multi-layered structures and nano-structured surfaces, layers and interfaces.
4. Development of validated methods for the thermal characterisation of thin films as a function of temperature and for multi-parameter characterisation of energy thin film materials under specific stress conditions.
5. Development of large-area characterisation methods for process optimisation in thin-film energy material production, including fast contact and non-contact methods.

3 Research results

3.1 Development of models for the interpretation of advanced materials measurements and their correlation to product performance.

A combination of X-ray and optical methods were demonstrated on highly complex thin films used in energy applications, such as solar cells and power electronics. The new data analysis models developed in this project represent a significant advance of the state of the art, and allow reliable characterisation that was not possible before. The new insight into the effect of film anisotropy (the difference in properties when measured along different axes) on optical properties and the ability to determine the depth gradient of composition with high accuracy allows the intelligent optimisation of product performance. These methods are now available for companies in Europe to use. Some project highlights are described below.

3.1.1 Combined procedure for Grazing Incidence X-Ray Diffraction and Grazing Incidence X-Ray Fluorescence for determination of depth gradient of complex thin films solar cells

The microstructure of polycrystalline thin films solar cell absorbers, such as chalcogenides or perovskites is crucial to performance and significantly affected by the manufacturing process. A detailed understanding of the impact of deposition parameters on microstructure is critical to allow cost-effective manufacturing. For instance, high efficiency Cu(In,Ga)Se_2 (CIGS) solar cells are manufactured in a 3-stage co-evaporation process to generate a complex elemental composition that changes through the thickness of the film to optimism performance.

Grazing Incidence X-Ray Difraction (GIXRD) can provide information about crystal phase and relative fraction of multiphases of materials, however it does not allow quantification of elemental composition. In contrast, grazing Incidence X-Ray Fluorescence analysis (GIXRF) can provide information about the elemental in-depth distribution of the composition in thin films in the nano-meter and micro-meter range. In both cases, different angles of incidence are used to tune the information depth from a few nano-meters using very shallow angles up to few micro-meters information depth for standard geometry (e.g. XRF with an angle of incidence of 45°). This variation of the information depth allows for the determination of an in-depth gradient by using a set of angles of incidence instead of a single one. Here, the highest sensitivity for a non-homogenous in-depth distribution is in the region of grazing incidence with angles up to a few degrees. The information depth of a characteristic X-ray fluorescence radiation depends on both the element itself (atomic number) and the compositional matrix making depth analysis using GIXRF methodology very challenging to quantify.

CIGS samples were provided by a researcher excellence grant (REG(HZB)). GIXRD and GIXRF measurements were performed separately on these samples. A new data format structure for elemental depth gradients in thin film layers was defined as input parameter for GIXRF and GIXRD calculation and fitting algorithms.

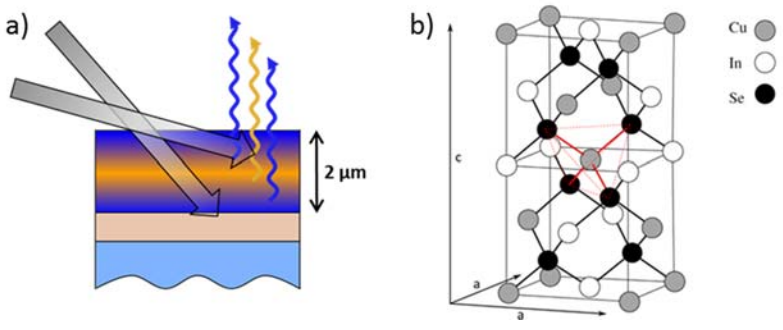

***Figure 1**: a) The 2 µm thick CIGS-layer grown on molybdenum coated glass will be measured under different angle of incidence to tune the information depth of the characteristic fluorescence lines for depth dependent NEAFS and EXAFS. b) The tetrahedrally bonded CIGS semiconductor has a chalcopyrite crystal structure. The lattice positions of In can also be occupied by Ga depending on the composition.*

To calculate the fluorescence intensities from a non-homogenous thin film the elemental in-depth gradient can be approximated by a layer-stack of homogenous sub-layers. For this procedure a partitioning in non- equidistant sub-layers is performed, where the top-layer which corresponds to the side of the front-contact is the thinnest layer and the layers towards the back layer become gradually thicker (see Figure 2, left). In

Figure 2 at the right hand side the contribution of the sub-layers to the total fluorescence intensity of the Cu Ka line is calculated. The variation of this contribution over the angle of incidence is shown. The top-layer (n=0) has the highest contribution for the smallest angles but decrease to nearly '0' for an angle of incidence of 3.2°, whereas the bottom layer (n=25) has nearly no contribution up to an angle of incidence of 1.3° and the highest contribution to the total fluorescence intensity from an angle of ~ 5°.

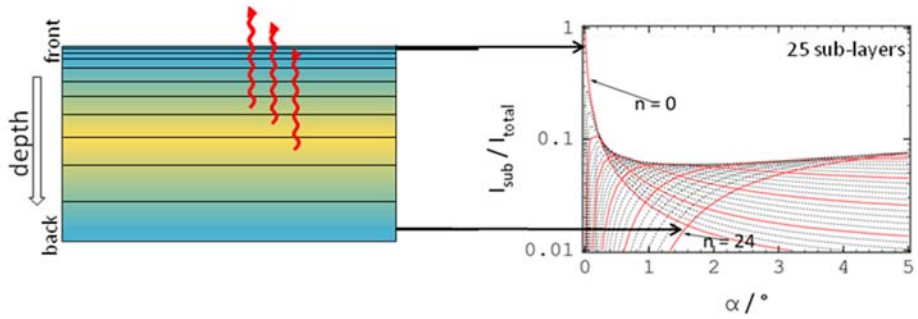

***Figure 2**: Partitioning of the in-homogenous thin film into a layer-structure of sub-layers. The elemental in-depth gradient will be approximated by this stack of homogenous sub-layers. It allows calculation of the fluorescence intensities from the sub-layer-stack.*

A GIXRD software tool was developed which enables quantitative simulations of full GIXRD patterns. The software tool is capable of simulating 2D XRD patterns for samples with elemental gradients and texture. Simulation studies were performed to analyse the uniqueness of the GIXRD results and hence uncertainties of the GIXRD fit. Numerical simulations for GIXRD and GIXRF were performed containing different kinds of test model samples to determine parameter regions for stable fitting results and therefore to optimise the GIXRF and GIXRD fitting strategies.

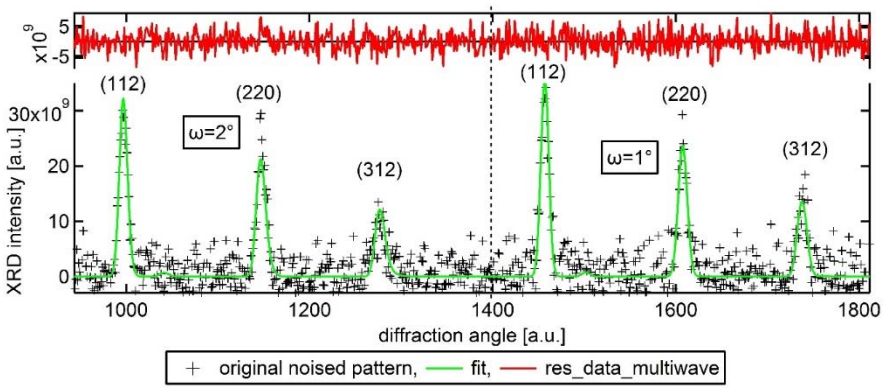

***Figure 3**: Example of fit of the original GIXRD at incidence angles of 1° and 2° including a noise function with standard deviation of 1e9. Only the areas around the main peaks were used and are plotted. The standard deviation of the Gaussian noise function is 3e9.*

Simulations for GIXRD test models show that an improved knowledge of the composition of the surface near region (angular range from 0° up to 3° for these CIGS samples) can provide better starting parameters for the fit and more stable results for the elemental depth gradients determined. It was also noted that the uncertainty in fundamental X-ray parameters, such as fluorescence cross section, are critical to achieving improved quantification of depth resolution. To support this work the X-Ray fluorescence yield of the K shell (the principal energy level) of Gallium (Ga) was determined with a low relative uncertainty of 4 %.

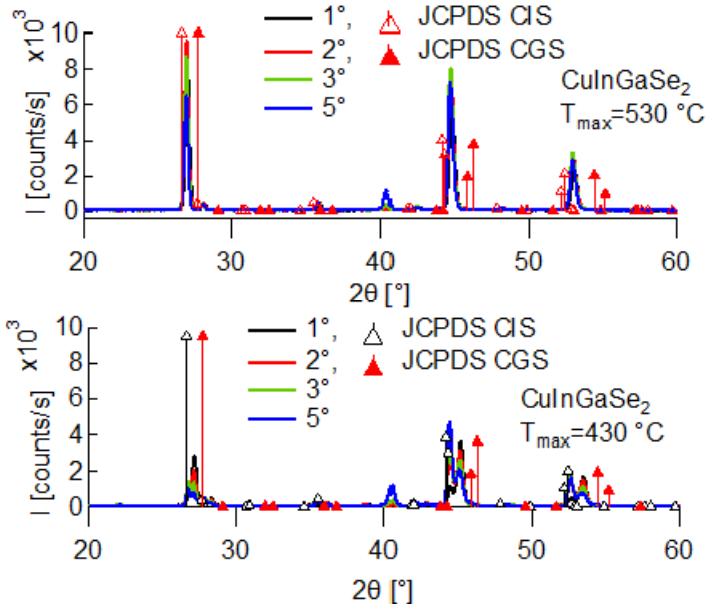

***Figure 4**: GIXRD patterns of CIGS samples produced at two susbtrate temperatures (530 °C and 430 °C) exhibiting pronounced Ga depth profiles. Based on these measurements we have developed an improved fitting routine that allows the determination of a distinct elemental depth profile which fits to both GIXRF and GIXRD measurements, providing higher accuracy that what can be otained by the separated analysis of each measurement.*

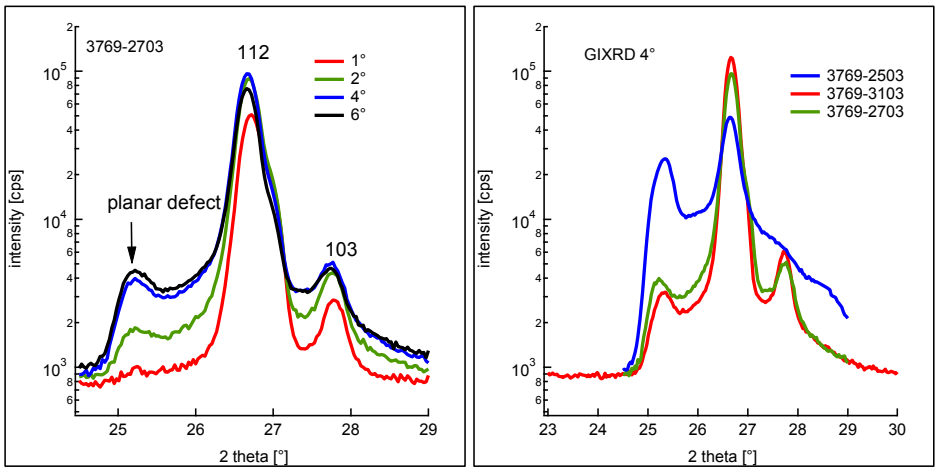

***Figure 5**: GIXRD pattern of CIGS samples with pronounced Cu depth profiles are shown. An important feature is a peak left of the 112 peaks which we are able to assign to planar defects. The GIXRD measurements at different incident angles allow us to model a depth profile of the amount of the planar defects that was correlated to elemental depth profiles obtained by GIXRF.*

In summary, a new data analysis procedure combining GIXRF was developed that allows the determination of the in-depth distribution of chemical elements in CIGS thin-film solar cells without prior knowledge about the gradient nor restriction on the elemental composition within the thin film. This is crucial for the optimisation and improvement of efficiency of complex thin film solar cells. Funding for future R&D development through a new EMPIR project 16ENG03 HyMET has been secured to transfer this capability into an online process control method during thin film deposition.

3.1.2 New model that allows measurement of complex refractive index of rough samples

It is a very challenging task to investigate and quantify optical properties, such as the complex refractive index, of CIGSe solar cells due to substantial roughness. Nevertheless, such properties are critical when

optimising the performance of the solar cell as they define how light is absorbed by the thin film before it is transformed into electricity. In this project we demonstrated that

- Mueller Polarimetry is a better method for investigating rough samples than ordinary ellipsometry.
- Mueller Polarimetry and surface roughness measurements are a strong combination for obtaining insight into the optical material properties.
- The observed dielectric function values are smaller than reported in the literature indicating that there are voids in all the thin film absorber layers used in the CIGS solar cells investigated.

Experiments

The sample was a CIGS standard absorber layer manufactured by REG(HZB). The CIGS layer was deposited on a glass substrate which had previously been coated with a molybdenum contact. No further layers were deposited on top of the CIGS. The recorded signal from the Mueller polarimetry may be written as:

$$I = I_{DC} + I_{f_0}\sin(\omega_0 t + \phi_0) + I_{f_1}\sin(\omega_0 t + \phi_0) + I_{2f_0}\cos(2\omega_0 t + 2\phi_0) + I_{2f_1}\cos(2\omega_1 t + 2\phi_1)$$
$$+ I_{f_0+f_1}\cos((\omega_0+\omega_1)t + \phi_0 + \phi_1) + I_{2f_0+f_1}\sin((2\omega_0+\omega_1)t + 2\phi_0 + \phi_1)$$
$$+ I_{f_0+2f_1}\sin((\omega_0+2\omega_1)t + \phi_0 + 2\phi_1) + I_{2f_0+2f_1}\cos((2\omega_0+2\omega_1)t + 2\phi_0 + 2\phi_1) + \ldots$$

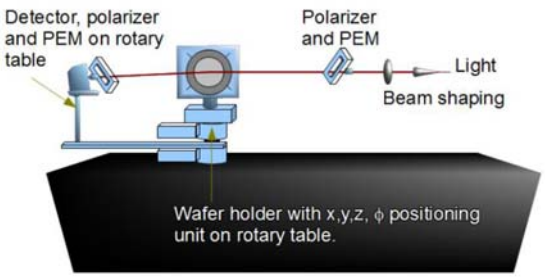

***Figure 6**: Illustration of the Mueller polarimetry setup.*

Where $\omega_j = 2\pi f_j \; j = 0,1$ are the angular modulation frequency of the Photo Elastic Modulators (PEMs) and $\phi_j \; j = 0,1$ are phases and

$$I_{DC} = I_{DC0} + J_0(A_0)I_{Y0} + J_0(A_1)I_{Y1} + J_0(A_0)J_0(A_1)I_{Y0Y1}$$
$$I_{f_0} = 2J_1(A_0)(I_{X0} + J_0(A_1)I_{X0Y1})$$
$$I_{f_1} = 2J_1(A_1)(I_{X1} + J_0(A_0)I_{Y0X1})$$
$$I_{2f_0} = 2J_2(A_0)(I_{Y0} + J_0(A_1)I_{Y0Y1})$$
$$I_{2f_1} = 2J_2(A_1)(I_{Y1} + J_0(A_0)I_{Y0Y1})$$
$$I_{f_0+f_1} = -2J_1(A_0)J_1(A_1)I_{X0X1}$$
$$I_{2f_0+f_1} = 2J_1(A_1)J_2(A_0)I_{Y0X1}$$
$$I_{f_0+2f_1} = 2J_1(A_0)J_2(A_1)I_{X0Y1}$$
$$I_{2f_0+2f_1} = 2J_2(A_0)J_2(A_1)I_{Y0Y1}$$

In these equations J_n is Bessel functions of the first kind of order $n=0,1,2$ and A_j is the Bessel amplitude. In the experiment the data was normalised in the following way:

$$A_f = I_f / I_{DC}, \quad f \in \{f_0, f_1, 2f_0, 2f_1, f_0+f_1, 2f_0+f_1, f_0+2f_1, 2f_0+2f_1\}$$

In this way nine components of the Muller matrix were measured simultaneously. The remaining elements may be obtained by rotating the PSG (Polarisation State Generator) and the PSA (Polarisation State Analyser).

Roughness measurements

Roughness measurements of the sample were performed with a commercial NX20 AFM from Park Systems equipped with PPP tip(s) and with a commercial confocal microscope Sensofar Plu Neox equipped with a 150 times magnifying lens. The two methods gave very similar results for the average rms roughness R_q (σ),70 nm and 68 nm, respectively. However, a very different result was observed in the measured correlation length by the two methods. The AFM correlation length was much longer. We believe that the longer correlation length measured by the AFM is due to the fact that the sample roughness is so high that we are not only using the outmost part of the tip. Therefore the correlation length obtained by the confocal microscope will be used. The measurements were analysed with the SPIP software from Image Metrology using the SPIP classical roughness calculation methods. This method calculated the surface roughness without applying any S or L filter.

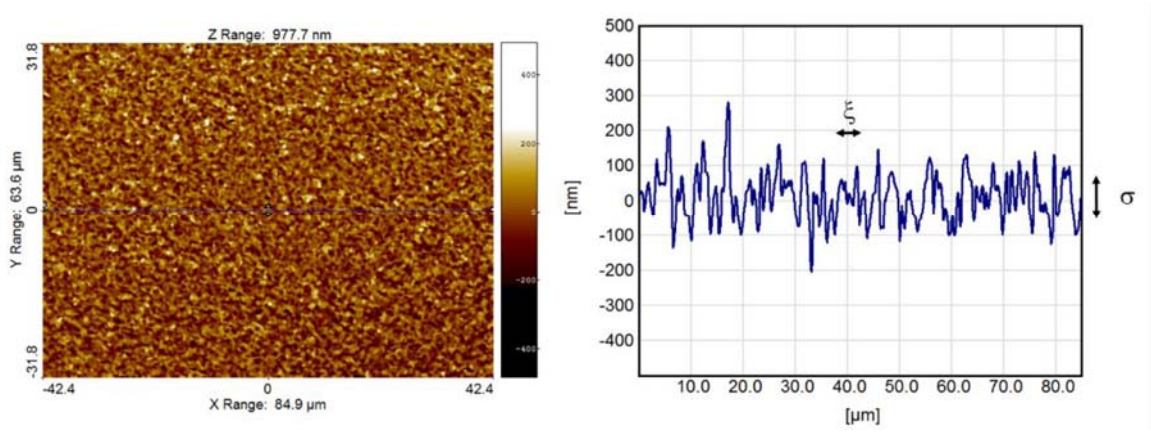

Figure 7*: Confocal microscopy image (height plot) of CIGS film acquired a 150x magnifying lens (left) and cross section illustrating the rms roughness σ and autocorrelation length ξ (right). An rms value of the heights of roughness irregularities σ = 68 ± 4 nm was extracted from the data using the commercial software SPIP from Image Metrology.*

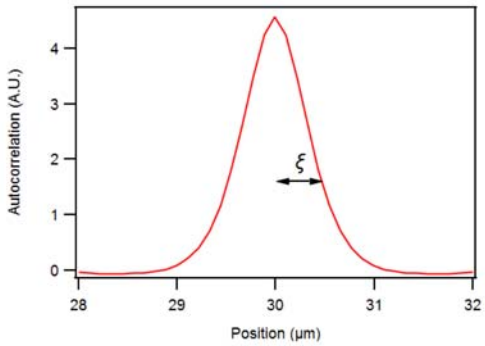

Figure 8*: Autocorrelation function of the data shown in Figure 6. The autocorrelation length ξ can be found as the length for which the function decreases by a factor 1/e; we find ξ = 465 nm.*

Modelling the effect of roughness

CIGS is an absorbing film in the wavelength range 300-900 nm; we can therefore consider the sample as a substrate. Figure 9 show two ways of simulating the optical response from a rough surface. The effective medium theory (A) is widely used and is very effective for characterisation of samples with low to medium roughness. Modelling of true surface (B) is hardly ever done because it is difficult and very time consuming, however this is the only predictable method for large roughness.

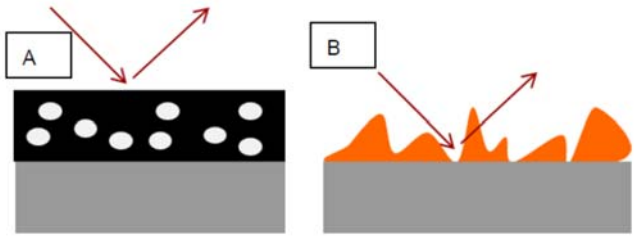

***Figure 9**: The figure illustrates two ways of calculation the optical response from a rough surface. A) Effective medium theory and B) Modelling of the true surface*

Effective medium theory

In effective medium theory, the opto-electronic properties of a complex medium such as an alloy, a colloidal solution or a medium with air intrusions, for instance a rough surface, are described by a single homogeneous effective medium. In this formalism, the complex permittivity $\langle\varepsilon\rangle$ of the effective medium (also called the 'effective permittivity') can be expressed in terms of the permittivities and volume fractions of the individual media making up the effective medium. A popular effective medium model to find the effective permittivity is the Maxwell-Garnett mixing formula, however, in a two phase system this model is only valid when the volume fraction of one phase is significantly larger than the other [1]. Instead we apply the Bruggeman formula which is symmetric with respect to the constituent media. For a two component system with permittivities ε_1, ε_2 and volume fractions f_1, f_2, respectively, the effective permittivity is given by

$$\langle\varepsilon\rangle = \frac{b + \sqrt{8\varepsilon_1\varepsilon_2 + b^2}}{4}, \quad b = (2f_1 - f_2)\varepsilon_1 + (2f_2 - f_1)\varepsilon_2$$

Modelling the true surface

The complex optical properties of an isotropic rough surfaces can be found using the Rayleigh-Rice formalism as described by Franta and Ohlidal [2,3]. The Rayleigh-Rice method is different from the traditional approach in the sense that the roughness layer does not have a set of dielectric constants of its own; it has the same dielectric constants as the bulk layer. The roughness is described by surface texture parameters that can be measured using optical and stylus profilometers. The best choice for a rough interface would be a confocal microscope with a high numerical aperture (NA) objective, since the tip of a stylus profilometer will give a depth depending influence of one of the parameters called the correlation length.

The change in the complex Fresnel reflection coefficients for a randomly rough surface characterised by the rms roughness σ and the correlation length ξ can be calculated as

$$\Delta r_{s,p} = \sigma^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_{s,p}(K_x, K_y) \times w(K_x - n_0 k_0 \sin\theta_0, K_y) dK_x dK_y$$

Where n_0 is the (complex) refractive index of the ambient, k_0=2π/λ is the wavenumber of the radiation, θ_0 is the angle of incidence and Kx and Ky are reciprocal lattice space coordinates. The kernel functions fp, are given by:

$$f_p(K_x, K_y) = A_p + (b - c)\frac{B_{31}K^2 + B_{62p}(K_y^2 + bc)}{K^2} + K_x\frac{B_{61p}[K^2(b-c)^2 + (K^2 + bc)^2] - B_{32p}}{K^2 + bc}$$

$$f_s(K_x, K_y) = A_s + B_{5s}\frac{(b - c)(K_x^2 + bc)}{K^2 + bc}$$

where

$$b = \sqrt{n_0^2 k_0^2 - K^2}$$

$$c = \sqrt{n_1^2 k_0^2 - K^2}$$

$$K = \sqrt{K_x^2 + K_y^2}$$

[1] V.A. Markel, J. Opt. Soc. Am. A **33**, 1244 (2016).
[2] D. Franta and I. Ohlídal, Opt. Commun. **147**, 349 (1998).
[3] D. Franta and I. Ohlídal, Opt. Commun. **248**, 459 (2005).

And

$$A_p = k_0^2 n_0 n_1^2 X/D$$
$$B_{31p} = k_0 n_0^2 n_1^2 \sin(\theta_0) W/D$$
$$B_{62p} = k_0 n_0 n_1 \cos(\theta_1) X/D$$
$$B_{61p} = n_0 n_1 \cos(\theta_1) W/D k_0$$
$$B_{32p} = k_0^3 n_0^2 n_1^2 \sin(\theta_0) X/D$$
$$A_s = -2k_0^2 n_0 n_1 \cos(\theta_0) \cos(\theta_1) r_{s0}$$
$$B_{5s} = -2k_0 n_0 \cos(\theta_0) r_{s0}$$

With

$$D = (n_0 \cos\theta_0 + n_1 \cos\theta_0)(n_0^2 \sin^2\theta_0 + n_0 n_1 \cos\theta_0 \cos\theta_1)$$
$$X = (n_0^2 - n_1^2)\cos(\theta_1)\, t_{p0}$$
$$W = (n_1/n_2 - 1/n_1) n_0 \sin(\theta_0) t_{p0}$$

Here n_1 is the complex refractive index of the material with the rough surface, θ_1 is the transmission angle and r_{s0}, r_{p0}, t_{p0}, t_{s0}, are the Fresnel reflection and transmission coefficients for flat interface.

The normalised power spectral density function w can be parametrised with the widely used Gaussian function:

$$w(K) = \frac{\xi^2}{4\pi} e^{-K^2\xi^2/4}$$

Results

If the pseudo-permittivity ε, or equivalently the complex refractive index n, is known, either from extraction from measured $\langle\varepsilon\rangle$ with the Bruggeman formula or from direct measurements on a flat homogeneous material, the Rayleigh-Rice formula can be used to calculate the ratio of the 'effective' complex reflection coefficients $r_p r_s = (r_{p0}+\Delta r_p)(r_{s0}+\Delta r_s)//$, from which the ellipsometric parameters *N*, *S* and *C* may be calculated.

From the measurements on our samples, we were unable to obtain satisfactory values for *n* using the Bruggeman analysis described above, which threats the roughness as a homogeneous layer with one permittivity. A more advanced Bruggeman analysis approach [4] might have been successful, but would require many more variables than the Rayleigh-Rice approach.

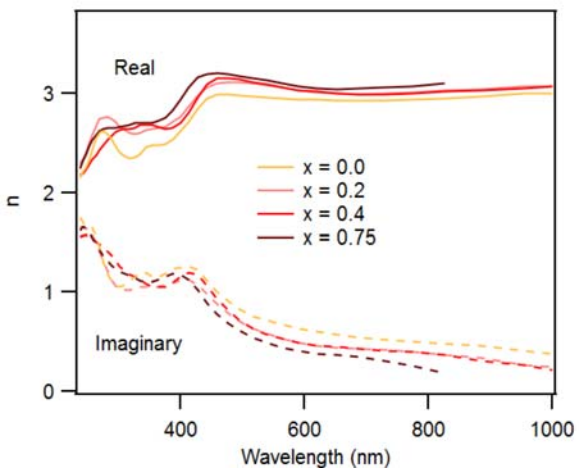

***Figure 10**: Real and imaginary (dashed line) components of the complex refractive index (n) for CIGS samples with different Ga concentrations $x = [Ga]/([Ga]+[In])$, from literature. The n value for x = 0.0 is taken from [5], the values for x = 0.2, 0.4, and 0.75 are taken from [6]. According to this data, the refractive index only change slightly with Ga concentration.*

[4] D. Lehmann , F. Seidel and D. RT Zahn SpringerPlus 3:82 (2014)
[5] M.I. Alonso, K. Wakita, J. Pascual, M. Garriga, and N. Yamamoto, Phys. Rev. B 63, 75203 (2001).
[6] M.I. Alonso, M. Garriga, C.A. Durante Rincón, E. Hernández, and M. León, Appl. Phys. A Mater. Sci. Process. 74, 659 (2002).

We used the roughness value of σ = 68 nm found from the confocal microscopy data as input parameter in the Rayleigh-Rice equation; in order to determine the correlation length ξ we calculated a library using a range of ξ values with a spacing of 5 nm. An optimal solution from this library was found by minimisation of the squared sum of errors (χ^2) between the calculated and measured Müller parameters [7].

Figure 11 shows the measured Müller matrix elements as well as *N*, *S*, and *C* parameters found by calculating a library for a range of ξ values and performing χ^2 minimisation. The *N*, *S*, and *C* parameters were calculated for the four *n* values shown in Figure 5, corresponding to different *x* values. The values found for ξ are 320 nm, 310 nm, 305 nm, and 305 nm for x = 0.0, 0.2, 0.4, and 0.75 respectively.

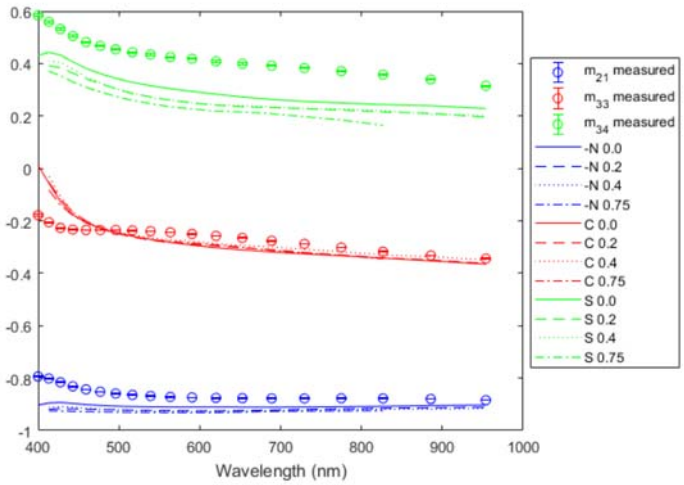

***Figure 11**: Measured Müller matrix elements and best fit elements calculated for n values corresponding to different values of the Ga concentration x.*

Despite the deviation at low wavelengths, the best fit to data is shown for Gallium (Ga) concentration value x = 0.0. As we know these CIGS samples do have a homogeneous chemical composition as a function of depth. A more precise determination of x would require treatment of the film as a multilayer system with varying values of x and a top layer that is rough. The modelling developed here allows for these calculations to take place due to the correct treatment of roughness in such optical measurements.

Summary

In summary, a new model that allows measurement of complex refractive index of rough samples, such as thin film solar cells, was successfully developed and demonstrated. It includes a new data analysis method to combine Mueller Polarimetry data with the real surface roughness allowing the characterisation of samples where it was not possible before using traditional ellipsometry. The new hybrid metrology approach uses the measured surface roughness, correlation length on the actual surface together with the measured complex refractive index of bulk CIGS material in a broadband wavelength range (300 nm to 1700 nm). These data were inserted into the Rayleigh-Rice theory and the ellipsometric parameters were fitted. We demonstrated that the hybrid approach were very stable and gave excellent results.

Conclusions

The project met the objective of developing models for the interpretation of advanced materials measurements and their correlation to product performance. It did this using a combination of X-ray and optical methods which were demonstrated on highly complex thin films used in energy applications, such as solar cells and power electronics. The new data analysis models developed in this project represent a significant advance of the state of the art, and allow reliable characterisation that was not possible before. The new insight into the effect of film anisotropy (the difference in properties when measured along different axes) on optical properties and the ability to determine the depth gradient of composition with high accuracy allows the intelligent optimisation of product performance. These methods are now available for companies in Europe to use. Some project highlights are:

[7] M.H. Madsen and P.-E. Hansen, Surf. Topogr. Metrol. Prop. **4**, 23003 (2016)

- A new data analysis procedure combining Grazing Incidence X-Ray Diffraction and Grazing Incidence X-Ray Fluorescence (GIXRF) was developed that allows the determination of the in-depth distribution of chemical elements in Copper-Indium-Gallium-Sulphur (CIGS) thin-film solar cells without prior knowledge about the gradient nor restriction on the elemental composition within the thin film. This is crucial for the optimisation and improvement of efficiency of complex thin film solar cells. Funding for future R&D development through a new EMPIR project 16ENG03 HyMET has been secured to transfer this capability into an online process control method during film deposition.
- A new model that allows measurement of complex refractive index of rough samples, such as thin film solar cells, was successfully developed and demonstrated. It includes a new data analysis method to combine Mueller Polarimetry data (a mathematical model) with the real surface roughness allowing the characterisation of samples where it was not possible before using traditional ellipsometry (an optical technique for investigating dielectric properties). The new method, in a broadband wavelength range (300 nm to 1700 nm) was applied to Copper-Indium-Gallium-Selenide and was able to identify internal stress in selected samples. Internal stress introduces unwanted polarisation dependent absorption that reduces the efficiency of the solar cell. The ability to measure internal stress in such complex thin films allows manufacturers to optimise the manufacturing process to improve performance.
- Innovative ellipsometry models for materials with anisotropic permittivity were developed that allow investigation of optical properties of complex thing films such as those with periodic structures used for increasing performance of solar cells or reducing energy losses in light emitting diodes.

3.2 Traceable determination of the correlation between material composition and electronic structure over a broad spectral range.

The expansion of the spectral range for electronic structure characterisation allows more accurate measurements and facilitates correlation with material composition as it provides a complete image of the electronic behaviour of thin film energy materials under working conditions. The work in this project and the demonstration of applicability of such methods for thin films used in different energy applications highlighted the need for standard and reliable calibration methods for ellipsometry. Significant input from this project has helped to generate a new standard at the German Institute for Standardisation (DIN) and is expected to lead to an international (ISO) standard in the near future. Some highlights are described below.

3.2.1 Combined analysis of far-UV to far-IR ellipsometric analysis of transparent oxide samples

The quality of thin film transparent oxides is critical for applications in power electronics, solar cells, solid state lighting, among others. The dielectric constant, measured via optical methods such as ellipsometry is typically used as an indication of quality. However, different companies and R&D institutes may measure only a limited spectral range, making comparison of data very challenging and can delay manufacturing process upscaling.

The aim of the activity was to optically characterise materials relevant for energy applications in a broad spectral range. For this purpose, indium free transparent conducting oxide (TCO) layers were produced by a researcher excellence grant (REG(CEA)). A set of Aluminium (Al) and Ga doped Zinc Oxide (ZnO) layers were prepared on thermally oxidised Si substrates and sent to partners BAM and PTB for ellipsometric investigations. The composition of the samples is schematically presented in Figure 12.

***Figure 12**: Schematic of the investigated TCO layers produced on thermally oxidised Si substrates*

Spectroscopic ellipsometry measurements in the energetic range 0.7-6.5 eV were performed using a M2000DI (J. A. Woollam Co.) rotating compensator ellipsometer (RCE), under different angles of incidence (50°-75°). The measurements performed by this instrument are traceable to the SI length definition by calibration with film thickness standards from PTB. The optical constants and the thickness of the samples were derived from fiting the experimental data using the multilayer system surface roughness/(doped) ZnO layer/Silicon Dixode (SiO_2) layer/Si substrate. The thickness of the SiO_2 layer was determined to be ~502 nm for the reference sample. This thickness slightly varies from sample to sample, fact directly noticeable from the measurements performed in the mid-infra-red (IR) range (and discussed in the Ga doped ZnO section below).

Undoped ZnO film

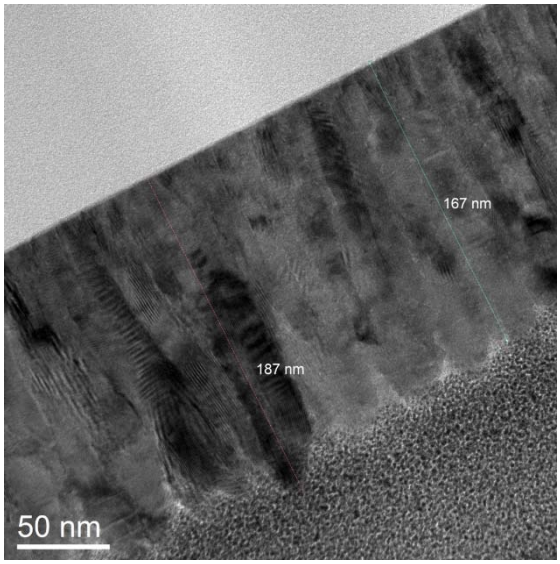

***Figure 13**: TEM image of a ZnO layer deposited on thermally oxidised Si substrate. The image shows a wavy surface due to the presence of columnar crystallites. The thickness determined in the measured region varies from 165 nm to 200 nm and indicates the importance of considering a roughness layer in the ellipsometric theoretical model. Similar results were obtained from REM and WLIM measurements.*

The first sample investigated, **AZO_P01,** was an undoped thin film of ZnO on thermally oxidised Si substrate. The thickness of the ZnO film was determined considering a Cauchy dispersion model in the transparent range 0.7-2.3 eV. A thickness of 20.3 nm and a roughness of 3 nm were obtained. The optical constants were determined in the extended measured energetic range. The comparison between experiment and simulation is shown in Figure 14. A very good agreement was met by considering the Herzinger-Johs parameterised semiconductor oscillator function (Psemi-M0). A 3.26 eV optical band gap was calculated for the sample.

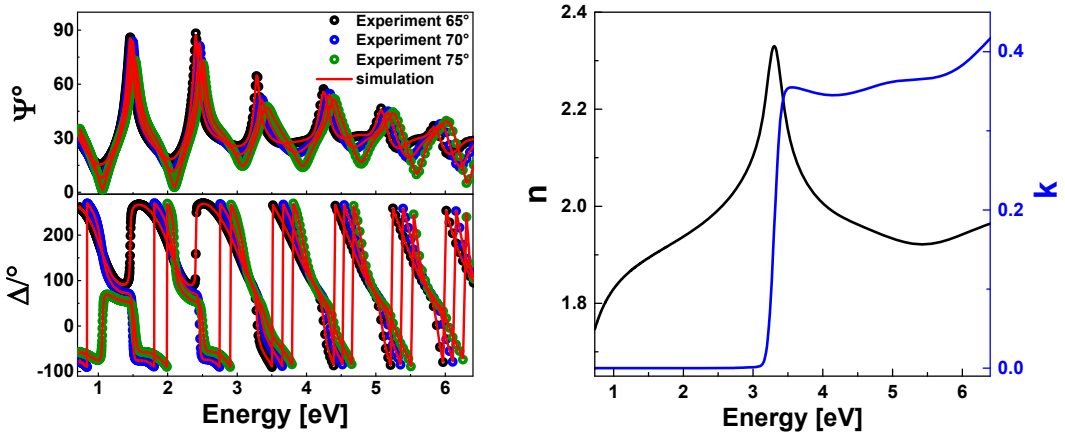

***Figure 14**: left: Measured and simulated Ψ and Δ ellipsometric parameters for 3 different angle of incidence; right: calculated n and k for a 20.3 nm thick ZnO layer*

Our next step was to extend the measured energetic range from mid IR to far UV. The measurements in the mid IR range were performed at BAM and the analysis was performed using the Spectraray software, while the measurements in the ultra-violet (UV) range were performed at the PTB facility. The analysis was performed by BAM using the WVASE software. For that, the experimental parameters measured by BAM in the near ultra-violet-visible-near infra-red (NIR-VIS-NUV) and the ones measured by PTB in the UV range were merged and simultaneously fitted. The result of the analysis in the range 0.7-15 eV is presented in Figure 15.

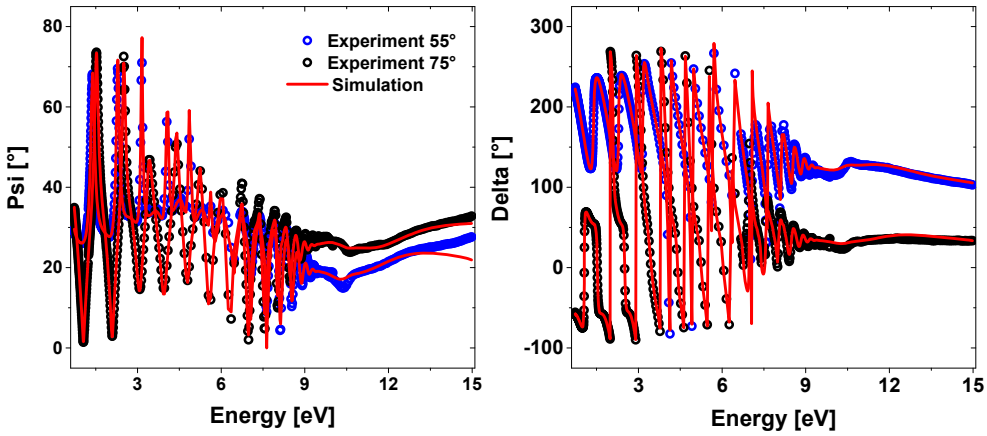

***Figure 15**: Experiment vs. simulation for parameters Psi and Delta for a ZnO layer deposited on thermally oxidised Si substrate*

The results of the analysis in the mid-IR range are shown in Figure 16.

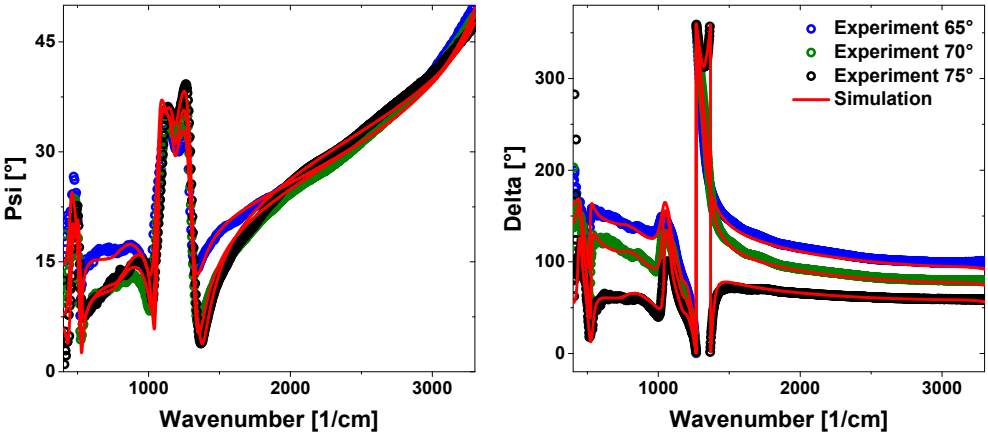

***Figure 16**: Comparison between experiment and simulation in the mid IR spectral range; the ZnO film was measured at three angles of incidence (65°, 70°, 75°)*

From the analysis presented above, the refractive index and the extinction coefficient was determined in the entire measured energetic range. The calculated optical constants are shown in Figure 17. For a better view, a logarithmic scale was chosen.

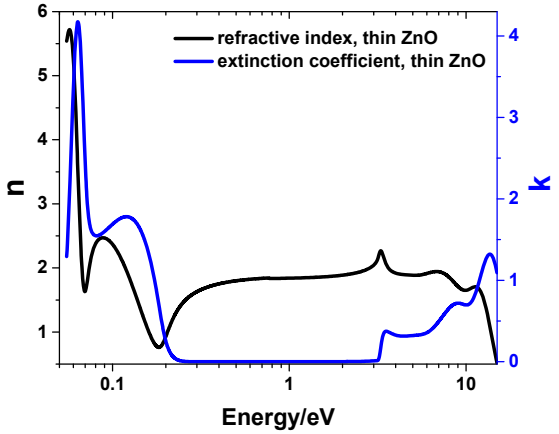

***Figure 17**: Refractive index and extinction coefficient from mid-IR to UV.*

Al doped ZnO films

Similar analysis and measurements were performed for doped ZnO films produced by atomic layer deposition.

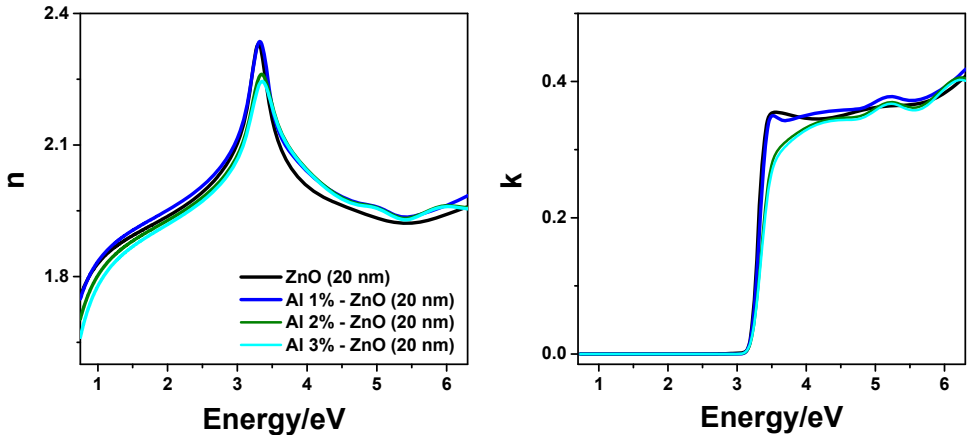

***Figure 18**: Comparison between the optical constants of the Al (0%-3%) doped ZnO films; left: refractive index, right: extinction coefficient.*

Ga doped ZnO films

The thickness and roughness of three 5% Ga doped ZnO layers were determined considering a Cauchy dispersion in the energetic range 1.8-2.8 eV. The dielectric function of the Ga doped ZnO layers in the NIR-VIS-NUV range was calculated using a combination of Drude model in the near infrared energetic range, Tauc- Lorenz model in the the band gap range and a Gauss model in the higher energetic range.

$$\varepsilon(En) = \varepsilon_D(En) + \varepsilon_{TL}(En) + \varepsilon_G(En)$$

with the Drude term being described by the equation:

$$\varepsilon_D = \frac{-\hbar^2}{\varepsilon_0\rho(\tau \cdot E^2 + i\hbar E)}, \qquad where \quad \rho = \frac{m^*}{Nq^2\tau} = \frac{1}{q\mu N}.$$

Ga doping in ZnO film	Thickness/nm	Roughness/nm	Band gap/eV
0% Ga	20.3	3	3.26
5% Ga	18.3	4	3.63
5% Ga	33	4.7	3.78
5% Ga	43.2	8.8	3.82

***Table 1**: Information obtained (thickness, roughness and optical band gap) for the investigated samples using the Herzinger-Johs parametric optical model in the extended energetic range.*

Figure 19 shows the refractive index and the extinction coefficient for the Ga doped and undoped ZnO layers. A clear difference between the undoped sample and the doped ZnO layers is observed. The refractive index decreases significantly in the range 0.7-3.5 eV with increasing the concentration of the Ga and increases in the range 3.5-6.5 eV. The extinction coefficient shows an important increment of the Drude component in the near infrared spectral range with introducing the Ga dopant. We also observed a slight variation with variating the thickness of the ZnO layer (for the same concentration of the Ga).

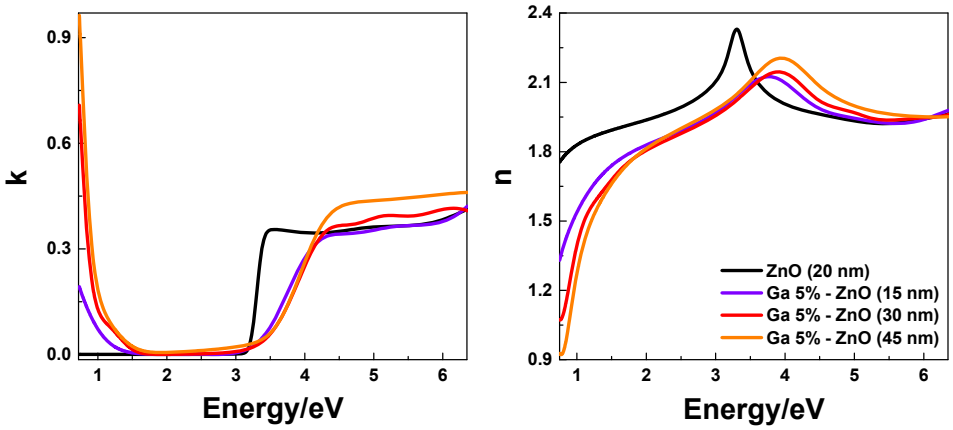

***Figure 19**: Extinction coefficient and refractive index for Ga doped ZnO layers*

An analysis of free-carrier absorption in Ga doped ZnO layers (using solely ellipsometry) was carried out. As mentioned at the beginning of the section, the free carrier effects are described using a Drude oscillator.

5% Ga doped ZnO sample	N/cm^{-3}	μ/cm^{2}V^{-1}s^{-1}	ρ/Ω-cm	τ/10^{-15}s
18.3 nm	2.24*10*^{20}	21.1	0.0013	3.36
33 nm	3.56*10*^{20}	16.8	0.001	2.67
43.2 nm	4.76*10*^{20}	16.9	0.0008	2.7

Table 2: *Calculated resistivity, carrier concentration, carrier mobility and scattering time for the three 5% Ga doped samples. Note that the carrier effective mass was kept constant (m^*/m_0=0.28).*

Summary

In summary, a new data analysis method was developed, taking into account a broad spectral range (from ultra violet to infrared) in order to determine traceable optical properties of surfaces and thin films. This method was demonstrated in transparent conducting oxide layers used in a range of energy applications, such as power electronics, solar cells and solid state lighting. Additional studies not shown here, demonstrated that these optical properties were not affected by long term exposure to UV irradiation. Stability of the optical and dielectric constant is crucial for energy applications as the performance of energy devices rely on these parameters.

Conclusions:

The project met the objective of traceable determination of the correlation between material composition and electronic structure over a broad spectral range. The expansion of the spectral range for electronic structure characterisation allows for more accurate measurements and facilitates correlation with material composition as it provides a complete image of the electronic behaviour of thin film energy materials under working conditions. The work in this project and the demonstration of applicability of such methods for thin films used in different energy applications highlighted the need for standard and reliable calibration methods for ellipsometry. Significant input from this project has helped to generate a new standard at DIN and is expected to lead to an international (ISO) standard in the near future. Highlights delivered by the project include:

- A new data analysis method was developed, taking into account a broad spectral range (from ultra violet to infrared) in order to determine traceable optical properties of surfaces and thin films. This method was demonstrated in transparent conducting oxide layers used in a range of energy applications, such as power electronics, solar cells and solid state lighting. Additionally, the effects of UV irradiation on the optical and electronic properties of the layers were analysed. Stability of the optical and dielectric constant is crucial for energy applications as the performance of energy devices rely on these parameters.
- The consortium contributed to an inter-laboratory study between DIN and the International Organisation for Standardisation (ISO) related to the ellipsometry calibration methods developed in this project. This study comprised the traceable determination of dielectric functions of different classes of carbon-based thin layers and will inform the development of new standards.

3.3 Validation of measurement techniques for elemental depth, selectivity and sensitivity for thin film energy materials such as novel compound materials with matrix elemental depth gradients, organic/inorganic hybrids, multi-layered structures and nano-structured surfaces, layers and interfaces.

Complex thin film energy materials often have non-uniform composition that directly affects their performance. Such variation in composition is notoriously difficult to measure. This project validated new non-destructive methods for determining elemental depth, selectivity and sensitivity of such complex thin films. In order to improve the accuracy and reliability of the new methods, the project also determined fundamental X-ray parameters of elements of interest for energy applications with significant lower uncertainties. These fundamental parameters, such as absorption cross section and fluorescence cross section, are used for the quantification of X-ray measurements, therefore a reduction in the uncertainty of fundamental parameters means more accurate determination of microstructures via X-ray measurements. The project's new methods are now available for EU companies to use, and additionally this work resulted in a CMC entry within BIPM for quantification of thin CIGS layers. Some highlights are described below.

3.3.1 Combined GIXRF and NEXAFS to allow measurement of depth dependent elemental composition and chemical speciation

Emerging liquid phase crystallisation techniques provide excellent material quality and open circuit voltages in crystalline Si thin-film photovoltaic devices. Nanophotonic light harvesting structures by nanoimprint-lithography further enable near-perfect sunlight absorption and improved efficiencies. But the interface between nanostructured substrate and Si absorber has lead so far to strong recombination losses and, as a consequence, to non-satisfactory efficiency. Thus the ability to chemically analyse the buried interface structure in these 3D nanostructured thin films would allow optimisation of the light trapping and improvement of solar cell efficiency.

Experimental

A set of nanostructured liquid phase crystallised silicon thin films on glass was fabricated for GIXRF- near edge X-ray absorption fine structure spectroscopy (NEXAFS) analysis. The glass-silicon interfaces under investigation are 750nm-periodically textured and exhibit varying aspect ratios h/p (h: texture hight; p: period) as shown in Table 3. The aspect ratio of this interface texture has been shown to influence the solar cell performance[8]. Two samples had a periodical sinus structure, two samples a cylindrical structure and one sample had no further structure for the sake of comparison.

GIXRF-NEXAFS measurements were performed in the soft X-ray range using PTB's plane grating monochromator beamline (PGM) at the synchrotron radiation facility BESSY II in Berlin. The PGM monochromator beamline for undulator radiation provides high photon flux of high spectral purity within an photon energy range of 78 eV up to up to 1860 eV. The angle of incidence was varied using 0.15°, 0.6°, 1° and 15° as excitation angle between sample surface incidence beam. This tunes the information depth for the respective element from only a few nm in the topmost surface region up to few 100 nm into the bulk.

[8] *Preidel et al., Journal of Applied Physics 117, 225306 (2015)*

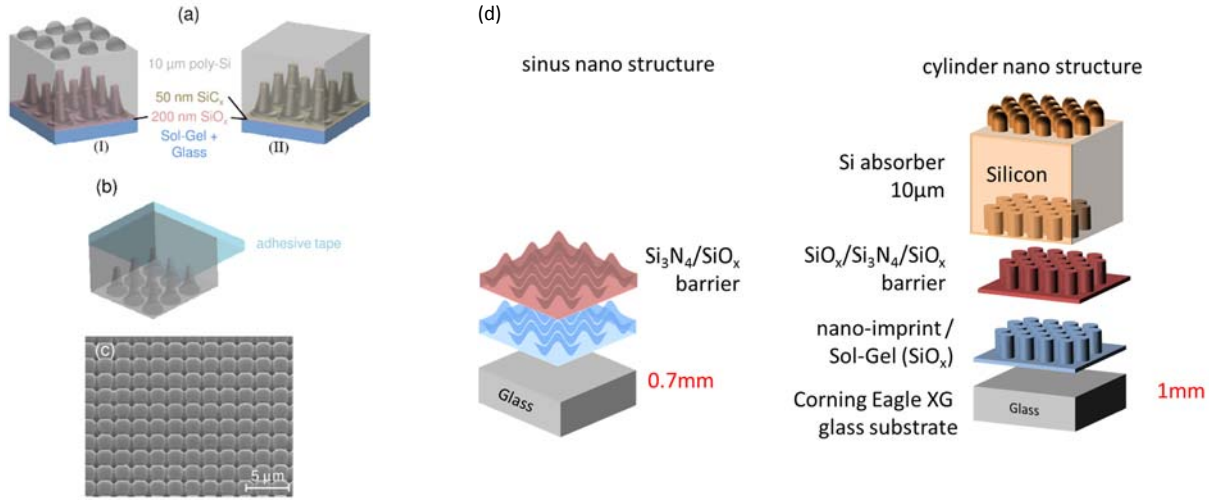

***Figure 20**:* Schematic illustration of the sample preparation. a) Solar cell absorber stack with a 200 nm SiO_x interlayer (left, (I)) and a 200 nm SiO_x / 50 nm SiC_x stack (right, (II)). b) Absorber supported by adhesive tape after glass/Sol-Gel removal in concentrated hydrofluoric acid. c) Scanning electron microscope image of the exposed textured silicon back surface after etching, showing the inverse Sol-Gel tip structure. d) Examples of types of nanostructured cells investigated: sinus and cylindrical.

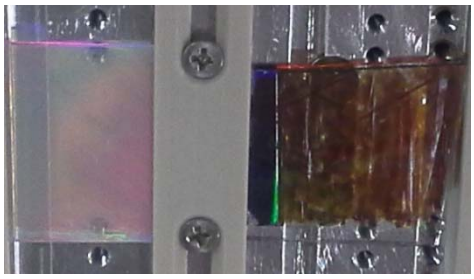

***Figure 21**: Photograph showing the nanostructure substrate without any further top layers (on the left side) and a sample with two areas including top layers on the nanostructured substrate (on the right side): one area with the microcrystalline thin film of about 10 µm and the etched area of about 300 nm thickness on top of the nano-structure.*

Results

Table 3: Nanostructured Si solar cell sample characteristics

Name	structure	period	height	aspect-ratio (h/P)	Si
Sample 1	sinus structure	500nm	130-140nm	0,27	No
Sample **2**	sinus structure	750nm	150nm	0,2	No
Sample **3**	cylinder structure	750nm	290nm	0,39	Yes d~ 100nm -400nm
Sample 4	cylinder structure	750nm	290nm	0,39	Yes d~ 300nm -600nm
Sample 5	No structure				

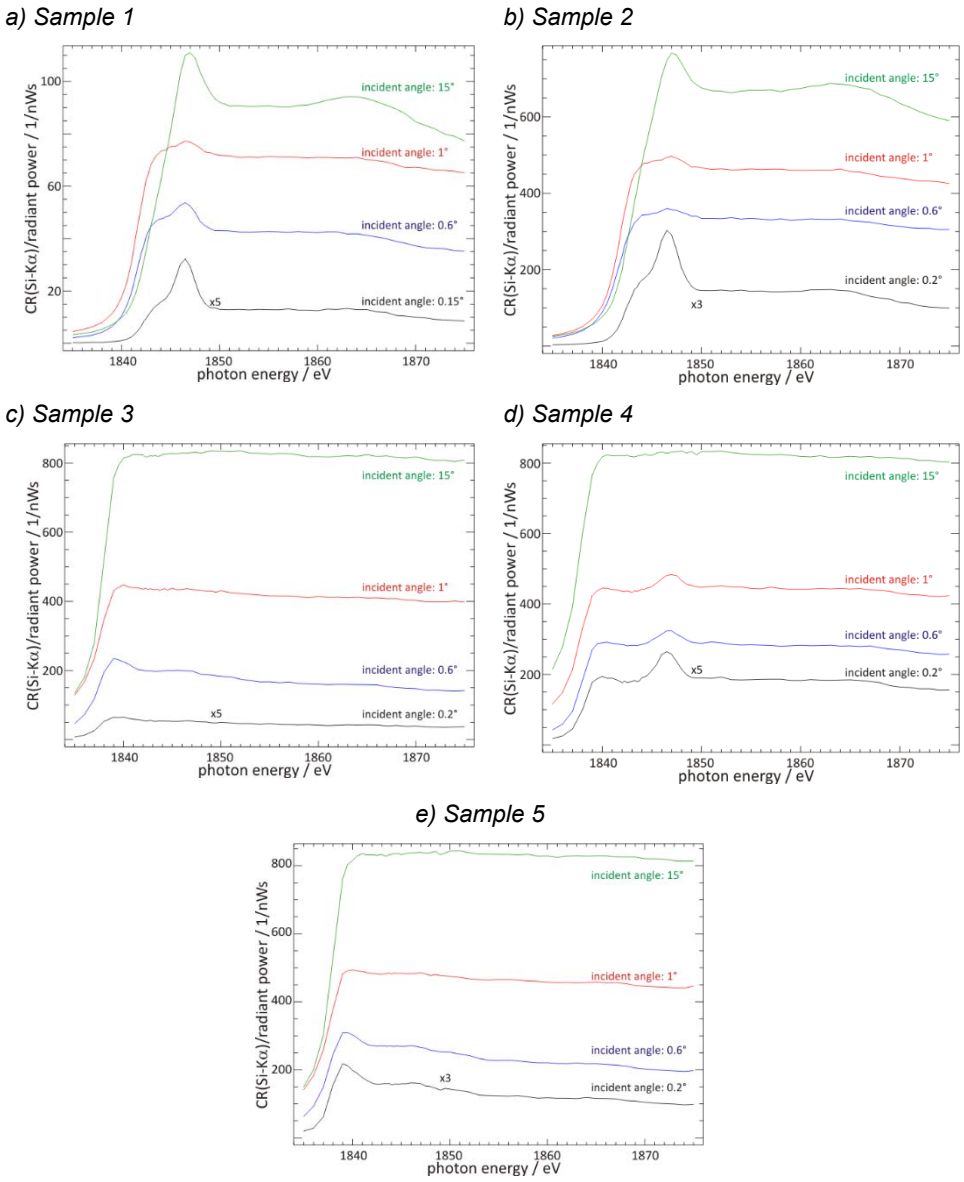

***Figure 22**: Combined Si-K GIXRF-NEXAFS measurements of all samples are shown for the different angles of incidence for samples 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e) indicated in table 1.*

In Figure 22 the Si-K GIXRF-NEXAFS measurements of all samples are shown for the different angles of incidence. Clear differences can be observed between the different samples and as a functions of angle of incidence. Quantification as a function of depth requires that the X-ray standing wave is taken into account. By developing a model that includes this contribution we are able to measurement the depth dependent elemental composition as well as chemical speciation. Analysing the elemental depth profiles of such materials, it is possible to determine the chemical binding states at the buried interfaces as: Si-Si (1840), Si-N (1847) and Si-O (1852).

3.3.2 Advances in quantification of grazing incidence X-ray spectroscopy for determination of multilayer thin film interface quality

The quality of multilayer thin films, including their interfaces are critical for the performance and reliabiity of power electronics. Therefore this project further developed of GIXRF for chemical analysis and elemental depth profiling in multilayer stack used in power electronics.

New traceable measurement facility

As part of this project, the CASTOR (Chamber for Analysis and Spectrometry in Transmission Or Reflection) setup dedicated to GIXRF, has been successfully installed and calibrated on both branches of the CEA-LNHB Metrology beam line of the SOLEIL Synchrotron facility in France and was used to characterise multilayer thin films for power electronic applications.

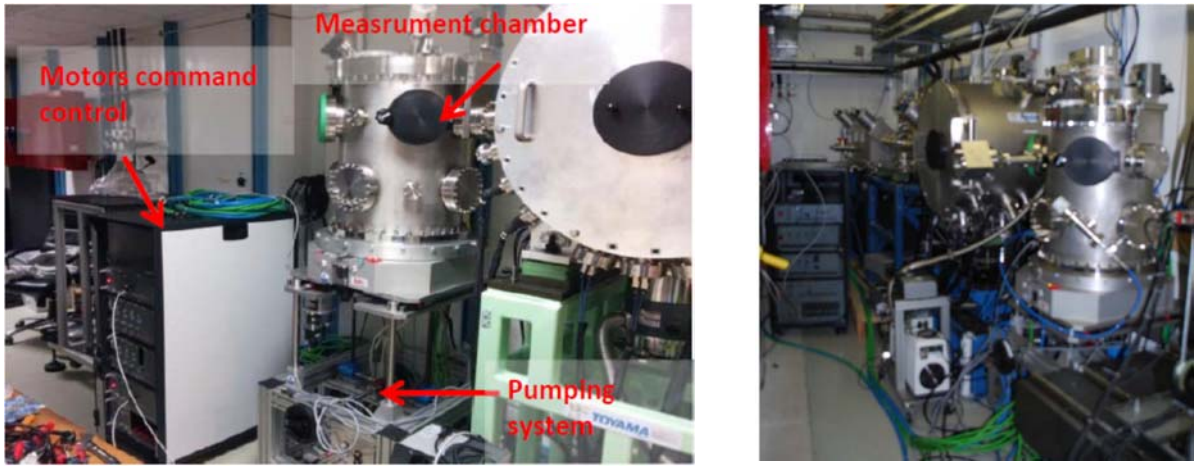

***Figure 23**: CASTOR Installed in the X-UV branch (left) and in the hard X-rays branch (right).*

The calibration of the instruments was obtained in several steps:

I. Checking of the motors movements

The vacuum chamber is equipped with 7 motors with the aim of moving the samples and the detection systems. The checking of the motors movements insures the stability and reproducibility of movements for high accuracy X-ray Spectroscopy (XRS) and X-ray reflectivity (XRR). Each each axis was thoroughly studied.

II. Determination of the alignment procedure and tests

The alignment procedure was established and applied on both branches of the Metrology beamline for which the beam entrances are opposite each other, thus the whole manipulator must be rotated by 180°. This step is crucial for reaching high quality GIXRF measurements.

III. Efficiency calibration of the detectors

The absolute efficiency calibration of detectors is required to get reliable quantitative results. There are two kinds of detectors which can be installed in the chamber: photodiodes and energy-dispersive detector (Silicon Drift Detector – SDD)

IV. Validation

The quality of the calibration procedure was checked by comparing GIXRF measurements at CASTOR with measurements on the same thin films samples measured at PTB. Both the qualitative angular dependence of the signal and total dose at high angles corresponded to the expected values.

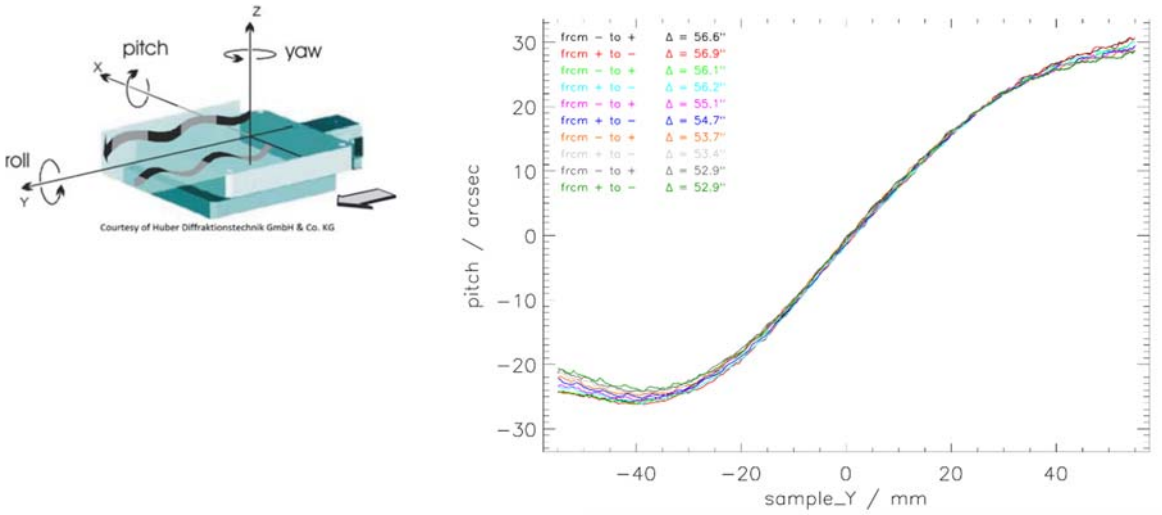

***Figure 24**: Left: Schematic showing the sample holder degrees of freedom. Right: Test results of the picth of sample holder Y axis.*

CASTOR was also equipped with a specific heating module that was designed and installed in order to subject the samples to temperature stress.

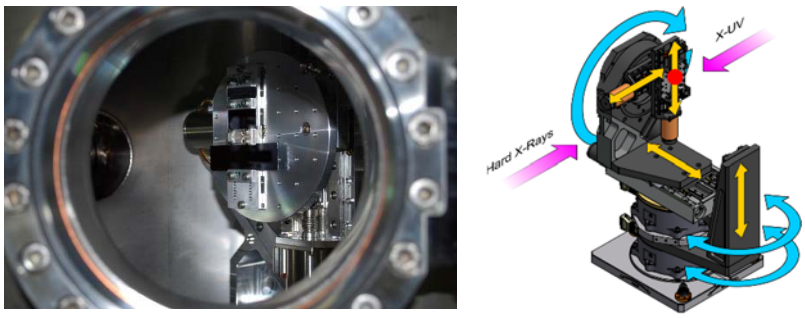

***Figure 25**: Left: picture of sample holder inside CASTOR that allows high precision multi-axial manipulation. Right: Schematic representation of the experimental set-up used for combined XRR and GIXRF analysis performed at the Metrologie beamline at the SOLEIL synchrotron, in France.*

<u>Investigation thin film samples for power electronics.</u>

CASTOR is designed to perform both XRR and GIXRF measurement simultaneously, however, results presented here were measured sequentially due to software restrictions at the time of the experiments.

Samples name	Substrate	Thin Film	Lateral size
HK_10_GN	GaN//Si(111)	10 nm Al_2O_3	2 cm*4 cm
HK_10_AGN	AlGaN//GaN//Si(111)	10 nm Al_2O_3	2 cm*4 cm

***Table 4**: Description of samples shown in this report. They consist of a very thin layer of a high-k material (alumina) deposited by Atomic Layer Deposition (ALD) technique on a III-N semiconductor based stack, which we call a substrate. This III-N stack consist of several layer, as described in Figure 26.*

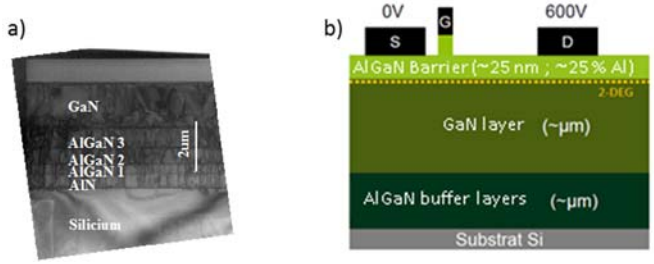

***Figure 26** : a) Example of the thin film III-N stack epitaxially grown on Si (111) substrate; b) schematic representation of the III-N stack.*

The first Aluminium nitride (AlN) layer is the nucleation layer which allows a better crystallisation of the Aluminium gallium nitride (AlGaN) buffer layers on the Si (111) substrate. The buffer layers composition increase gradually in Ga content in order to adapt the lattice parameter mismatch going from AlN crystal structure to GaN structure. This process allows to get good quality epitaxial GaN layer with a very few amount of defects. This is compulsory before depositing the AlGaN barrier, as shown in Figure 27b in order to get good electrical properties for the 2D electron gas. The dielectric material is then deposited above the AlGaN barrier.

In order to get a better insight about the interface between the high-k layer (10 nm Al_2O_3) and the III-N stack (GaN and AlGaN upper layer), a combined XRR-GIXRF analysis was performed.

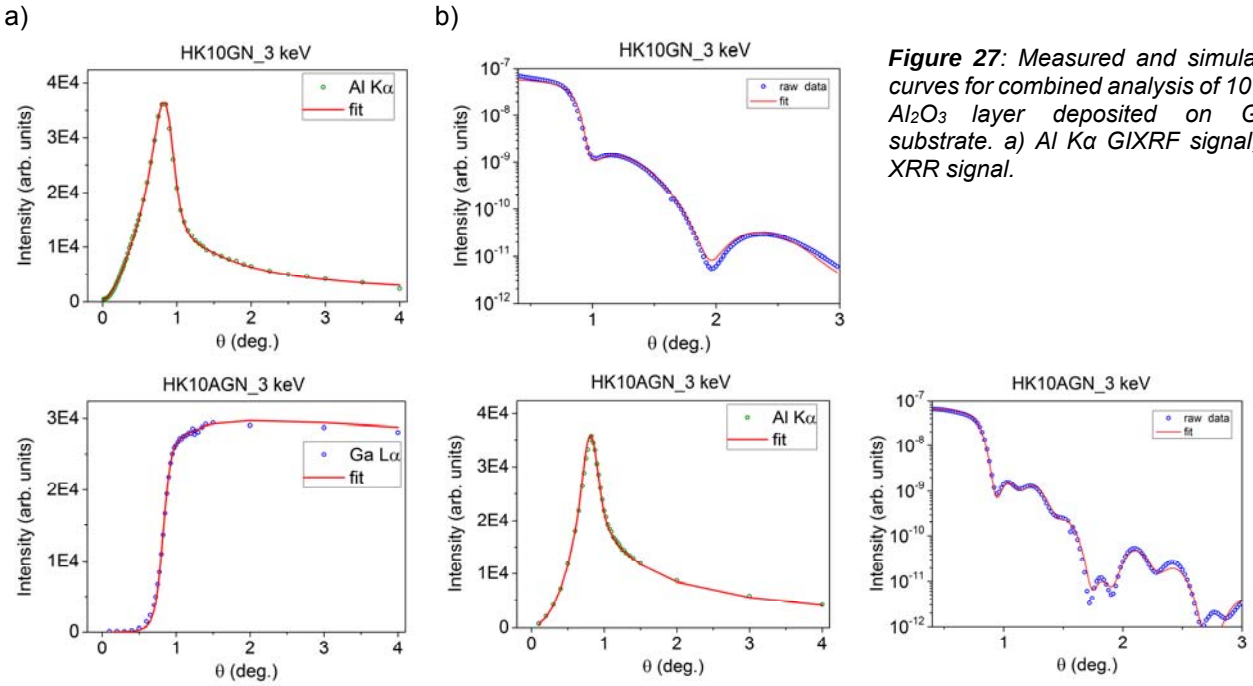

***Figure 27**: Measured and simulated curves for combined analysis of 10 nm Al_2O_3 layer deposited on GaN substrate. a) Al Kα GIXRF signal; b) XRR signal.*

Using the JGIXA software [9] for the combined analysis, we obtain the fitted parameter results reported in table 5. The results reveals in both case that the aluminium elemental profile is consistent with a homogeneous layer of Al_2O_3 with a good interface quality which is critical for the performance of such thin films in power electronics applications.

Sample	Layers	Thickness (nm)	Density ($g.cm^{-3}$)	Al content (%)	Roughness (nm)
HK_10_GN	Al_2O_3	9.5(8)	3.2(1)		0.6(3)
	GaN	--	6.1		0.1(3)
HK_10_AGN	Al_2O_3	10.9(3)	2.7(1)		0.6(2)
	$Al_xGa_{1-x}N$	25.0(9)	5.24(2)	30.0	0.6(3)
	GaN	--	6.1		0.2(2)

Table 5: Parameters obtained by combined XRR-GIXRF data analysis on samples with 10 nm Al_2O_3 thin films on both GaN and AlGaN substrates

Summary

X-ray spectroscopy measurements in grazing incidence geometry and analysis of a series of multilayer thin film samples based on dielectrics (high-k) on semiconductors for power electronic application were performed. The combination of different methods allowed the determination of thin film interface quality which is critical to high electronic performance. Additional NEXAFS measurements also demonstrated a slight change in substrate strain within the first atomic layers that could potentially lead to reliability issues in the longer term.

[9] *D. Ingerle et al., (2016) Spectrochimica Acta Part B. 118, 20-28.*

The ability to perform such measurements and analysis will help manufacturers to optimise the performance of power electronic devices.

The new measurement facility developed in this project allows correlation of the effect of temperature and irradiation on parameters of thin films energy materials and is now available for users at the SOLEIL synchrotron, in France. The new instrumentation allows synchrotron-based XRR and GIXRF of samples under controlled temperatures.

Conclusions

The project met the objective of validation of measurement techniques for elemental depth, selectivity and sensitivity for thin film energy materials such as novel compound materials with matrix elemental depth gradients, organic/inorganic hybrids, multi-layered structures and nano-structured surfaces, layers and interfaces. This project validated non-destructive new methods for determining elemental depth, selectivity and sensitivity of complex thin films. In order to improve the accuracy and reliability of the new methods, the project also determined fundamental X-ray parameters of elements of interest for energy applications with significant lower uncertainties. These fundamental parameters, such as absorption cross section and fluorescence cross section, are used for the quantification of X-ray measurements, therefore a reduction in the uncertainty of fundamental parameters means more accurate determination of microstructures via X-ray measurements. The new methods are now available for EU companies to use, and additionally this work resulted in a Calibration and Measurement Capability entry within BIPM for quantification of thin CIGS layers. Some highlights are:

- A new X-ray standing wave method was developed for GIXRF and near edge X-ray absorption fine structure that allows the measurement of depth dependent elemental composition as well as chemical speciation (the distribution of an element amongst chemical species). This information is crucial for the development of highly efficient solar cells and was applied to nanostructured Si solar cells.
- A new measurement facility developed in this project that allows correlation of the effect of temperature and irradiation on parameters of thin films energy materials and is now available for users at the SOLEIL synchrotron, in France. The new instrumentation allows synchrotron-based X-ray Reflectivity and GIXRF of samples under controlled temperatures. To validate the facility optimised measurement protocols were developed to reliably and traceably analyse power electronic materials and transparent conductive oxide stacks under controlled temperature conditions.
- The X-Ray fluorescence yield of the K shell (the principal energy level) of Gallium (Ga) was determined with a low relative uncertainty of 4 %. This significantly improves the quantification of X-ray fluorescence analysis of thin films that rely on fundamental X-ray parameter values with low, reliable and traceable uncertainties. Ga is an important element in CIGS thin film solar cells and this result has allowed better quantification of depth profiling of these compound materials with matrix elemental depth gradients.
- The X-Ray fluorescence yield of the oxygen K-shell was determined experimentally with a significant reduction in uncertainty from approximately 20 % to 5.2% (in comparison with the available literature data) and represents a significant improvement in the current state of the art. This atomic fundamental parameter is important for reference-free quantitative analysis of oxides, which are formed on most surfaces in ambient air conditions and can lead to a loss of performance in energy products.
- X-ray spectroscopy measurements in grazing incidence geometry and analysis of a series of multilayer thin film samples based on dielectrics (high-k) on semiconductors for power electronic application were performed. The combination of different methods allowed the determination of thin film interface quality which is critical to high electronic performance. But it also demonstrated a slight change in substrate strain within the first atomic layers that could potentially lead to reliability issues in the longer term. The ability to perform such measurements and analysis will help manufacturers to optimise the performance of power electronic devices.
- A novel combined Grazing Incidence X-Ray Diffraction - GIXRF measurement method and analysis was developed to allow reliable characterisation of depth profiling. The new method was successfully validated through comparison with cross-section scanning electron microscopy measurements of a series of complex CIGS solar cells.

3.4 Development of validated methods for the thermal characterisation of thin films as a function of temperature and for multi-parameter characterisation of energy thin film materials under specific stress conditions.

The diversity of energy applications, sometimes in extreme conditions (for example high temperature) requires a detailed knowledge of their behaviour under stress. Furthermore, the development of models to describe the materials or predict their behaviours requires reliable input data. This project successfully developed and validated a new traceable facility for thermal diffusivity measurements on thin films as a function of temperature. It has also developed facilities, now available for EU companies that allow characterisation of thin film energy materials under controlled stress conditions. Some highlights are described below.

3.4.1 New facility for thermal diffusivity of thin films as a function of temperature

The thermal properties of materials are linked by the equation:

$$k = a.\rho.C_p \qquad [1]$$

where $\mathrm{k}\,[\mathrm{W.m^{-1}.K^{-1}}]$ is the thermal conductivity, $\mathrm{a}\,[\mathrm{m^2.s^{-1}}]$ is the thermal diffusivity, $\rho\,[\mathrm{kg.m^3}]$ is the density and $\mathrm{C_P}\,[\mathrm{J.kg^{-1}.K^{-1}}]$ is the specific heat; the volumetric specific heat $\rho.\mathrm{C_p}$ can also be determined when measuring k and a. In the previous project JRP IND07 Thin Films, LNE developed a modulated IR photo thermal radiometry facility for traceable thermal conductivity measurements of thin films (from a few tens of nanometres to a few micrometres thick) up to 1000°C [[10]]. However, measurement of thermal diffusivity remained a challenge.

In this project we have developed a pulsed photothermal facility for traceable measurements of thermal diffusivity in thin films as a function of temperature, up to 1000 °C, as shown in Figure 28. A calibration procedure has been developed as part of the validation of the facility.

Pulsed photothermal radiometry consists of illuminating the sample front face surface (at the interface between the thin film and its substrate) by a single laser pulse or a train of Dirac light beam pulses and then the detection of the thermal response of the opposite thin film face by means of an IR detector. The tested sample (thin film deposited on substrate) is heated at a chosen studied temperature, under vacuum or inert gas, by a furnace. The thermal excitation is carried out by a continuous laser (1.55 µm) that its beam is shaped by an acousto-optic modulator driven by the signal issued from a function generator. The thermal excitation is a pulse or a train of laser pulses. An IR detector measures the thermal response versus time (also called thermogram) of the thin layer on the opposite side of the excitation. An off-axis parabolic mirror coupled with an IR transmitting lens collects the IR radiation emitted by the specimen, and focuses it on the sensitive element of the detector. The signal delivered by the IR detector is recorded by an ultrafast and high resolution oscilloscope and is triggered by the signal provide by the function generator that drive the exciting beam.

The project developed a thermal model that links the thermal rear face response of the thin film to the front face excitation of the sample. We then use a thermal quadrupole method to fit to the experimental thermogram (thermal response versus time) by inverse technique in order to determine the thermal diffusivity of the investigated thin film.

[10] *N. Fleurence et al., (2015) physica status solidi (a) 212, 535-540.*

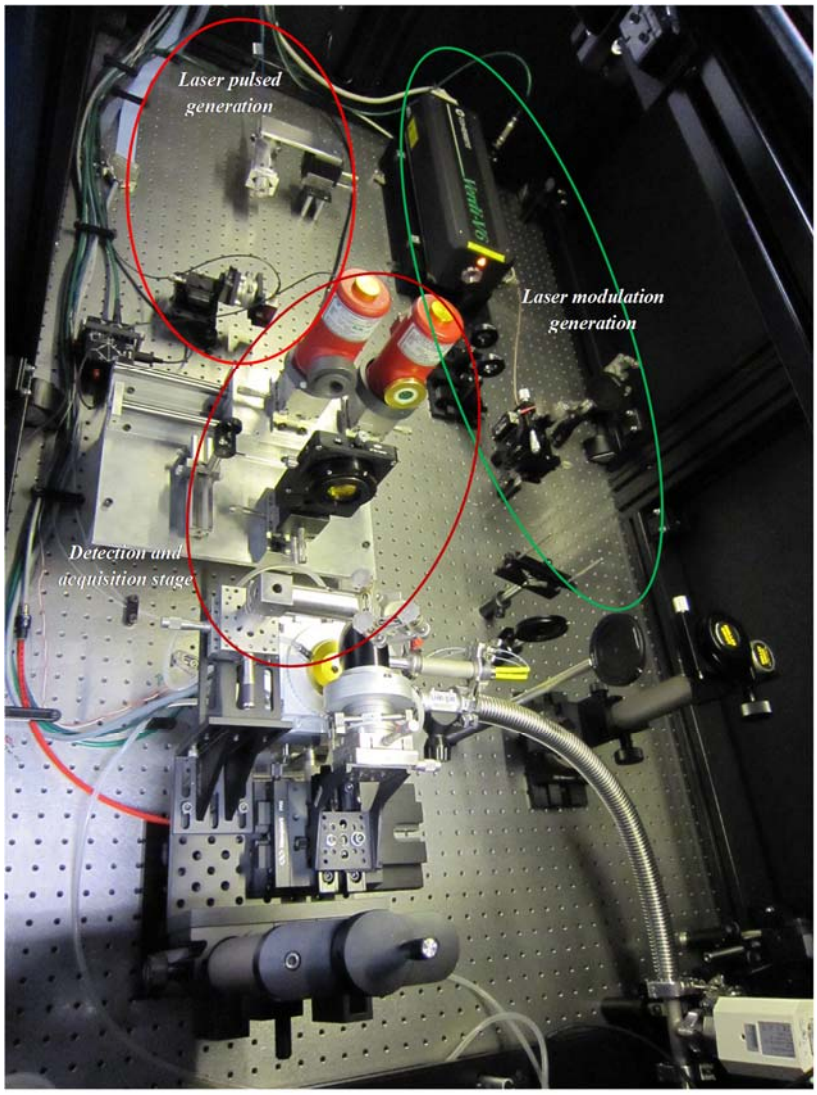

***Figure 28**: Photograph of the photothermal radiometry facility for traceable thermal diffusivity measurements at LNE, France.*

Summary

A new facility was developed for thermal diffusivity measurements on thin films as a function of temperature, from room temperature up to 1000°C, and is available for European companies to access. New protocols for temperature and frequency calibration were also developed, and a best practice guide written which is now available on the project website.

3.4.2 Validated methods for Multiparameter characterisation under specific stress conditions

In situ measurements of electrical and optical properties when thin film electronic materials as subjected to stress (temperature, oxygen, humidity, etc) is critical to understanding reliability and failure modes. In this project a novel facility has been developed to allow multiple characterisation methods to be performed either simultaneously or in a sequence, while samples are subjected to controlled stress conditions. The facilities are particularly focused on flexibility so that tests can be quickly adapted to the changing requirements of new materials and device geometries as used for numerous energy applications.

Leak-free portable environmental chamber

NPL has developed a leak-free portable environmental chamber that can be coupled to different measurement instruments and is now commercially available. The low leak rate (see Figure 29) allows the chamber to be moved between measurement instruments without affecting the sample environment, which is critical for

accurate correlation of results from multiple measurement methods. The static leak test for three different time spans shows that the static leak rate is less than 1 ppm per hour for both oxygen and water, which is the design specification of the chamber. It permits in-situ measurements under different stress conditions, such as well controlled levels of humidity and oxygen, which allows identification of degradation modes and improvement of product lifetime.

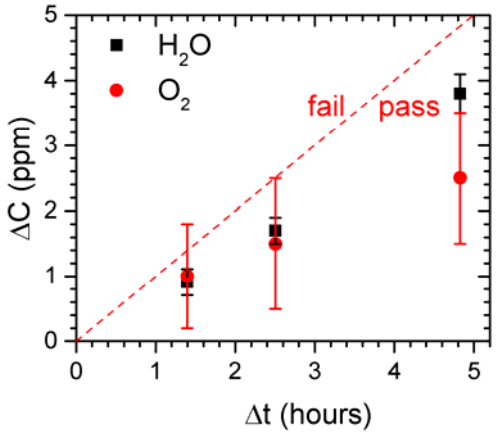

***Figure 29**: Results of static leak test for oxygen and water vapour for the large portable environmental chamber developed at NPL. Chamber has internal volume of 1.25 L and can accommodate samples of up to 10 cm x 10 cm. in lateral dimensions*

World's first measurement facility for resolution mapping of transient photovoltage and transient photocurrent

Transient photovoltage (TPV) and transient photocurrent (TPC) response measurements are established tools for analysing the charge carrier dynamics of photovoltaic samples, which help to direct progress towards high efficiency solar cells. In this measurement, the time-resolved electrical response to a nanosecond optical excitation pulse is recorded providing information about charge recombination rate, density of states, charge transport, among others. Traditional TPV and TPC experiments measure the whole device macroscopically, therefore not providing information about spatial variations, which can critically influence performance and reliability. In this project NPL has developed the first measurement facility that for high resolution mapping of TPV and TPC and applied it to investigate defects in solar cells.

The profiles of the expanded and focused laser beams were measured using a biased photodiode with a mounted pinhole (100 µm diameter for expanded beam and 10 µm for focused beam) and mapping the response. These beam intensity profiles are shown in Figure 31. The diameter of the focused beam at full width half maximum (FWHM) is 16 µm giving an indication of the spatial resolution of mapping that can be achieved with the system.

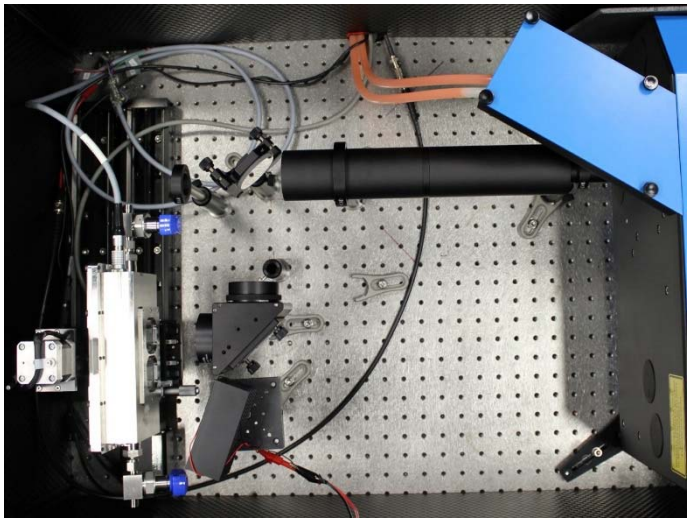

***Figure 30**: Photograph showing partial view of the spatially resolved transient photovoltage and transient photocurrent measurement facility developed at NPL, UK.*

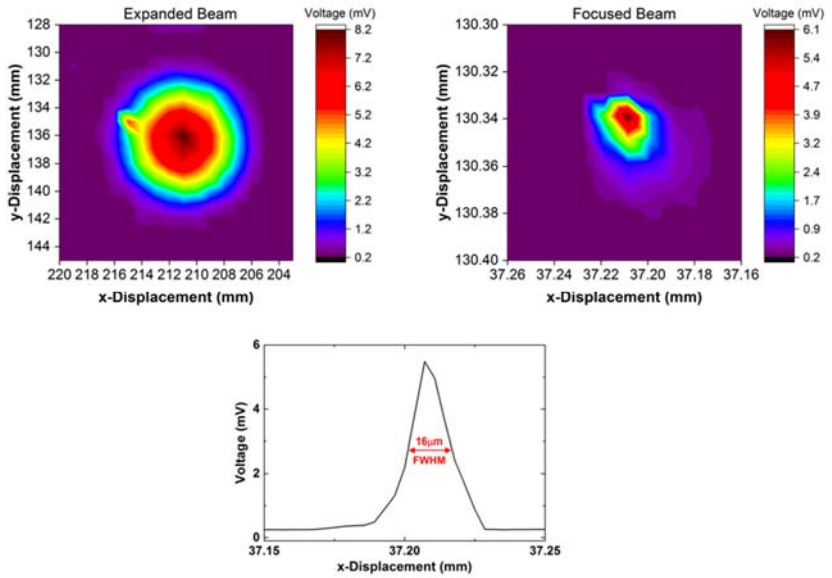

***Figure 31**: 2D intensity profiles of expanded and focused laser beam, and cross section of focused beam intensity.*

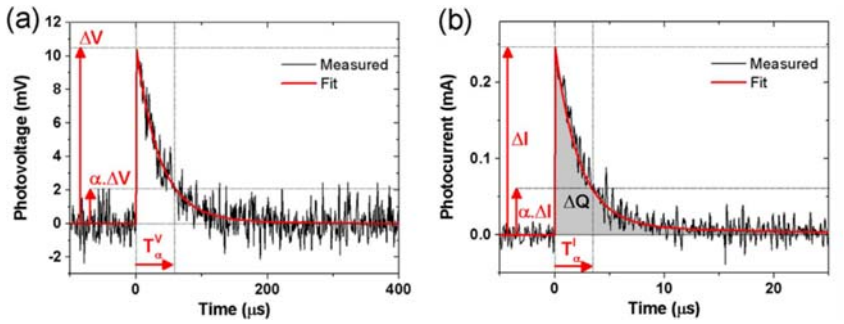

***Figure 32**: Examples of a) photovoltage and b) photocurrent transients measured at a single point showing double exponential fitting lines and illustrating the parameters that can be extracted. Adapted from [11].*

The new measurement facility was demonstrated as a powerful method to characterise solar cells.

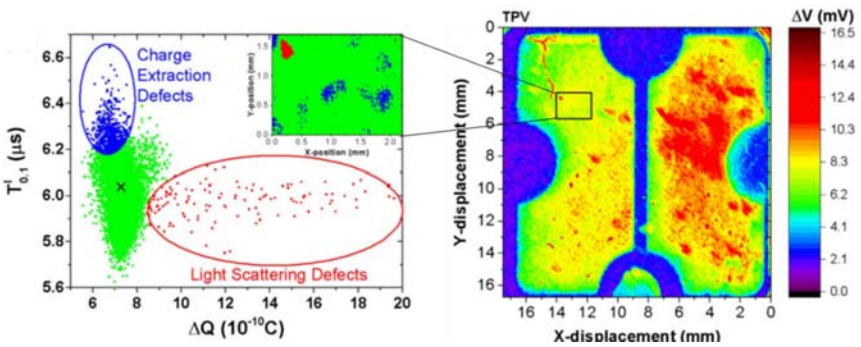

***Figure 33**: Example of high resolution TPV map of a solar cells (right) and identification of defscts by combined TPV and TPC analysis. Adapted from [11] where further details are discussed.*

Summary

A new facility that allows multiparameter characterisation and ocntrol of stress conditions has been developed and is currently available at NPL. The portable environmental chamber has been licensed to an EU company and is commerically available. Although not shown here, the chamber has also been used for assessment of the quality of manufacturing of large area printed solar cells (~ up to 100 cm^2) and the combination of

[11] *S. Wood et al, (2017) Solar Energy Materials & Solar Cells 161, 89-95.*

environmental control and multiparameter analysis will continue to be developed through two further projects H2020 CORNET and EMPIR project 16ENG03 HyMET.

Conclusions

The project met the objective of the development of validated methods for the thermal characterisation of thin films as a function of temperature and for multi-parameter characterisation of energy thin film materials under specific stress conditions. This project successfully developed and validated a new facility for thermal diffusivity measurements on thin films as a function of temperature. It has also developed facilities, now available for EU companies that allow characterisation of thin film energy materials under controlled stress conditions. Highlights are:

- A new facility was developed for thermal diffusivity measurements on thin films as a function of temperature, from room temperature up to 1000°C. New protocols for temperature and frequency calibration were developed, and a best practice guide written which is now available on the project website and other online platforms.
- A world first measurement facility that allows high resolution mapping of transient photovoltage and transient photocurrent was developed. These measurements are critical for the analysis of performance loss in solar cells and the facility has already been used to identify and classify defects in organic solar cells.
- A leak-free portable environmental chamber that can be coupled to different measurement instruments was developed and is now commercially available. It permits in-situ measurements under different stress conditions, such as well controlled levels of humidity and oxygen, which allows identification of degradation modes and improvement of product lifetime. Through a collaboration with Surrey University, this chamber was used for assessment of the quality of manufacturing of large area printed solar cells (~ up to 100 cm2). Further engagement with Surrey University and additional collaborators will continue in a new EC funded R&D project (H2020 CORNET).
- It was shown that integration of a portable environmental chamber with Muller Polarimetry can identify causes of performance loss in solar cells due to UV and O2 exposure. Measurement protocols were also developed that allowed investigation of degradation in-situ via measurement of the chemical binding states using X-ray photoemission spectroscopy.

3.5 Development of large-area characterisation methods for process optimisation in thin-film energy material production, including fast contact and non-contact methods.

This project designed, developed and validated a series of novel instrumentation for fast, contact and non-contact large area characterisation of thin film energy materials. These methods provide low uncertainly, high sensitivity and a significant increase in measurement speed. These developments have attracted significant industrial interest, which so far has led to one patent application, consultancy agreements, a new calibration service and a spin-out company being formed. Some highlights are described below.

3.5.1 Traceable large area non-contact optical scatterometry

This work has brought the accuracy of optical scatterometry to a scale where it can impact on large thin films foils. It has designed, built and validated a new two-colour Coherent Fourier Scatterometry measurement facility at VSL that is able to perform optical characterisation of thin films with sub-nanometre uncertainty and is capable of measuring pitches down to 200 nm as well as thickness and refractive indices of materials. The system can also be integrated with a large-area robotic system with six-degrees of freedom which allows measurements over an area of 75 x 75 cm^2 on samples of different shapes and formats. The outcomes of this will impact the metrology and process control of structured thin films materials, which are increasingly used for light harvesting applications and lighting, as well as in power electronics.

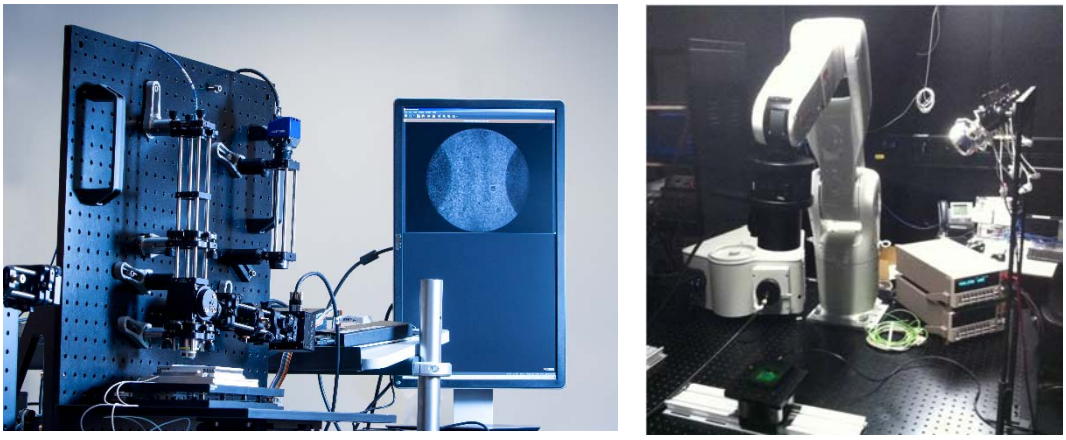

***Figure 34**: Photograph of the coherent optical scatterometer and the robotic arm system at VSL, Netherlands.*

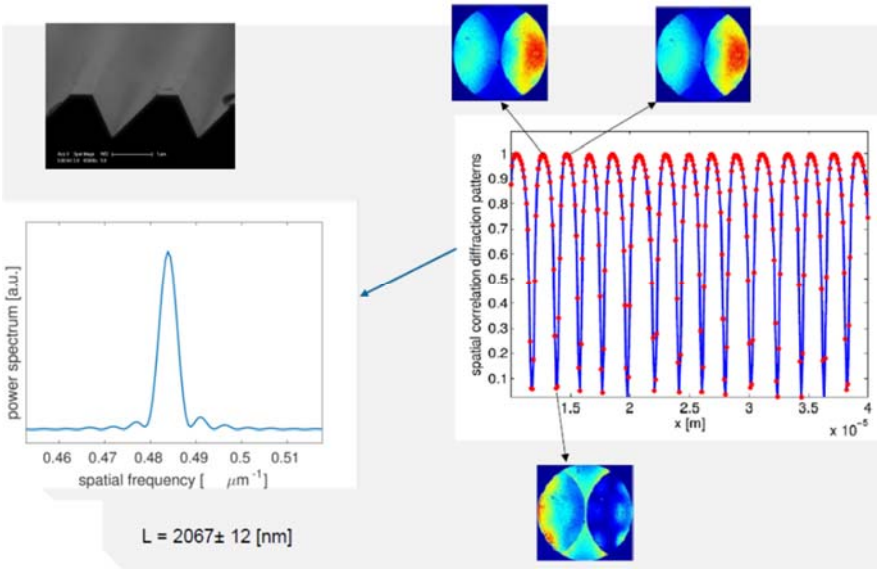

Figure 34: Example of results obtained measuring a grating indicating pitch purity and effect of stray-light.

The scatterometer works in a back-scattering configuration where the light coming from a laser is focused on the target and the scattered light is collected by the same objective. The advantage of using a microscope objective (MO) is that one does not need to physically scan the incident and reflected angles, since this is done by the objective itself. The largest angle of incidence is limited by the numerical aperture of the MO.

The method has also been used to investigate GaN power electronic thin films. Simulations have been performed, with different values of thickness for the AlGaN barrier and the GaN by steps of 1 nm. This gave a wide range of possible measured far fields intensity profiles. It is easy to recognise some of the features presented by the measured data in the simulated profiles (Figure 35).

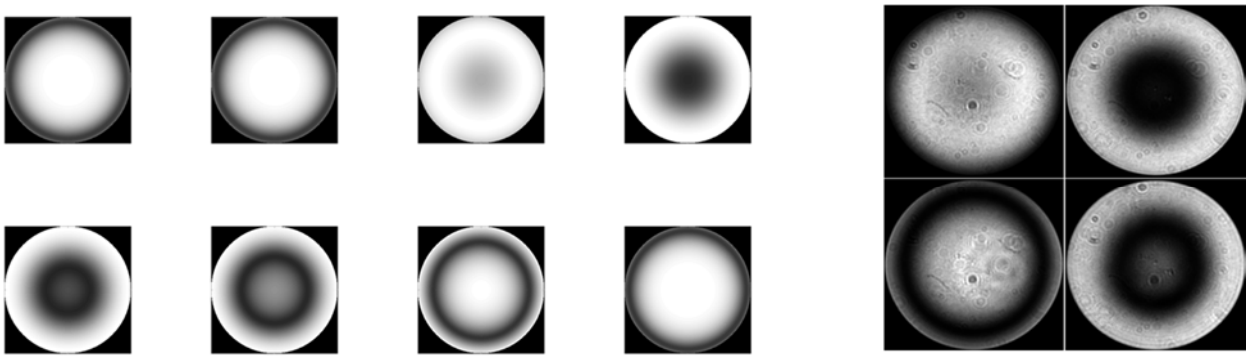

***Figure 35**: Left: Different simulated intensity profiles for the GaN sample, obtained by tuning the thickness of the AlGaN and GaN layers by a few nanometers. Right: Experimental results of measured GaN samples.*

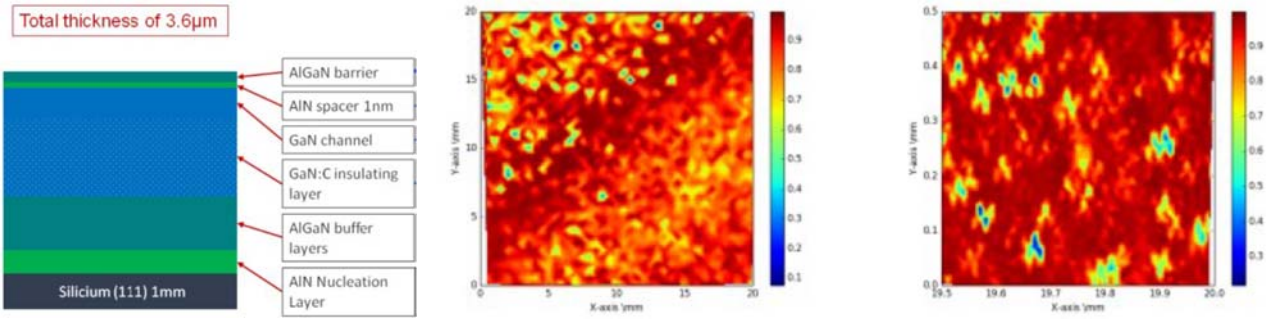

***Figure 35**: Left: Schematic of thin film power electronic sample measured. Scatterometry measurement results showing relative variation of thickness on samples. Measurements with 500 µm step size (middle) and 10 µm step size (right).*

3.5.2 Spatial characterisation of solar cells

The spatial characterisation of electrical, optical and morphological properties of a photovoltaic cell is a fundamental step in the quality assessment of a device. Two new measurement instruments have been developed to allow spatial characterisation of electrical properties of solar cells, (1) that allows fast photocurrent mapping, reducing measurement speed from hours to a few minutes (i.e. fast photocurrent mapping), and (2) that allows non-contact non-invasive spatial characterisation (i.e. photomagnetic detection).

Photomagnetic detection

A non-contact, non-invasive measurement setup for spatial characterisation of performance of solar cells using non-cryogenic photomagnetic detection was designed, developed and demonstrated at PTB. The photomagnetic method allows contactless characterisation of thin films and complete solar cells for identification of defects and reduced performance in small and large area solar cells. It measures the magnetic field generated by the photocurrent within the thin film while scanning the sample with the laser. Therefore the spatial resolution is determined by the laser spot which, in the current configuration can achieve 10 µm. To increase sensitivity and avoid noise, the laser intensity is modulated and a double lock-in method is used to detect the magnetic signal, detecting the signal in phase and with 90º shift.

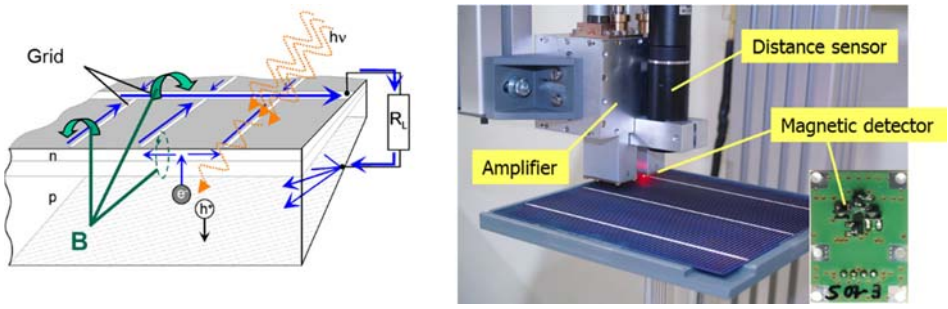

***Figure 36**: Left: schematic of photomagnetic detection in a silicon solar cell. Right: Photograph of the photomagnetic detection instrument at PTB, Germany.*

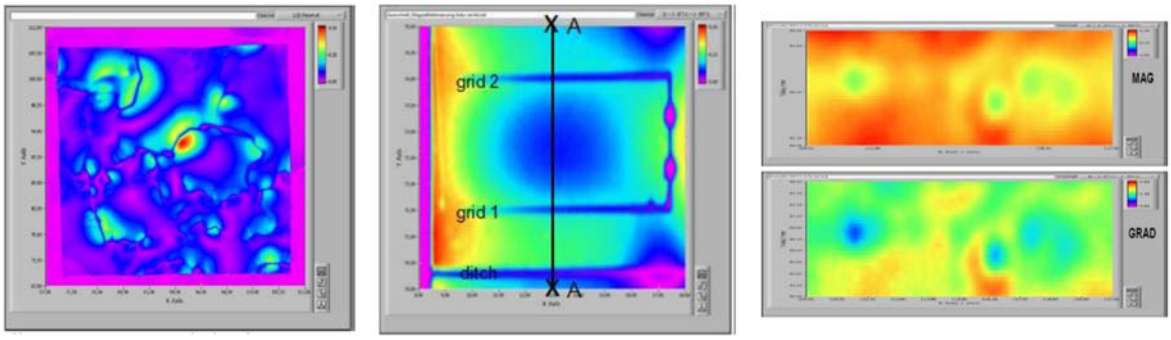

***Figure 37**: Example of photomagnetic detection photocurrent maps in polycrystalline Si (left), CIGS (middle) and organic (right) solar cells.*

The photomagnetic technique was applied to different types of solar cells, including multicrystalline silicon, CIGS and organic solar cells (Figure 37). The measuring method is well suited to identify spatial variations in light conversion efficiency without physical contact with the sample. The most interesting results are obtained from solar cells which are nearly fully processed, and not covered with metal grids. Taking into account the measuring time, this new non-destructive measuring method seems to be mostly suitable for research labs, rather than solar cell fabrication lines with a high throughput.

Fast Photocurrent mapping

A new measurement facility and software was developed at NPL for fast photocurrent mapping measurements of the homogeneity of solar cells. This method is significantly faster than the current state of the art for photocurrent mapping, and reduces the measurement time from a hours to a few minutes, thereby opening up the possibility to implement such a technique as part of quality control during the manufacturing of photovoltaics (Figure 38).

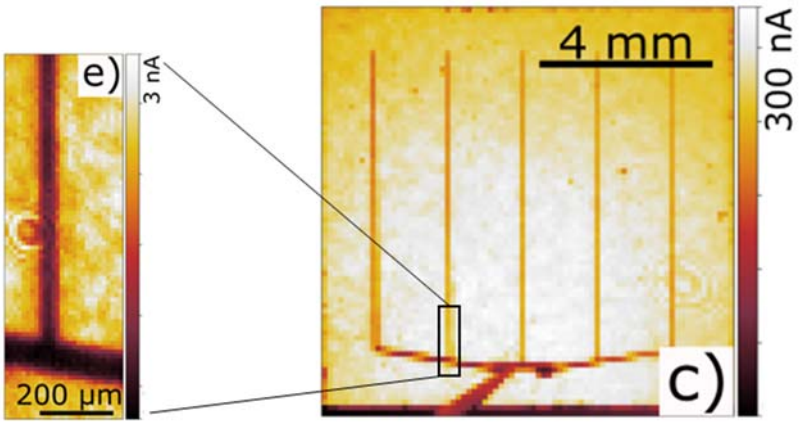

***Figure 38**: Fast mapping of a CIGS solar cell using new measurement instrument and software developed at NPL. Right: 5852 pixels (100 µm resolution), scanning time 35s. Left: 2784 pixels, scanning time 16s.*

Conclusions

The project met the objective of the development of large-area characterisation methods for process optimisation in thin-film energy material production, including fast contact and non-contact methods. This project designed, developed and validated a series of novel instrumentation for fast, contact and non-contact large area characterisation of thin film energy materials. These methods provide low uncertainly, high sensitivity and a significant increase in measurement speed. These developments have attracted significant industrial interest, which so far has led to one patent application, consultancy agreements, a new calibration service and a spin-out company being formed. Highlights include:

- A new measurement facility and software was developed for fast photocurrent mapping measurements of homogeneity of solar cells. This method is significantly faster than the current state of the art for photocurrent mapping, and reduces the measurement time from hours to a few minutes, thereby opening up the possibility to implement such a technique as quality control during the manufacturing of photovoltaics.
- A theory translating the microwave implementation of the Electro-absorption interferometry technique to the optical domain was developed. This will allow the future development of an experimental setup for fast, non-contact optical characterisation of thin films over large areas.
- A non-contact, non-invasive, fast optical measurement facility was designed and built that allows optical characterisation of periodically patterned or flat thin films with sub-nanometer uncertainty. Integration of coherent Fourier scatterometry with a large-area robotic system with six-degrees of freedom was achieved which allows measurements over an area of 75 x 75 cm2 on samples of different shapes and formats.
- A new two-colour Coherent Fourier Scatterometry system was designed, built and validated. It is able to perform optical characterisation of thin films with sub-nanometre uncertainty and is capable of measuring pitches down to 200 nm as well as thickness and refractive indices of materials.
- A non-contact, non-invasive measurement setup for spatial characterisation of performance of solar cells was designed, developed and demonstrated on a range of different photovoltaic technologies. The photomagnetic method allows contactless characterisation of thin films and complete solar cells for identification of defects and reduced performance in small and large area solar cells.
- A set of characterisation tools suitable for non-contact characterisation of the electrical quality of nanostructured thin films and related interfaces has been developed to allow fast mapping of samples up to 8 inches in size. The methods were tested with a variety of thin film samples to optimize the process parameters and from this the best parameters were selected to fabricate high-efficiency Si solar cells.

4 Actual and potential impact

This project developed a measurement framework for reliably characterising thin films, and has delivered new instrumentation, industrial consultancy, calibration services, standards documents, new solar cell technology, and a spin out company.

Dissemination of results

This project engaged with a wide range of stakeholders, resulting in the direct uptake of the technology and knowhow developed. The consortium delivered a series successful events:

- A large 4-day symposium on Analytical techniques for precise characterisation of nano materials (ALTECH 2017) at the spring meeting of the European Materials Research Society including dedicated sessions and a workshop to disseminate the results of the ENG53 ThinErgy project. 140 high quality papers from 23 countries were presented during ALTECH and allowed significant dissemination of project results to the 4000 attendees of the whole conference.

- 4 successful targeted workshops (in Portugal 2015, Germany 2016, UK 2016, and France 2017), two on Fundamental X-ray parameters and two on advanced optical characterisation.
- Summer School on Metrology for Thin Film Materials targeted at early stage engineers and scientists and organised as part of the European Optical Society Annual Meeting (EOSAM) in Berlin in September 2016.
- Four training sessions on novel experimental methodologies for synchrotron radiation to the scientific community were attended by members of the scientific community from higher education and public research organisations.

Twenty four peer-review papers were published and 42 conference presentations were delivered to conferences such as the EU Photovoltaic Science and Engineering Conference (PVSEC) Solar Cell Conference, European Conference on X-ray Spectrometry (EXRS), the International Congress of Metrology and the European Conference on Applications of Surface and Interface Analysis (ECASIA).

In order to facilitate update of know-how developed in the project, the consortium published the following 4 Good Practice Guides:

1. Grazing incidence X-ray fluorescence analysis
2. Photoelectron spectroscopy in the VUV spectral range
3. Calibration of IR photothermal radiometry
4. Ellipsometry measurements on solar cells

These Good Practice Guides are available from the project website, through the technical website ResearchGate and through society's websites, such as the European X-ray Spectrometry Association (EXSA). They have also been presented at key conferences and will be used as teaching material in universities such as the Danish Technical University.

Impact on standards and policy

The consortium actively engaged with standardisation bodies, international metrology committees and policy makers. Results from this project were presented and discussed with the BIPM, DIN, ISO and the Versailles Project on Advanced Materials and Standards (VAMAS).

- Part 1 of draft standard (DN 50989-1) on data analysis in spectroscopic ellipsometry was published with significant input from this project and is now available online. Input to other parts of this standard are ongoing and discussions with ISO are in place to bring this work into the international level (objective 2).
- The consortium contributed to an ISO inter-laboratory study on elllipsometry measurements of thin films that will inform standards development in the field (objective 2).
- Presentations were delivered to the BIPM's Consultative Committee Task Group for Thermophysical Quantities and to the steering committee of VAMAS to inform future activities in the international arena.
- The consortium contributed to the successful completion of the BIPM CCQM (Surface Analysis) Pilot Study P140 on Quantitative Surface Analysis of Multi-Element Alloy Films and to the BIPM KC125 CCQM Key Comparison on amount of substance, these studies are crucial to ensure international agreement in the measurement of thin films.
- A new CMC for the quantification of thin film CIGS layers was registered with and approved by BIPM, the highest international authority in metrology (objective 5).

Results from the project have also informed Government policy. Members of the consortium gave a presentation about metrology strategy to the Board of Experts for the Ministry of Economic Affairs in the Netherlands, and contributed as invited experts in a round-table discussion with the Government Office for Science in the UK on policy for materials for energy technologies.

Early impact

- A new measurement facility that allows correlation of the effect of temperature and irradiation on parameters of thin films energy materials and is now available for users at the SOLEIL synchrotron, in France (objective 3).
- Multiple parameter characterisation under the same stress conditions is crucial for the determination of reliability of performance of new thin film energy materials and is now available at NPL (objective 4).
- Increased solar cell efficiency was demonstrated when compared with current technology in the production line of a German Solar Cell Manufacturer by applying the passivated Si high efficient solar cells thin films developed in this project.
- A patent application for high efficiency Si thin film technology has been submitted and based on this the spin-off company ElFys Inc. has been established and started operating.
- New instrumentation has been made available to end users via license agreements. For instance, a portable environmental chamber that can be coupled to existing instrumentation for on-site characterisation, was developed at NPL and licensed to a company and is now commercially available. It allows in-situ electrical and optical measurements under well controlled environmental conditions and can be coupled to existing measurement instrumentation (objective 4).
- Several NMIs are providing consultancy and other services to large EU companies using know-how developed in this project, this will help with increase competitiveness. For instance, one large European equipment manufacturer has signed a long term consultancy agreement with VSL to develop new instrumentation for thin film characterisation.
- A new guide for calibration of scatterometer measurement is being used to deliver commercial projects (e.g. measurement service) to companies in the EU (objective 5).
- The new CMC entry within BIPM for quantification of thin CIGS layers is now available for European companies (objective 3).
- The project attracted additional collaborations leading to follow-on projects i.e. 16ENG03 HyMET and H2020 CORNET that will further develop results from this project into a wider range of applications. This includes companies contributing to standards development and to development of new

instrumentation as well as application of methods developed in this project to new energy materials systems.

Potential future impact

The know-how, new facilities and instrumentation developed in this project will facilitate the development of new technologies and increase competitiveness of European energy technologies. By extending Europe's leadership in energy technology and innovation, this project has helped to ensure economic growth and an energy efficient future for Europe.

5 Website address and contact details

https://www.ptb.de/emrp/thinergy-home.html

https://www.ptb.de/emrp/thinergy-contact.html

6 List of publications

[1]. ***Elemental depth profiling in TCO thin film by XRR-GIXRF combined analysis***
Helene Rotella, B. Caby, Yves Ménesguen, Y. Mazel, A. Valla, D. Ingerle, Blanka Detlefs, Marie-Christine Lépy, A. Novikova, G. Rodriguez, Christina Streli and Emmanuel Nolot, Spectrochimica Acta Part B: Atomic Spectroscopy (2017) DOI: 10.1016/j.sab.2017.06.011

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M. Juntunen, P. Repo, V. Vähänissi, J. Heinonen, D. Valluru and H. Savin, Nature Photonics, DOI:10.1038/nphoton.2016.226

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D.I. Kutsarov, E. New, F. Bausi, A. Zoladek-Lemanczyk, F.A. Castro, S.R.P. Silva. Solar Energy Materials and Solar Cells http://www.sciencedirect.com/science/article/pii/S0927024816305402

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