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1   Overview

The EU's 2050 targets for energy efficiency and renewable energy generation stimulate fast growth of a multibillion multi-technology industry based on innovation. Two key challenges in the development of new technologies for energy generation, distribution and storage/conversion are to ensure long-term durability at the required performance and short time-to-market of innovative products. This project has developed a cross cutting European hybrid metrology capability for the characterisation of thin film performance and durability in energy applications; developing experimental and mathematical methods to enable datasets from multiple measurements to be combined to deliver new or better results than the sum of individual methods.

2   Need

At the time of this project over 50 % of the EU's energy is imported, leading to a lack of price control due to volatility of international markets. This scenario is further complicated by increasing demand and the significant detrimental impact of fossil fuels on the environment. To combat that situation, Europe's strategy is to focus on more efficient ways of generating and using energy, which should lead to reduced CO_2 emissions, improved energy security, creation of local jobs and increased exports of EU expertise and products. The EU's targets for the use of renewable energy and energy efficient devices have stimulated fast growth of a multi-technology market based on innovation. Two key challenges in the development of new technologies for energy generation, distribution and storage/conversion are to ensure long-term durability at the required performance and short time-to-market of innovative products.

New, efficient energy technologies currently face barriers to market entry due to the challenge of demonstrating required lifetimes before product deployment. Predictive modelling of aging would reduce investment risks in new technologies and provide a link between laboratory tests and real-life operation. It also would provide a ranking method for different materials and manufacturing processes, accelerating the cost-effective development of new energy technologies. The key challenge for predictive modelling is that degradation is affected by a complex mix of different parameters which would require a new analytical approach to combined data analysis.

In parallel, faster and more cost-efficient development and transfer of manufacturing processes from laboratory to factory would accelerate uptake of new energy-efficient products. The complexity of thin films used in energy applications means that device performance is affected by a combination of different sample characteristics. The requirement to use complementary characterisation methods leads to major challenges related to reliable correlation of datasets from different metrology tools. The result is increased scale-up time and costs that adversely affects the uptake of better performing energy technologies.

3   Objectives

The aim of this project was to develop a cross-cutting European hybrid metrology capability for the characterisation of thin films' performance and durability in energy applications; it has developed experimental and mathematical methods to combine datasets from multiple measurements, delivering new or better results than the sum of individual methods.

The specific objectives of the project were to:

1. Develop hybrid experimental methods for improved analysis of complex energy thin film material properties and study their impact on the performance of energy products.

2. Develop data analysis, data fusion and mathematical models to implement the hybrid metrology methods.

3. Develop measurement methods for 2D and 3D chemical, structural, optical, and optoelectronic properties of nano-structured thin film energy materials and devices capable of identifying inhomogeneities at multiple scales.

4. Identify key measurement parameters for improved stability of thin film energy products and generation of new materials datasets as a function of aging.

5. Facilitate the uptake of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (DIN, ISO) and engage with industries that exploit thin films in energy

4 Results

Objective 1: Develop hybrid experimental methods for improved analysis of complex energy thin film material properties and study their impact on the performance of energy products.

This objective was achieved. The project developed new experimental methods that make use of multiple measurement techniques to improve analysis of complex thin film materials used in energy applications. Examples are described below of the benefits of using these methods on improving the performance of energy products, such as photovoltaics, electrocatalysis and power electronics.

Hybrid metrology for photovoltaics – combination of X-ray diffraction (XRD), X-ray fluorescence (XRF) and white light reflectometry (WLR) to characterise depth dependent microstructure.

Thin films for photovoltaics are often composed of multiple chemical elements and structural phases. The microstructural composition of these films has a major impact on the energy generation performance and long-term reliability of solar cells. The motivation for combining X-ray diffraction (XRD), X-ray fluorescence (XRF), and white light reflectometry (WLR) was to obtain a more complete model of the microstructure of the analysed thin film than would be possible with each method alone. This approach is exemplified here for the determination of the Ga depth distribution in $CuIn_{1-x}Ga_xSe_2$ (CIGSe) films, i.e. the value of x as a function of film depth. The depth dependent chemical composition is an important property for photovoltaic absorber films consisting of compound semiconductors, because it strongly influences the band gap energy of the material. Controlling this depth-dependence enables tuning of the band gap as a function of film depth. In the case of $Cu(In,Ga)Se_2$, this is utilised to create an electron barrier at the back-contact to reduce performance loss due to charge carrier recombination.

The challenge was to measure the depth profile of the chemical composition during deposition of these thin films in real time to give better understanding and control of this important material property, and hence to achieve higher solar cell efficiencies and improved reproducibility of the fabrication process. This is difficult because each method on its own is unable to uniquely resolve such a depth distribution within a time that allows its application as an in-situ or in-line process control method, i.e. within a few seconds up to a maximum of around 10 seconds. The main idea of this case study was to realise the three methods in a single, laboratory-scale setup. The approach developed for analysis of the hybrid XRD/XRF/WLR data analysis is explained in Figure 1.
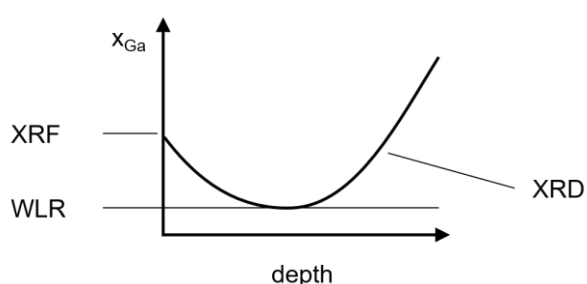

Figure 1: Approach used for the hybrid data evaluation: A Ga depth distribution x_{Ga} was evaluated by simulating the corresponding XRD signal and fitting this to the measured XRD signal. Since the solution in general is not unique, the degrees of freedom for the shape of the depth distribution are reduced by determining the surface chemical composition by XRF and the minimum composition of the depth profile by WLR.

Within the project the experimental setup was developed and optimised in collaboration with PTB. To enable short data acquisition times for the X-ray methods (XRD and XRF), a high-flux liquid-metal-jet X-ray source was employed in combination with a weakly focusing polycapillary optic. The absolute photon flux for the high-flux metal jet X-ray source was determined and reference calibration samples were validated. Polycapillary optics were chosen because they do not monochromate the radiation, which is an advantage for XRF and acceptable (but not ideal) for XRD, see Figure 2.

For XRD, the characteristic Ga-Ka radiation of the X-ray source and a large area X-ray photo counting detector were employed, which significantly accelerate the data acquisition compared with a line detector or point detector, because a wider range of diffraction and azimuthal angles can be detected at once. Moreover, information on crystal orientation was obtained with this setup. For the XRF measurements a silicon drift detector was employed.
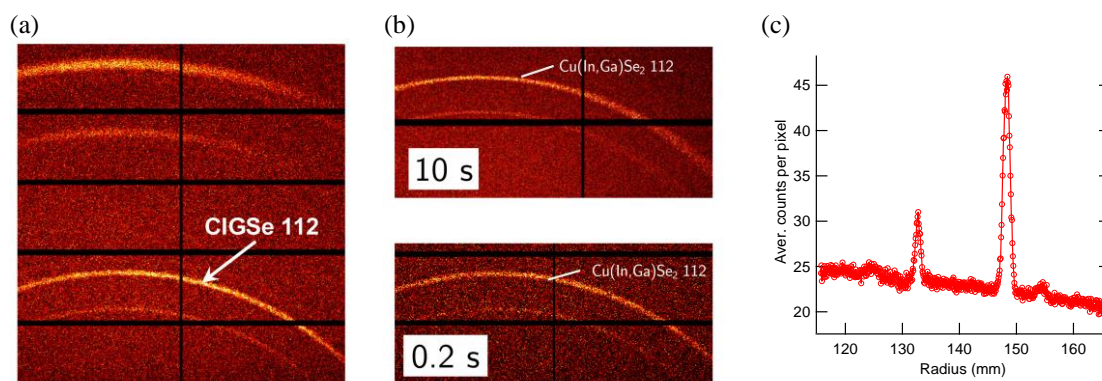
Figure 2: a) 2D-XRD diffraction image of a CIGSe sample measured with without optics. b) Comparison of a measurement without optics (top) and with polycapillary optics (bottom). c) Circular integration of the measurement shown in (a).

The WLR setup was developed such that it can be measured simultaneously with XRD and XRF at the metal-jet source. The acquisition time was not critical for WLR, where a spectrum could be recorded within seconds.

To extract the band gap of the sample from the WLR data turned out to be challenging, because the data could not be directly fitted with a physical model. The band gap was determined from the deflection point of the first rise of the background. The composition x was then calculated from the bandgap.

Even though elemental analysis within 10 seconds was possible with the laboratory-based XRF setup, it turned out that the absolute accuracy was not yet sufficient for the hybrid data evaluation. Therefore, we used data from synchrotron measurements performed by PTB.

The measured 2D-XRD data were circularly integrated to obtain a 1D-XRD diffractogram. Using the surface Ga concentration from XRF and the minimum Ga concentration from WLR as fitting constraints, the estimated Ga depth distribution was varied until a best fit was obtained between the simulated XRD profile and the measured XRD profile of the $Cu(In,Ga)Se_2$ 112 reflection. The Ga depth distribution obtained from this procedure is shown in Figure 3.
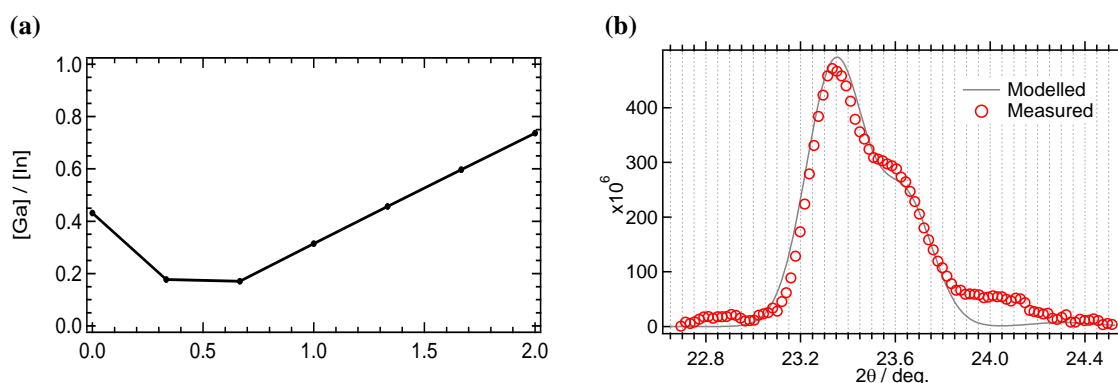

Figure 3: a) Ga depth distribution resulting from fitting the calculated XRD profile to the measured XRD profile. b) Measured and simulated XRD profiles of the $Cu(In,Ga)Se_2$ 112 reflection.

Understanding the mechanism of growth and how the final crystalline structure can affect the overall quantum efficiency is critical to methodically developing a good recipe for accurate and robust assessment of photovoltaic absorber films. Within the HyMet project HZB demonstrated that it is feasible to analyse chemical gradients in-situ as thin films are grown in a vacuum chamber, using laboratory equipment and a hybrid metrology approach. They also showed the applicability of the methods to photovoltaic samples prepared by Flisom who investigated the feasibility of transferring the technology for in-line quality assessment to accelerate development of high-quality photovoltaic products.

The market and technology applications for this technology includes:

- Thin film solar cells – such as chalcopyrites, perovskites and other new materials

• 	Wider functional thin films applications such as composites and metallic alloys

Hybrid metrology for electrocatalysts - Analysing electrocatalytic thin layers by means of multiple surface methods.

During the project, BAM together with TUB, and with support from PTB, VSL, CMI, CEA, NPL and Accurion investigated porous thin layer materials used in electrocatalytic water splitting. Green hydrogen is seen by the EU as a versatile renewable energy source that will drive the so-called "hydrogen economy". A better understanding of the materials used in electrolytic reactors is expected to lower the costs of installation and maintenance. Thus, the aim of this work was to demonstrate hybrid metrology methods to support improvement of electrocatalytic materials to increase yields of electrolytic ("green") hydrogen production.

The challenge was to develop a method for determining critical parameters of mesoporous doped oxide and carbon layers (both used in water splitting) that correlate with the electrochemical properties, which are critical for the performance of these materials in electrocatalysis. This was difficult because these are highly complex thin films consisting of porous layers, where the porosity and the chemistry within the pores critically determine their performance. The HyMet project evaluated a broad range of measurement techniques to identify the best approach for a multi-method metrological scheme that provides reliable results with direct impact on the performance of these materials in electrocatalysis.

Figure 4 compares a range of methods usable for mesoporous layer characterisation with their respective advantages and disadvantages. A good analysis strategy should obtain as much useful data as possible whilst considering the measurement and analysis expense. Here, the project sought a methodology that would yield maximal benefit for production purposes. This was achieved by developing spectroscopic ellipsometry analysis as a production-friendly technique, whilst making use of the strong metrological advantages offered by other methods to improve and quantify accuracy.
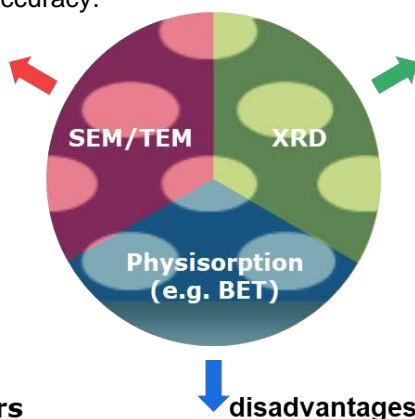
Figure 4: Overview over some possible analysis methods usable for complex mesoporous layer characterisation

The hybrid approach of the project enabled the development of new multi-method data analysis schemes combining the data from electron microscopy, optical spectroscopy, optical scatterometry, X-Ray scattering, and electrochemistry. The project has produced a large reference dataset of enduring value for advancing the properties of electrocatalytic layers. In a step not envisaged at the start of the project, a new *in situ* method for combining electrochemical measurements with optical spectroscopy was developed at BAM, in collaboration with TUB. This now serves as a basis for further optimisation of the materials investigated in the project as well as for future process quality assurance methods.
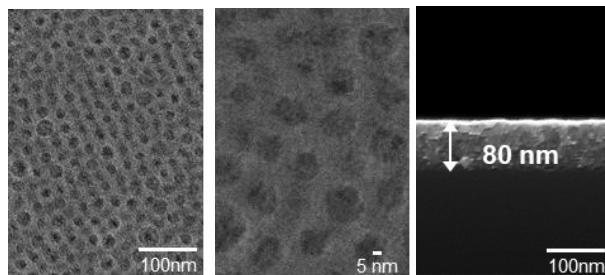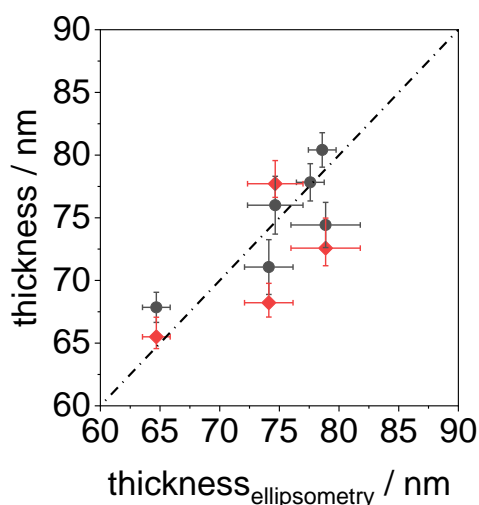
Figure 5: Electron micrographs of porous IrOx layers.

As an example, to improve the performance of electrocatalysts, like porous Iridium oxide layers, used in water splitting, the correlation between the manufacturing parameters and the performance of these materials must be found [1]. This project investigated porous IrOx layers like the one shown in these electron micrographs (**Error! Reference source not found.**). This shows the surface of an IrOx layer calcined at 300°C. The dependence of the material parameters on the calcination temperature is highly important for understanding and improving the materials. Therefore, a study was conducted on how to non-destructively analyse IrOx layers using spectroscopic ellipsometry, which showed that the values obtained for the layer thickness correlate well with the results obtained from electron microscopy (Figure 6).

Figure 6: Comparison of thickness measurements obtained from spectroscopic ellipsometry and electron microscopy.

Further, the project found a correlation between the optical constants spectrum of the IrOx material and the electronic structure (shown in Figure 7):
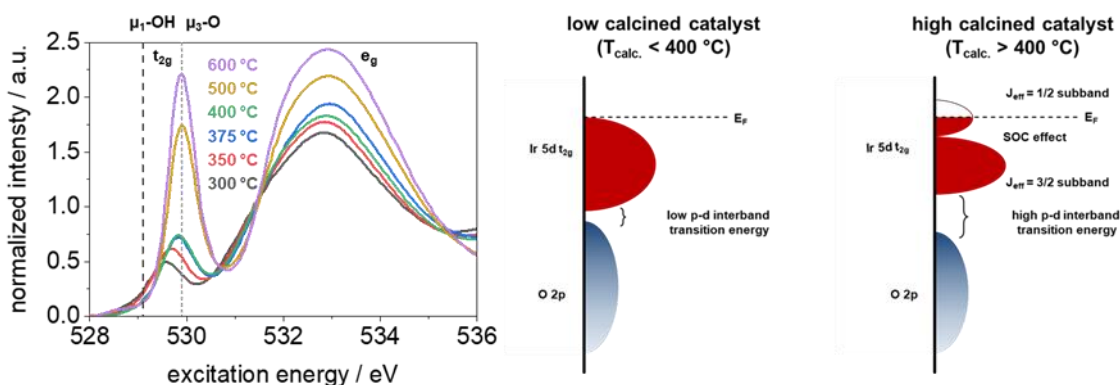

Figure 7: Comparison of the optical constant spectrum of IrOx (left) and its electronic structure for low and high temperature calcination (right).

The goal of this work was also to establish correlations between the optical constants (dielectric function) of the electrocatalytic materials and the electrochemical performance so that one method could be used to infer information from the other. Figure 8, demonstrates how such a connection can be drawn.
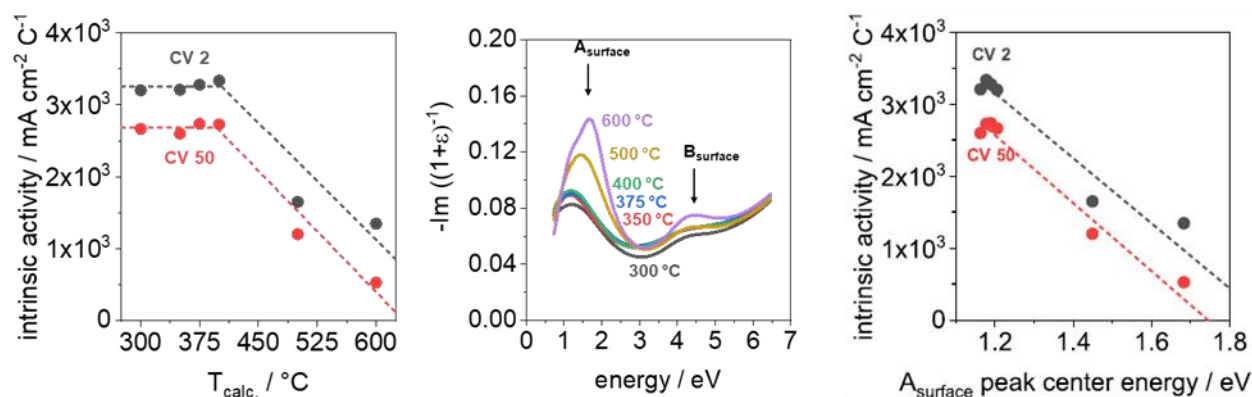
Figure 8: Correlations between the optical constants (dielectric function) of the electrocatalytic materials and the electrochemical performance (intrinsic activity).

The electrochemical activity depends on the calcination temperature of the IrO_x catalyst (Figure 8, left image). The dielectric function spectrum (depicted as energy loss function, middle image) also changes with this temperature. Therefore, spectroscopic features directly yield a measure of the expected catalytic performance (right image). This can be used as a fast and non-destructive activity monitor for the catalyst and potentially as an in-situ analysis tool.

With these results, the search for the optimal electrocatalyst for the hydrogen economy can be significantly faster in the future and *operando* monitoring of the catalysts to reduce maintenance costs becomes possible. Thus, this new hybrid metrology approach leads to a direct impact on the uptake and development of technology for the hydrogen economy.

Objective 2: Develop data analysis, data fusion and mathematical models to implement the hybrid metrology methods.

This objective has been achieved. The project has developed mathematical methods, data analysis and data fusion techniques to allow implementation of hybrid metrology methods.

Due to the complexity of thin film materials used in energy applications, which may include porosity, nanostructure, multi-element and multi-phase characteristics, their functional performance is determined by multiple physical and chemical properties. This means that single measurement methods are not sufficient to fully characterise these materials.

Often measurement techniques are developed individually, failing to build on synergies to deliver robust metrology for complex systems. The hybrid metrology concept of this project is the measurement paradigm where multiple complementary measurement techniques are applied in combination, and advanced data fusion is used to extract more information with higher confidence than can be achieved using each technique separately.

The focus of this objective was to tackle the complex challenge of hybrid metrology with multiple correlated measurands, which seeks to describe the sample with a model combining multiple measurements. Often, in thin film energy applications, the quantity of interest (known as the 'derived measurand of interest') is the reliability or quality of the material or device. These derived measurands of interest cannot be quantified by direct measurements nor by simple combinations of measurements through well-established mathematical equations. The more complex the system under investigation, the higher the number of input measurements that will affect these derived measurands of interest. A hybrid metrology approach aims to build hybrid models that combine different input measurement data to generate a derived measurand of interest.

The benefits of successfully applying a hybrid metrology approach include:
- Reduced uncertainty in the derived measurand of interest
- Optimised use of available data by understanding which measurements are more critical to the measurand of interest
- Reduction of the amount of data required, by removing redundancy in information, which ultimately reduces cost and material/product development time.

- Translation of results between measurement methods, facilitating comparison of results between laboratories and transfer of knowledge between laboratories and industry, where typically different measurement methods are available.

There are, however, several challenges associated with adopting a hybrid metrology approach, the seriousness of which depends on the level of maturity of each technology.

- The mathematical relationships between the different input measurement parameters are often unknown and/or dependent on the specific thin film application.
- The relationship between the derived measurand of interest (e.g. quality, reliability, efficiency) and the input measurement parameters is often unknown.
- The best data fusion approach to combine the input measurement parameters is case dependent

These challenges point to the conclusion that implementation of hybrid metrology needs to be optimised for the specific application of interest, which makes implementation costly and time consuming. Thus, in order to facilitate uptake of the hybrid metrology approach, NPL and TWI, in collaboration PTB, HZB and CMI, has identified key steps in a general procedure to implement hybrid metrology that is proposed as a guide to others who would like to implement this approach.

Define the problem and identify all parameters of interest

1) Define the aim. What information you want to obtain (e.g. performance, identify defects, ageing etc.)?
2) Define the aim as a quantifiable measurand of interest (e.g. dimensions of feature on an image, voltage vs time, physical sample parameter such as charge mobility, etc)
3) Identify the control measurement parameters that may induce change in what is being measured/observed (e.g. temperature, time, spatial position, processing condition, etc)
4) Identify what physical understanding you have of the problem. Are there equations, known relationships, boundaries for range of parameters, etc. that can be used?
5) Identify the input measurement data: in particular, what "type of data" is being measured (e.g. images, dimensionality, voltages, time dependence, etc.)
6) Assess reliability of the data (e.g. uncertainties)
7) Additional questions if data is spatially resolved
   a. Is there cross talk between pixels?
   b. Is there blurring?
   c. Does the location remain constant between measurements (registration, drift)?
   d. Additional questions if multiple image types are used as input measurement data:
      i. are datasets co-located (registration)?
      ii. are pixel sizes the same?
8) Additional questions if data is time-resolved:
   a. Are datasets synchronised
   b. What is the sampling rate?
   c. What parameters may affect your data as a function of time (controlled or unknown, e.g. temperature, degradation)?

Data analysis - Data fusion

1) Before identifying the best data fusion method to combine and analyse datasets the steps below should be followed.
2) Check if the dataset is consistent: datasets need to be reproducible and of high quality. Methods to clean and pre-process data can be used if collected data has unusable data (e.g. data outside the range of interest) and/or known errors (e.g. data collected under incorrect conditions in a time series).
3) Identify what are the data formats that will be used and what data format will be used for the output of the fusion (e.g. raw data, analysed data, decision). If unsure, follow the steps below to identify best options
   o Plot features of interest vs control parameter of interest (e.g. voltage vs time, feature size vs environmental exposure level, etc)

- o Look for similar or functional behaviour. This can be achieved:
    - ▪ Visually
    - ▪ Via parametrisation (if analysing curves) or spatial correlation (if analysing images)
    - ▪ Via calculation of correlation between datasets
4) Apply physical interpretation/knowledge of the sample system. Questions to be asked include:
   - o Is there an expected correlation?
   - o Why is there a correlation?
   - o Can a mathematical relationship be derived that links the quantifiable measurand of interest to the input datasets?
5) Choose the most appropriate data fusion method to analyse the chosen data formats that will be fused. Figure 9 below provides some examples on the types of mathematical models. However, note that these will need to be optimised for the specific case of interest.
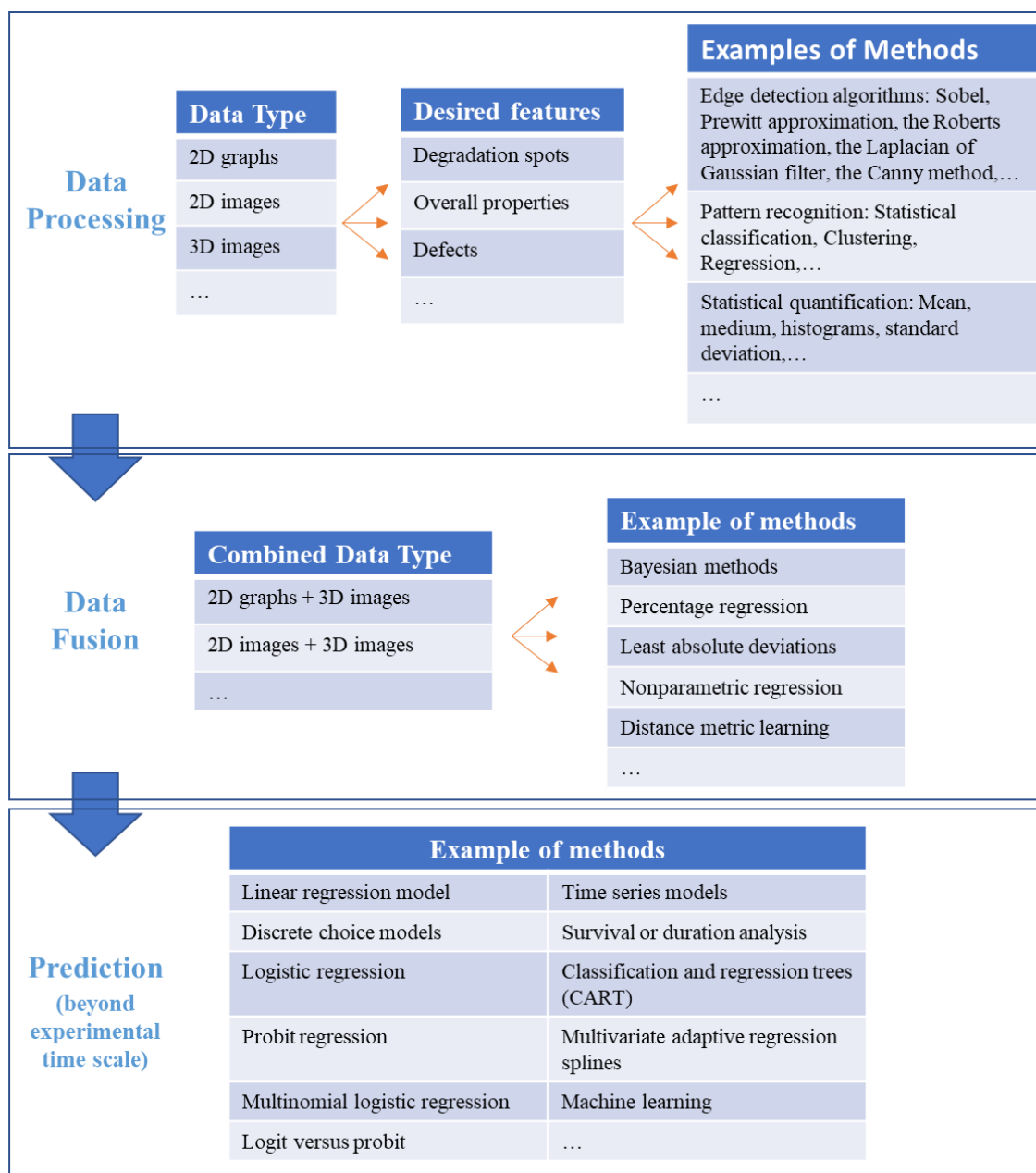

Figure 9: Example of data analysis, data fusion and mathematical methods for hybrid metrology.

Limitations or range of validity of generalised procedure
The generalised procedure above should only be applied if the following are fulfilled:

- Datasets are of good quality (e.g. reproducible, stable). See definition in [2]
- Samples are reproducible, which would affect the quality of the datasets.
- Measurements are taken using equipment that are calibrated and traceable to the International System of Units.
- Uncertainty of measurements is known or can be estimated. Good practice for the evaluation of measurement uncertainty is defined in the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and its supplements [4,5].

Two examples of advances in hybrid data analysis are shown below.

Hybrid metrology for power electronics – reference-based grazing -incidence X-ray fluorescence (GIXRF) and X-ray reflectometry (XRR) method to measure complex multi-layer thin films.

CEA, in collaboration with PTB and HF (Horiba), improved an industry-compatible hybrid methodology dedicated to the non-destructive metrology of inorganic thin-layered stacks. Such types of complex thin films are typically used for high performance power electronics applications, which are critical to reduce energy losses. The proposed methodology combines two X-ray techniques, grazing-incidence X-ray fluorescence (GIXRF) and X-ray reflectometry (XRR), to estimate thickness, composition and to reveal elemental depth-profiles with state-of-the art accuracy. CEA and partners optimised the analytical procedure and software and demonstrated the accuracy of this hybrid approach on samples specifically prepared for the project. The combination of XRR, which is more sensitive to the atomic density, and GIXRF, which is sensitive to element density, produces results of better accuracy compared with one technique alone. Such hybrid metrology is particularly suitable to support the development of advanced materials such as 2D materials and GaN-based stacks for energy applications, including power electronics. Importantly, the metrology toolset established during the HyMet project (analytical procedure and software) demonstrates to industrial partners – suppliers of X-ray tools and material deposition equipment, along with end-users, that hybrid XRR/GIXRF is mature enough to fulfil requirements for in-line measurements to accelerate development and deployment of high performance new energy technologies.
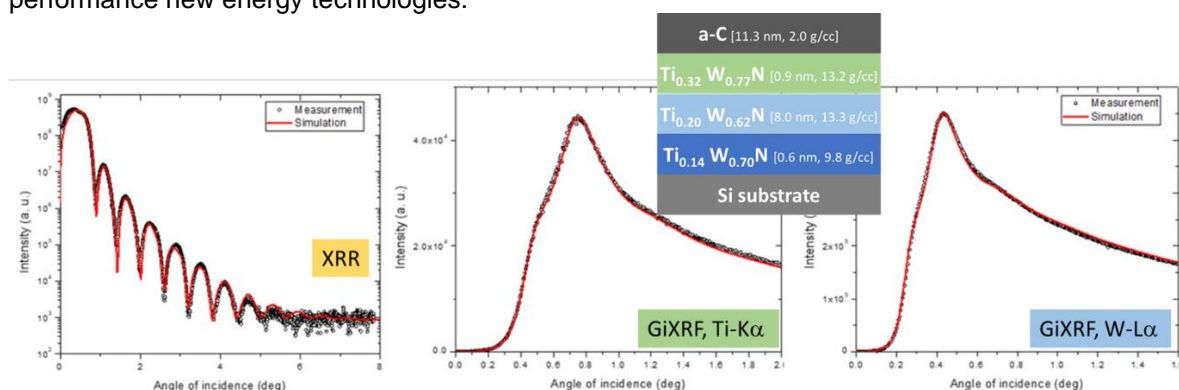

Figure 10: Experimental XRR and GIXRF data of a model sample developed in this project, where an amorphous carbon cap layer was used to protect the active TiWN layer from ageing, thereby permitting consistent characterisation of the sample by different partners. The developed software was used, first to determine the reduced instrumental function, then to determine the depth-dependent properties of the stack. The mass deposition of W and Ti were confirmed by reference-free GIXRF/XRR experiments conducted at PTB, and the elemental depth-profile was fully consistent with PP-TOFMS results from HF (Horiba).

The challenge was to demonstrate that the combination of GIXRF with XRR is adequate to probe thin-layered materials for industrial use (i.e. in the semiconductor industry). GIXRF is a highly sensitive elementary technique capable of probing chemical depth profiles in films with thickness ranging from few nm to ~ 200 nm. On the other hand, the XRR technique is a well-established technique widely available in laboratories and industry, which provides accurate values of mass density, thickness and roughness of smooth layered films in almost the same thickness range as GIXRF. The key advantage of combining XRR with GIXRF is in the drastic reduction in uncertainty due to the cross-correlated parameters' dependencies, e.g. between thickness and mass density in GIXRF-only analysis. GIXRF/XRR combines electronic density (XRR) and atomic density

(GIXRF) profiles, resulting in improved ability to determine accurate quantitative chemical depth-dependent information in thin-layered materials. This hybrid approach is already used in some laboratories and at synchrotron facilities but had not been introduced in industrial metrology due to the lack of standardised analytical procedure and software.

Therefore, CEA developed an alternative approach to hybrid GIXRF/XRR, in which a reduced instrumental function can be estimated from a limited number of samples. PTB and CEA worked together to demonstrate the accuracy of this industry-compatible reference-based approach, based on PTB's extensive experience of hybrid GIXRF/XRR analysis. In addition, an innovative technique developed by HF (Horiba) (plasma-profiling time-of-flight mass spectrometry, PP-TOFMS) was used for complementary analysis for the assessment of hybrid reference-based GIXRF/XRR. This resulted in the development of a GIXRF/XRR data analysis software to determine the depth-dependent properties of the complex thin film stack (Figure 10).

Hybrid metrology combining Grazing Incidence X-Ray Fluorescence (GIXRF) and Near-Edge X-ray Absorption Spectroscopy (NEXAFS).

NEXAFS is a sensitive method to reveal the chemical bonding environment of atoms. Combining this method with grazing incidence excitation X-ray geometry allows investigation of very thin films. Due to an incidence angle of only a few degrees, an X-ray Standing Wave (XSW) field can be used to tune the penetration depth of the exciting photons a few nanometres into the layers. Controlling the XSW field however is challenging. Therefore, in this project PTB developed data analysis tools to optimise the measurement conditions and assess the changes in the NEXAFS measurements, using simulation of GIXRF conditions and modelling of the measured spectra.

The standing wave field depends on the incident energy, the angle of incidence, and on sample properties, like the density, layer thickness (both as mass deposition or mass per area), roughness, and optical constants of the constituent elements. Figure 11 shows simulation results of the XSW field for a 20 nm thick aluminium oxide layer on a silicon wafer substrate. The graphs show how the XSW intensity distribution shifts with the angle of incidence (y-axis) and layer depth (x-axis) which allows the identification of optimum measurement angles for specific depths.
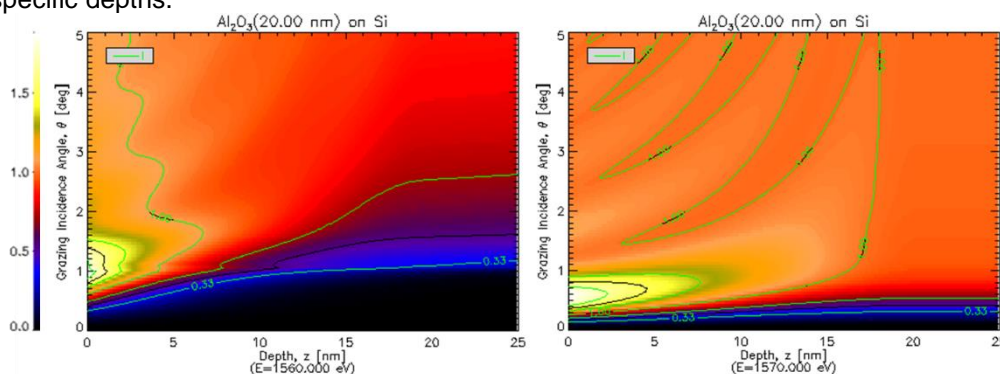

Figure 11 Simulation of the X-ray Standing Wave Field (XSW) for a 20 nm thick AlOx layer on a Si wafer. (left) The result for 1560 eV, just below the Al K absorption edge. (right) Results for 1570 eV above the edge.

These AlO$_x$ nanolayers provided by Aalto are proposed for use as surface passivation layers to improve performance and extend the lifetime of Si solar cells. Post-process annealing was seen to enhance the electrical properties of these devices. The hybrid GIXRF-NEXAFS method was used to investigate the reason for the enhancement. To allow for a stable and reliable evaluation and assessment of the measured GIXRF-NEXAFS spectra, a detailed modelling routine was developed (see Figure 12) to assign fixed resonances that describe the NEXAFS shape and thus enable the structural changes to be recognised on the basis of shifts in the intensity of these resonances. The modelling describes all NEXAFS spectra equally well (Figure 12), with a comparable small deviation between fit and measurement. Intensity ratios (P1-P8) were used to assess changes in spectra due to different post-processing annealing conditions. The results demonstrate that the observed improvement in the electrical properties cannot be attributed to a change in the crystalline bond structure.
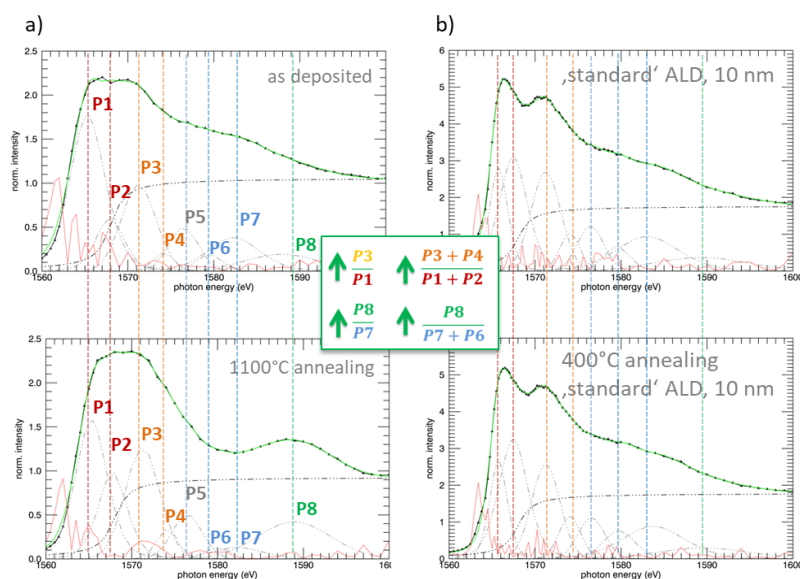
Figure 12 To deconvolute the NEXAFS spectra a fitting model with 8 Voigt lines and a step function was defined. The inset shows the resonance intensity ratios defined based on a reference sample set with an annealing temperature of 1100°C (a). In red the deviation between fit and measurement enlarged by the factor of 10 is shown.

Objective 3: Develop measurement methods for 2D and 3D chemical, structural, optical, and optoelectronic properties of nano-structured thin film energy materials and devices capable of identifying inhomogeneities at multiple scales.

This objective has been achieved. This project developed different measurement methods and improved measurement instrumentation to allow identification of inhomogeneities at multiple scales. Inhomogeneities are often a sign of local variation in performance, either due to manufacturing issues or to degradation. Some of the key advances achieved in this project included the design and realisation of a hyperspectral optical scatterometer at VSL, the development of advanced nanoscale electrical scanning probe microscopy methods at NPL and at METAS, time of flight secondary ion mass spectrometry (TOF-SIMS) at NPL and time resolved photoluminescence mapping at EMPA.

Application of these methods to identify inhomogeneity at multiple scales in complex thin films was demonstrated in samples provided by Surrey, OxfordPV, EMPA and Flisom, as summarised below.

High resolution 2D and 3D measurements of inhomogeneity in perovskite solar cells

Several of the complex thin films used in energy applications can suffer oxidation or other unwanted degradation when exposed to air, O_2 and/or humidity. For instance, when perovskite thin film solar cells are exposed to the atmosphere, they degrade rapidly due to oxidation or other reactions that may lead to irreversible microstructural, optical and electrical changes, directly reducing their performance. The ability to perform high resolution scanning probe measurements under controlled conditions significantly improve repeatability and reproducibility of measurements, providing higher confidence in the results and preventing unwanted contamination/degradation. Therefore, through this project NPL has upgraded their advanced scanning probe microscopy facility to allow structural, electrical and optical high-resolution measurements under controlled atmospheric conditions.

Error! Reference source not found. shows the NPL facility developed in this project, which includes an atomic force microscope able to perform nanoscale electrical measurements in contact (conductive, C-AFM, and photoconductive, PC-AFM) and non-contact (scanning Kelvin probe microscopy, SKPM) modes. Conductive atomic force microscopy is capable of mapping local current distribution with picoampere (pA) sensitivity. Photoconductive AFM is an extension of the technique where C-AFM experiments are carried out with additional optical illumination. Both techniques are powerful for correlating current and photocurrent characteristics in perovskite devices with microstructural features such as grains and grain boundaries to evaluate where charge trapping or recombination occurs [6,7], and can achieve lateral resolution below 200 nm. In contrast to C-AFM and PC-AFM, SKPM is a local measurement that is primarily sensitive to the sample surface underneath the tip and measures the electrical contact potential difference (CPD) between the probe and the sample. Assuming that the surface potential at the AFM tip remains constant, SKPM maps variations in the local work-function of a sample surface with nanoscale (> 200 nm) lateral resolution. For perovskite

devices SKPM offers valuable information on the interfaces which can be related to band bending, charge accumulation and ionic migrations [8].

The system is enclosed in a nitrogen filled glovebox that maintains very low levels of O_2 and H_2O. Laser illumination is also integrated allowing measurement with and without light. In addition, the output can be coupled to a Raman/Photoluminescence spectrometer for co-localised optical characterisation. A transfer port has also been installed to allow sample transfer between this SPM facility and the Secondary Ion Mass Spectroscopy (SIMS) measurement facility at NPL, while keeping samples in vacuum to avoid contamination or unwanted degradation.
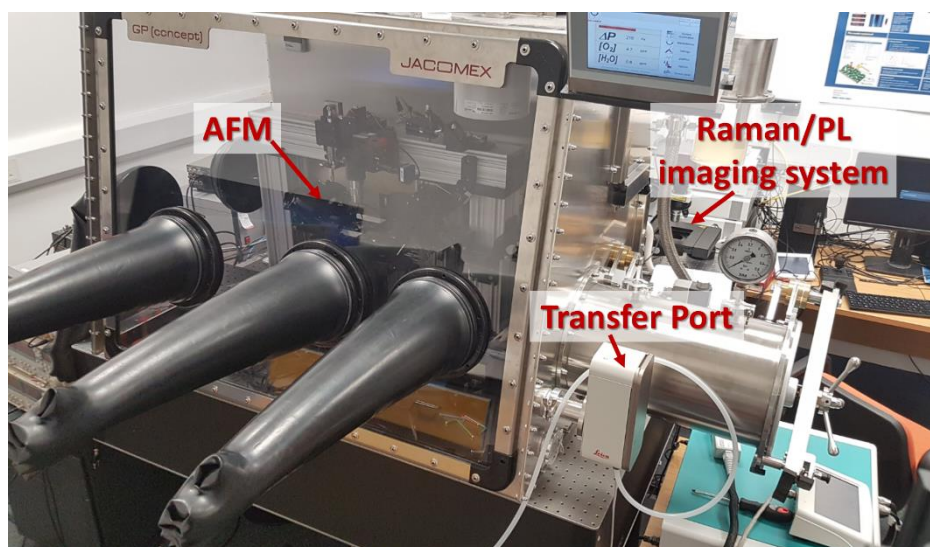

Figure 13. Image the advanced scanning probe microscopy facility at NPL showing AFM inside a glove box for environmental control with the additional transfer port, and Raman/ photoluminescence imaging system (obscured in image).

Secondary ion mass spectroscopy (SIMS) is a widely-used ion-beam technique used to probe the chemical composition of layered structures [9]. Typically, 3D structural information can be obtained throughout the sample thickness using dual ion beam depth profiling: one sputter ion beam erodes the surface and an analysis ion beam analyses the centre of the crater between sputtering cycles. Depth profiling of hybrid structures with SIMS represents a challenge in finding the optimal experimental conditions, *i.e.* sputtering conditions for all the materials represented in the structure, since sputtering rates vary by several orders of magnitude between inorganic and organic materials. The application of SIMS to complex thin films such as perovskites that present both organic and inorganic phases presents a significant technical challenge [10].

Within this project, NPL developed a sputtering method to create a circular bevel cross-section (Figure 14) to circumvent the issues of material dependent sputtering rate. The bevel expands the layered structure and interfaces by a factor of approximately 100 times. The bevel angle is nominally the same in each sample and can be accurately calibrated using a profilometer.
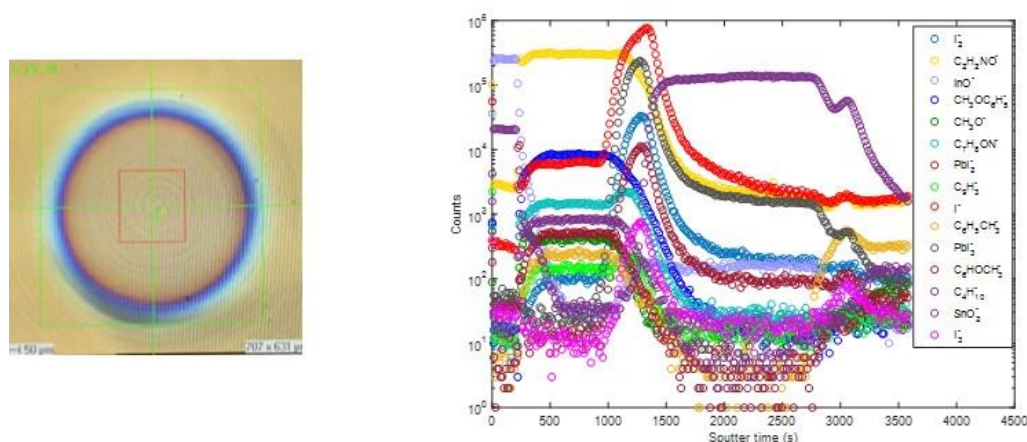
Figure 14. (left) Optical image of bevel cut in OxfordPV perovskite sample using 3 keV Cs⁺ for sputtering with sample rotation. (right) Corresponding perovskite secondary ion depth profile which illustrates different sample layers. The most intense signal in the first layer comes from InO⁻ (light purple) and corresponds with the transparent conductor ITO. The following layer is the organic hole transporting layer, which is in this case Spiro-OMeTAD with the most intense signal originating from the $C_2H_2NO^-$ fragment in yellow. The perovskite layer gives sharp depth profile curves with the most intense one originating from I⁻ in red. Finally, the dark purple signal originates from SnO_x representing the inorganic electron transporting layer.

Complementary depth-resolved chemical and nanoscale electrical characterisation using Secondary-Ion Mass Spectrometry (SIMS), and electrical modes of Atomic Force Microscopy (AFM), respectively offer high resolution imaging capable of probing chemical changes due to manufacturing defects or degradation, and correlate these with local changes in functional properties, exhibiting spatial resolution better than 200 nm. These techniques were used to investigate perovskite samples from Surrey, with the structure: glass/ITO/Poly-TPD/PFN-Br/perovskite/PCBM/BCP/Ag.

Chemical imaging using the 3D OrbiSIMS instrument (SIMS using an Orbitrap mass analyser [11]) are shown in Figure 15 for a non-degraded sample. The most intense signal corresponds to the perovskite layer which is represented by I⁻, PbI_3^-, CsI_2^-, I_2^-, PbI_2^-, the m/z 340.73 peak and $Br_2O_2^-$. PCBM related fragment ions also give a strong signal but further insights into the fragment chemical composition is needed. Further chemical identification of the less intense Poly-TBD and PFN fragment peaks (including the m/z 622.52 peak which corresponds to the PFN layer) is also required. The thin silver layer is clearly observed.
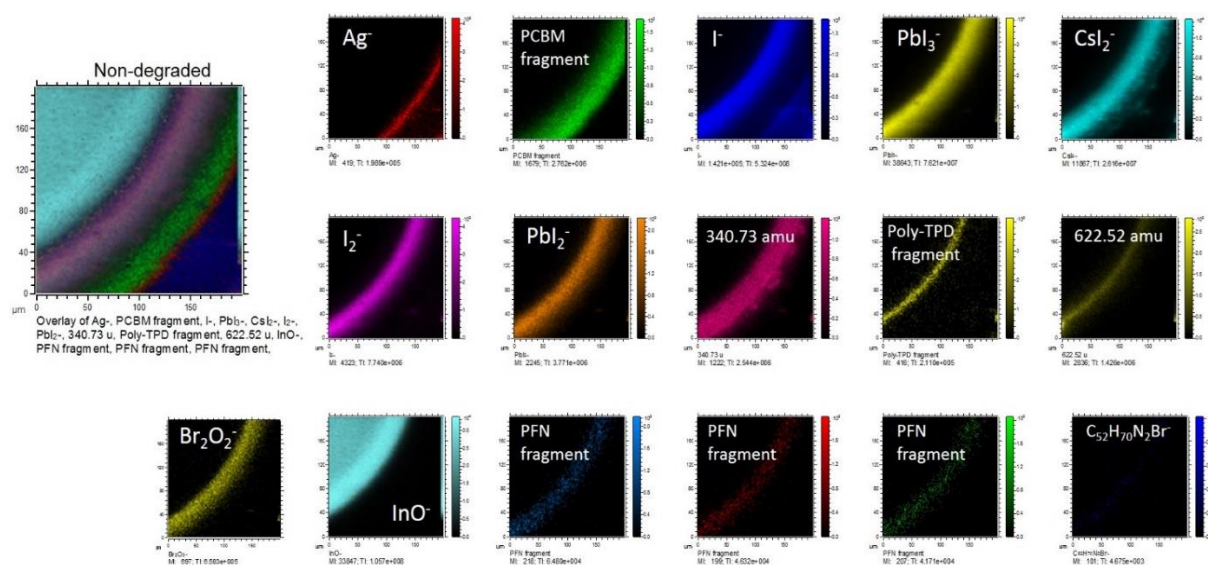

Figure 15. Chemical maps of the non-degraded perovskite solar cell from Surrey.

In order to correlate chemical changes due to degradation and its direct impact in electrical and optoelectronic performance, a registration method was developed to combine datasets for hybrid analysis. Co-registering the SIMS and electrical AFM data is challenging due to the very large difference in field of view and resolution. Nevertheless, feasibility is demonstrated below, which was achieved using coarse alignment markings and feature matching to overcome the challenge. This is demonstrated in Figure 16 where aligned datasets for cross-sections of a degraded perovskite sample are shown. The larger lateral resolution of AFM images can identify elongated periodic structures associated with degradation of the perovskite layer which are not visible in the TOF-SIMS data. The co-registration allows us to identify the chemical species in that position from TOF-SIMS data, which corresponds to PbI_2^-, a poly-TPD fragment, and InO^-. These chemical species are associated with the 'bottom', hole extracting contact of the perovskite device stack and indicate that this is where the observed structure develops. The strongest electrical currents measured in the PC-AFM image align with the light blue chemical signal (InO^-), indicating that the AFM tip is in contact with the bottom ITO layer of the device, where one might expect strong electrical conduction. This indicates the potential for this new hybrid approach to investigate inhomogeneities in complex thin films for energy applications.
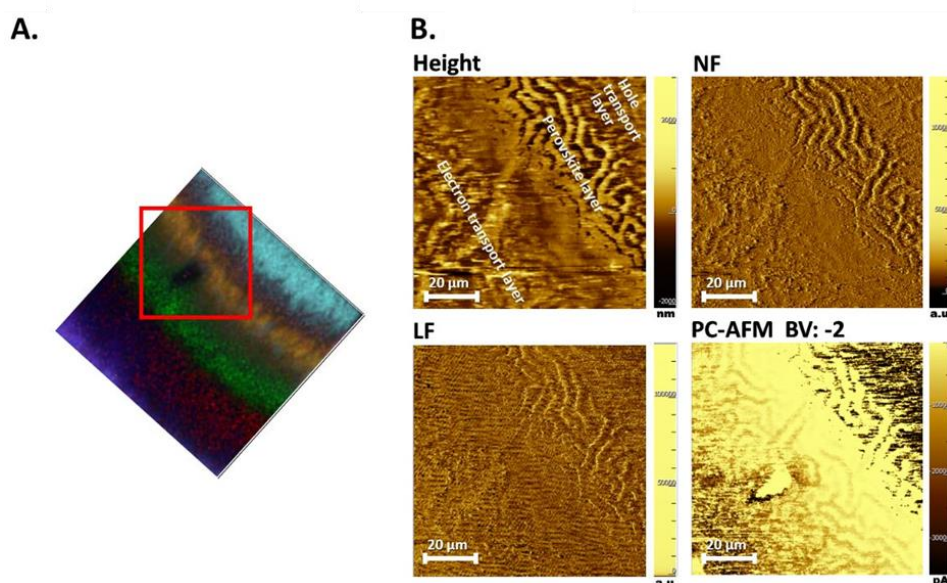

Figure 16. Alignment of SIMS chemical map with AFM images for a degraded perovskite Sample. (A) SIMS chemical map with rotation of 110° to match AFM image area indicated by red square. (B) AFM images showing Height, Normal Force, Lateral Force and PC-AFM current signal collected under 532 nm laser illumination and bias voltage of -2 V.

2D multiscale measurements of inhomogeneity in CIGS solar cells

Copper indium gallium sulphide (CIGS) thin film solar cells can be applied on flexible and lightweight substrates, opening numerous energy-harvesting applications [12]. However, these compound, polycrystalline materials, produced by co-sputtering or co-deposition, typically present inhomogeneities across the film which can affect operation and performance of the solar cells. A cross-section SEM image of a CIGS solar cell structure is shown in Figure 17. So far, large scale production of the CIGS cells remains a challenge, particularly due to quality issues, and various control techniques are in high demand for CIGS production.
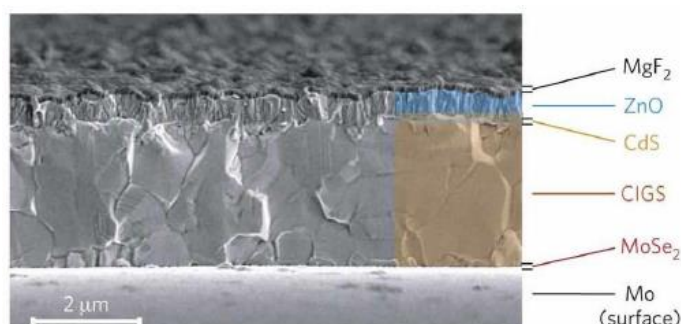

Figure 17: Scanning electron microscopy image of a typical CIGS solar cell structure.

This project utilised different spatially resolved techniques to investigate their applicability to determining inhomogeneities at multiple scales, from sub-micrometre level to large scale. Samples with different post-treatment methods were fabricated at EMPA and markers were used to facilitate co-localised measurements between time-resolved photoluminescence (TRPL) and high-resolution SEM imaging performed at EMPA, scanning Kelvin probe microscopy (SKPM) at NPL, and scanning microwave probe microscopy (SMM) at METAS.
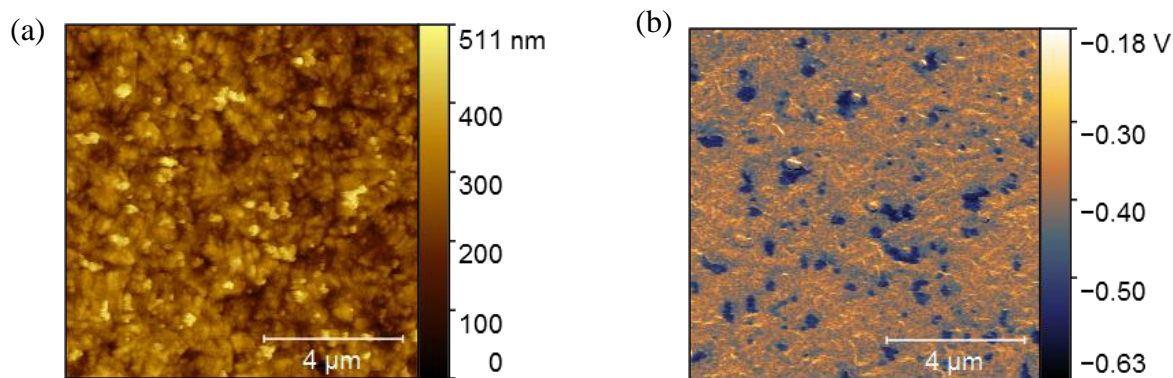
Figure 18: SPM measurements on sample CIGS sample without post-deposition treatment. (a) Surface topography and (b) contact potential difference.

SKPM was used to understand the role of various post-deposition treatment (PDT) steps in enhancing the performance of CIGS photovoltaic devices. In Figure 18 (a) higher lying features with round geometry are visible, correlating to regions of more negative CPD in Figure 18 (b). These are understood to be related to nucleation of CdS around contaminant particles during chemical bath deposition, and have been reported previously on similar structures [13]. Grain boundaries are visible in the SKPM map and show higher CPD. The data presented in Figure 18 is representative of features observed in the sample without post-deposition treatment.

While SKPM is sensitive only to the surface of the sample, scanning microwave microscopy (SMM) provides a way to probe deeper into the subsurface. SMM applies a microwave signal to the sample and measures the signal reflected from the point contact between the probe tip and the sample. The ratio between the reflected and applied signals is a complex number, the so-called S_{11}-parameter, that depends on the electrical properties of the sample, i.e. its dielectric constant ε, and its conductivity σ. Due to the skin-depth of the microwave radiation, different frequencies can be used to probe different depths into the subsurface of the films (ranging from ~100 nm at 50 GHz, to ~2 micrometres at 1 GHz in copper, and much larger in semiconductor materials) [14]. For this project, METAS upgraded the SMM instrumentation to allow measurements under illumination.
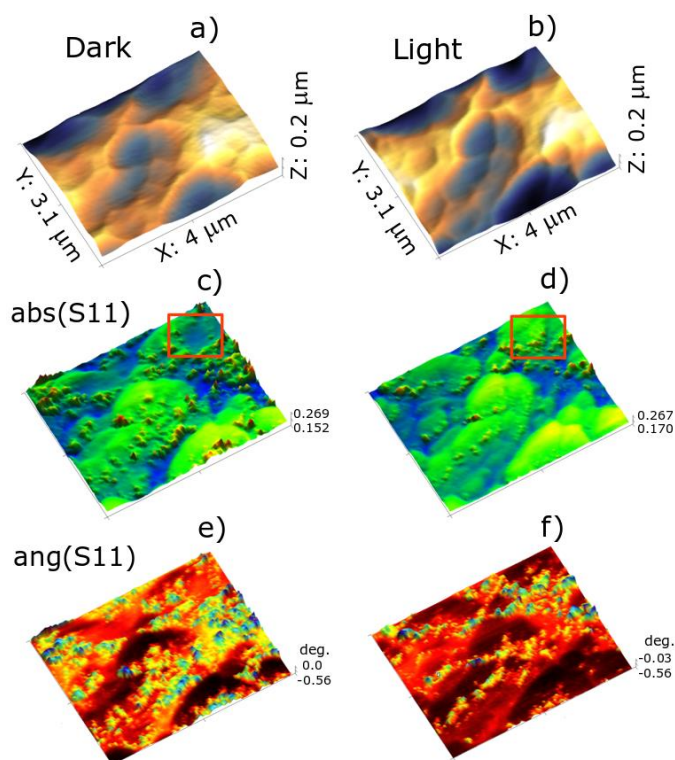
Figure 19: SMM measurements of the top surface of the CIGS samples from EMPA under white light illumination.

SMM measurements at the top surface of a CIGS sample in the dark and under white light illumination show topography (Figure 19 (a) and (b)) consistent with that obtained by KPFM; grainy structure with grain sizes ranging from 0.5 µm to 2.0 µm and height variations of up to 200 nm. The S11 parameter maps show additional features appearing when the sample is under white light illumination, as highlighted with red rectangles in Figure 19 (c) and (d). The spatial broadening of the features around grain boundaries and appearance of new features under illumination is attributed to optically generated charges, which become trapped and change the local depletion of the grain boundaries, thus modifying the local capacitance [15]. Such pockets of charge are expected to have a detrimental effect on the solar cell performance.

Transient photoluminescence (TRPL) mapping measurements allow extraction of the effective minority carrier lifetime (a key parameter determining the efficiency of a solar cell) in the absorber layer in order to identify the influence of grain-boundaries and inhomogeneities on the micrometre scale. EMPA's TRPL setup was coupled to a microscope to gather light from a micrometre-scale area, i.e. 1 µm to 25 µm optical resolution depending on the scan range. Spatial scanners complete the mapping tool built and used in this project to measure the TRPL decay curves for each pixel and for measurement regions on the cm-length-scale down to the nm-length-scale. Quantification of TRPL data is a challenge as some fitting parameters can be influenced by multiple factors, such as doping concentration, radiative coefficient, fast recombination processes or charge separation within the time resolution of the system, among others. Despite this, it provides a way to evaluate the amount of radiative recombination events, which correlates to the efficiency of the solar cell.

Figure 20 shows the TRPL parameters for each solar cell with different post treatment (PDT) applied. Black lines and rectangle on top of each image correspond to the grid lines of the device (acting as the front electrical contact), being regions where no light is absorbed in the solar cell. Although not fully homogeneous, there are no significant deviations for any of the TRPL parameters.
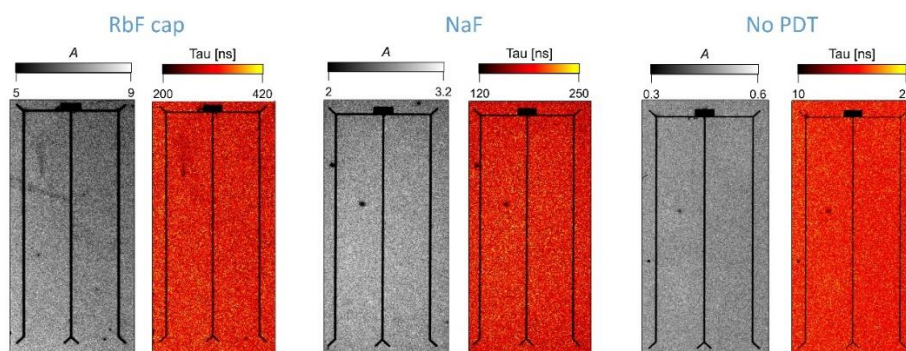

Figure 20: Maps of TRPL parameters for three different post deposition treatments for EMPA solar cells. Note the different colour scales.

Overall, all three methods are suitable for characterisation of CIGS, with complementary capabilities for in-line characterisation and post-production quality control and testing. The KPFM and SMM are suitable for revealing

small-scale (between ~100 nm and ~10 μm) inhomogeneities and TRPL is suitable for the detection of larger scale variations (from a few micrometres up to a few centimetres).

Objective 4: Identify key measurement parameters for improved stability of thin film energy products and generation of new materials datasets as a function of ageing.

This objective has been achieved. This project has developed in-situ metrology facilities that can generate realistic ageing conditions in a controlled way, transfer chambers and procedures to avoid sample contamination and uncontrolled ageing during transport and storage, and improve quantification of techniques. These facilities, combined with additional methods, were used to generate materials datasets as a function of ageing and to identify key measurement parameters that can be used as metrics for the stability of thin film materials in energy applications.

NPL developed a new measurement facility for in-situ characterisation of solar cells using multiple measurement methods. The new facility combines portable environmental chambers with simulated sunlight, electrical characterisation, and spatially resolved optical characterisation methods, allowing the simulation of realistic ageing conditions by controlling the gas environment, illumination, temperature and electrical bias conditions. Traceable control of temperature is achieved using a PT100 temperature sensor located in the sample plane, in combination with a transparent electrical heating element placed between the sample and the light source. A control program with a feedback-loop was set up to switch the power output of the heating element according to a temperature set-point. The proportional, integral and derivative parameters of the feedback loop (PID) were tuned to minimise the temperature overshoot, oscillations and time to reach the set-point. NPL also developed a new LED light source to allow controlled long term in-situ measurements under simulated sunlight. The light output qualifies as class ABA for spectrum, uniformity and stability, respectively, according to IEC 60904-9:2007 for the spectral range of < 700 nm only [16]. A spatial map showing irradiance spatial uniformity and the spectral profile of the LED array are presented in Figure 21.
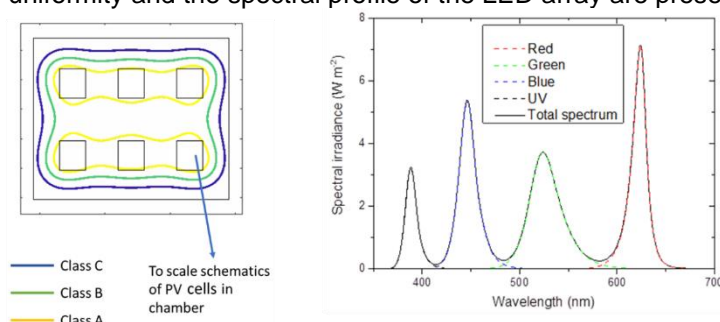

Figure 21. Left: layout of large sample chamber showing 6 samples in their positions, and contours indicating regions where illumination uniformity meets requirements for Class A, B, and C. Right: Emission spectrum for the LED array light source showing contributions from red, green, blue, and UV LEDs.

Current-voltage curves that are used to measure the power conversion efficiency of solar cells, are measured in-situ while samples are exposed to the ageing conditions of interest. NPL has also developed and implemented an optical measurement system that is compatible with the environmental chambers and capable of performing *in situ* photoluminescence (PL) and electroluminescence (EL) imaging as well as fast photocurrent mapping of samples through the optical window of the environmental chamber (Figure 21). This allows electrical and imaging measurements to be acquired and combined during degradation tests, linking performance changes with spatially resolved features that develop during degradation. Different aspects of spatial homogeneity and electrical performance of samples during ageing tests can be monitored and distinguished, such as the local charge collection efficiency, electrical contact failures and material degradation.
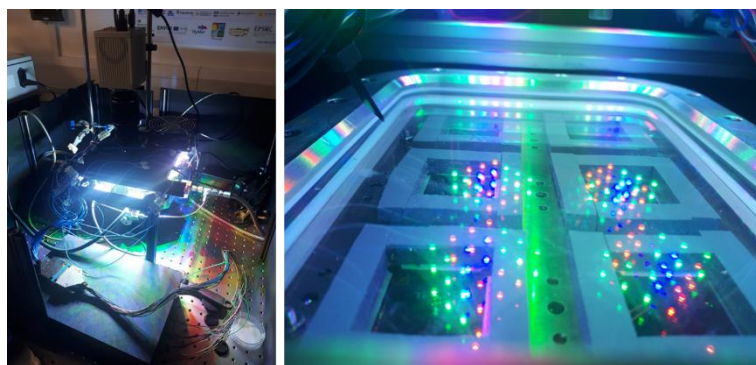

Figure 22. On the left, a picture of the system developed at NPL for in situ optical and electrical measurements, with one of the large portable environmental chambers connected to the gas mixing system. On the right a picture of top side of the chamber under the LED array of the system, the slots inside the chamber where the cell are placed can be observed.

Spatial uniformity as a key parameter for assessing stability of perovskite solar cells

Perovskite solar cells can degrade rapidly in environments containing oxygen but the mechanisms affecting this degradation are not clearly understood. There is widespread commercial interest in developing techniques to overcome this limitation to increase uptake of this solar cell technology. During this project, our studies found that the macroscopic reduction in perovskite solar cell device performance over time when exposed to light and oxygen originates from highly non-uniform degradation across the device film. Thus, lateral spatial homogeneity of perovskites can be used as a key parameter for assessing improved stability of solar cells.

NPL, in collaboration with Surrey, Oxford PV, and CPI, applied this new in-situ measurement facility to perovskite solar cell samples under realistic stress conditions in order to study the device degradation. Degradation studies consisted of experiments running for 4 days under pre-determined conditions (e.g. illuminated samples at constant temperature under specified O_2 concentration) and measured both current-voltage curves and spatial optical imaging (e.g. photoluminescence) as a function of time.

An example showing the variation in photocurrent generation at very low exposure to oxygen (4 ppm) is shown in Figure 23. The changes in short circuit current (I_{sc}) are similar for two out of three cells, having almost identical initial I_{sc} values, whereas the third cell, A51D3 had a lower initial I_{sc} value. Despite the difference in initial I_{sc}, the relative behaviour of this quantity over time is similar for three cells.
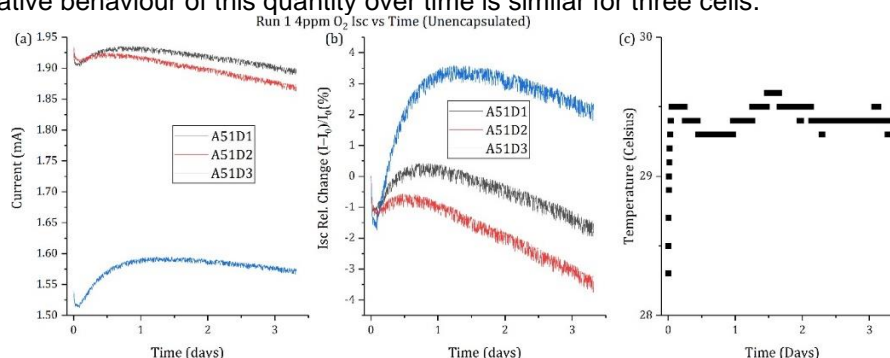

Figure 23. (a) I_{sc} and (b) relative change in I_{sc} plotted over time for Run 1 where the O_2 concentration was 4 ppm. (c) Substrate temperature monitored during this measurement.

The behaviour of the photoluminescence (PL), is markedly different. Figure 24 shows the average of all pixel values for each of the three cells plotted against the degradation time. At short times (< 0.5 days), the PL intensity drops and then recovers, which appears to correlate with the I_{sc} measurement, but at longer times the PL intensity continues to increase (whereas I_{sc} reaches a maximum at around 1.0 days and then declines). This indicates that there is not a simple relationship between PL and I_{sc}. Rather it suggests that there is a transition between two types of behaviour at around 0.5 days of measurement. In Figure 25, the spatial distribution of the relative change in PL intensity per pixel after 0.5 days is plotted, alongside a histogram of these values. The plots are ordered respectively from top to bottom: A51D1, A51D2 and A51D3. This analysis reveals different types of defects: some that show little change over 2.5 days and some that are strongly affected by degradation exhibiting more than 100 % change over time, such as the ring-shaped feature near the centre A51D2 (visible in Figure 25(c)).
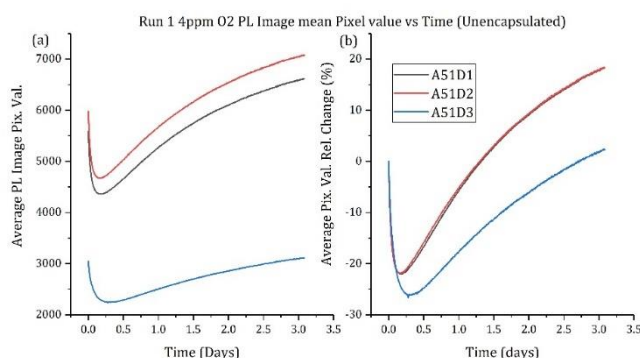

Figure 24. Average PL image intensity plotted over time for Run 1 with 4 ppm O_2.
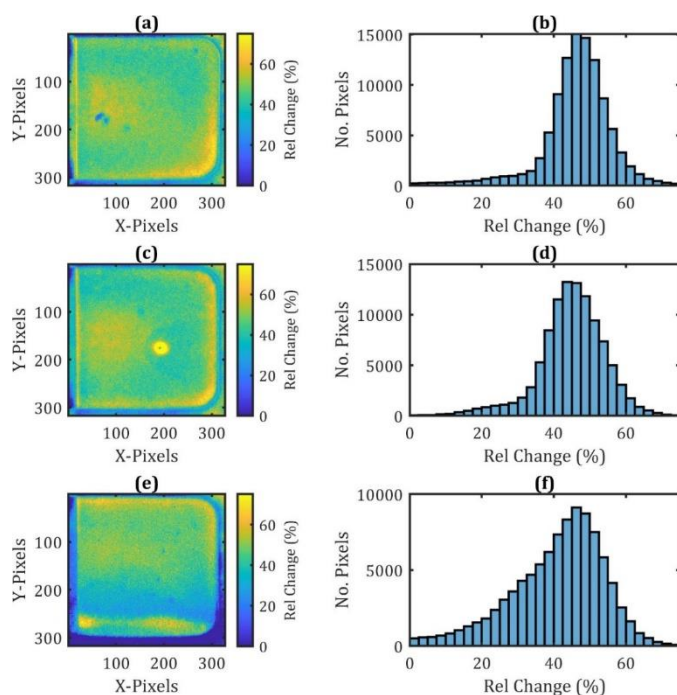
Figure 25. PL maps (a), (c) and (e) showing spatial distribution of relative changes in PL intensity alongside histograms (b), (d) and (f) for devices A51D1 A51D2 and A51D3, respectively under 4 ppm oxygen degradation conditions (Run 1).

Table 1: Device performance statistics for Run 2 (1,000 ppm O_2 degradation) comparing devices with and without ALD layer.

	Bare (mean ± standard dev.)	ALD (mean ± standard dev.)
Initial V_{oc} (V)	1.08 ± 0.02	1.04 ± 0.03
Final V_{oc} (V)	1.07 ± 0.02	1.04 ± 0.03
Relative change in V_{oc} (%)	-0.93 ± 0.01	-0.25 ± 0.62
Initial I_{sc} (mA)	1.40 ± 0.13	1.2 ± 0.08
Final I_{sc} (mA)	1.30 ± 0.09	1.20 ± 0.11
Relative change in I_{sc} (%)	-7.79 ± 1.37	-3.47 ± 2.55

In order to improve the operational lifetime of perovskite solar cells, this project considered the use of Atomic Layer Deposition (ALD) to deposit a thin barrier layer of aluminium oxide as a barrier layer. Table 1 compares device performance parameters for samples with and without ALD coating degraded under 1,000 ppm oxygen. Devices without the ALD layer experienced a loss in I_{sc} 7.79 % ± 1.37 %, whereas the ALD-coated devices lost 3.47 % ± 2.55 %. The large uncertainties exist due to the sampling limitations, as experiments had to be reduced due to COVID pandemic-related restrictions during the final year of this project. Nevertheless, the results indicate a benefit of using ALD coatings in terms of improved device stability against elevated levels of O_2. It is proposed that the ALD layer provides a barrier to oxygen ingress and thus reduces the rate of oxygen-induced degradation.

Charge carrier lifetime as a key parameter for assessing stability of black silicon solar cells

In the latest silicon photovoltaic technologies, such as PERC (Passivated Emitter and Rear Contact) cells and black silicon (b-Si) cells, high performance relies on the effectiveness of surface passivation. The bulk diffusion length of minority carriers is an order of magnitude larger than the thickness of cells, making surface recombination the dominant limitation on performance. Therefore, surface passivation degradation is an important degradation factor during ageing experiments. The minimisation of recombination processes is especially important in the case of nanostructured silicon surfaces. Black silicon (b-Si) solar cells appear black to the eye due to their superior optical absorption, but the surface area is greatly increased compared to planar silicon.

Atomic Layer Deposited (ALD) aluminium oxide (AlO_x) is an efficient material for silicon surface passivation in the case of both planar and black silicon. In this project, Aalto, NPL and PTB studied the stability of the passivation performance of ALD AlO_x under various ageing environments, especially at elevated temperature,

combined with intense illumination (i.e. light soaking) or high ambient moisture (i.e. damp heat). The effects were investigated on films deposited with conventional research-scale and industrial-scale ALD processes, different film thicknesses, and chemical treatments prior to film deposition.

PL measurements in the NPL in-situ facility were used as a qualitative metric of carrier lifetime of Si wafers. The intensity of the PL emission depends on the amount of minority charge carriers present in the sample during the exposure time set for acquiring the PL image; higher lifetime values result in a higher density of minority carriers present within this time window, providing higher PL intensity values. PL imaging results at NPL are compared with photoconductance decay (PCD) measurements at Aalto in order to validate results.

During this project, Aalto developed an in situ measurement system for the characterisation of charge-carrier lifetime in silicon wafers under illumination and elevated temperature (shown in Figure 26) based on photoconductance decay measurements. The LED lamp provides an intensity up to 0.6 kW/m2, which is relevant for lifetime degradation measurements. The temperature range is from room temperature up to 200 °C. The measurement procedure has been automated, so measurements with a high temporal resolution can be conducted with no risk of sample damage due to handling.
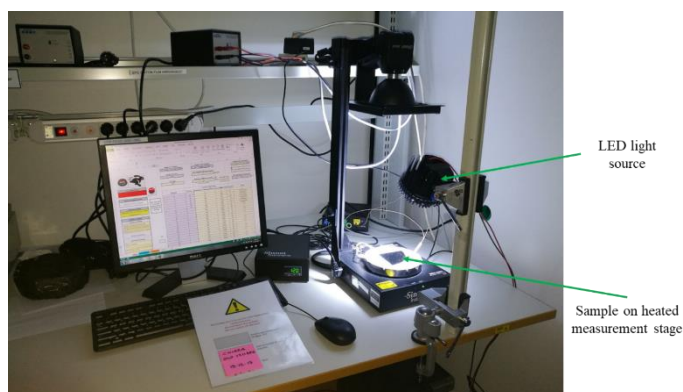

Figure 26: The in situ degradation setup developed in this project combining a light source and a heated sample plate with an automated setup used to measure carrier lifetime.

The measurement parameters that probe the performance of thin film passivated silicon wafers during degradation tests were investigated. Samples with different texture features and thicknesses of thin film passivation layers were prepared by Aalto using both standard ALD and industrial spatial ALD (SALD). Light soaking and damp heat stress tests for 1000 hours were carried out for all samples at NPL.

Figure 27 (a) shows effective charge carrier lifetime τ_{eff} measured from planar and black silicon samples passivated with 2 nm, 5 nm, and 20 nm thick SALD AlO$_x$ films. The lifetime achieved with 20 nm thick films on both planar and black silicon was highly stable throughout the exposure, but the 5 nm samples showed slight degradation with lifetime dropping from approx. 600 µs to 570 µs for planar and 580 µs to 400 µs for black silicon. The 2 nm samples were the least stable under light soaking, with lifetime decreasing from 120 µs to 32 µs for planar, and from 30 µs to 17 µs for black silicon.
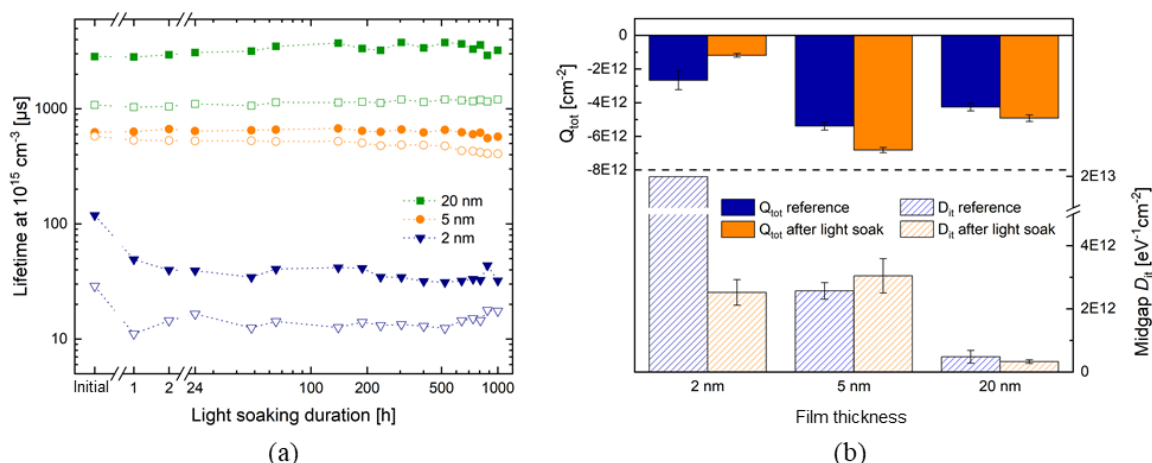
Figure 27: (a) Effective lifetime results over the course of 1000 h-long light soaking. Filled symbols refer to samples with a planar texture, while the open symbols refer to black silicon samples. (b) Passivation film total charge Q_{tot} and interfacial defect density D_{it} for planar samples with different film thicknesses.

Figure 28 presents the PL signal (a) and examples of PL images (b) of the SALD-passivated black silicon samples. The stable PL signal of the 20 nm samples correlated with the unchanged lifetime, but the 5 nm and 2 nm samples showed different degradation rates: the PL signal of the 5 nm samples degraded gradually, while for 2 nm samples the signal had degraded close to the background level already after 100 h of exposure. It is noteworthy that in the case of 5 nm films the black silicon sample degraded slightly faster than its planar counterpart. For the 2 nm samples there were no significant differences between the degradation rate of planar and black silicon with these measurement intervals. The decrease of passivation quality is demonstrated in Figure 28(b), which shows that the signal of the 5 nm black silicon sample was significantly less intense than initially, while for the 20 nm sample the signal intensity had not decreased at all. In all samples, the intensity of the PL signal decreased uniformly across the whole wafer
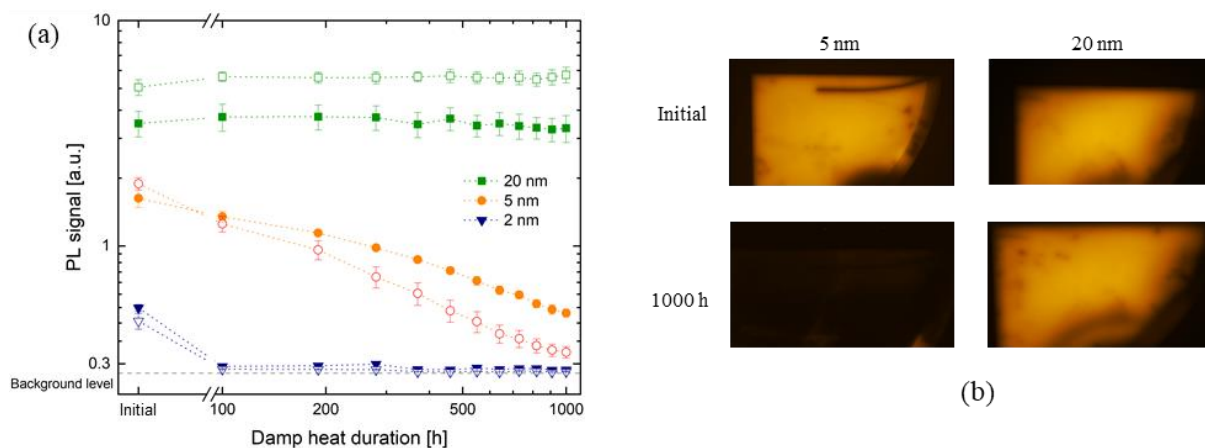

Figure 28: (a) The total PL signal of SALD-passivated samples throughout the damp heat exposure with filled symbols referring to planar samples and open symbols to black silicon. (b) PL images of black silicon samples passivated with 5 nm and 20 nm SALD AlO$_x$ initially and after 1000 h of damp heat exposure.

The effective charge carrier lifetime of the samples was assessed during degradation using PCD (at Aalto) and PL imaging (at NPL). Both techniques demonstrated that effective charge carrier lifetime is the key parameter that reflects passivation quality. Surface texture did not play a major role in passivation stability. However, it was observed that films deposited with different techniques had dramatic differences in stability, and that thicker films yielded more stable passivation. Photoelectron Spectroscopy measurements at PTB showed differences in the chemical bonding of the degraded samples, but additional research would be required to correlate them with the observed changes in the passivation performance. A surprising and significant result was that the chemically grown interfacial silicon oxide layer between the passivation film and the substrate greatly enhanced the passivation stability.

5 Impact

Close interaction with stakeholders and a well-designed plan of knowledge transfer, training, dissemination and exploitation activities was central to this project. The project actively engaged with stakeholders and disseminated knowledge from the project. That has included input to standards, organisation of workshops and training events, as well as publications and conference presentations. As a result, several results from the project started to be taken up while the project was running and concrete plans for exploitation have been developed. This included end-users evaluating technology developed by this project in its manufacturing line, new measurements services and consultancy services from results of the project already delivered to industry, project results already supporting development of better energy products and a new company being formed to commercialise results from the project.

Impact on industrial and other user communities

- Three case studies championed by stakeholders have been produced, covering stability of solar cells, impact of porosity and chemical composition on electrocatalytic activity and quality assessment of thin film power electronics. These demonstrate the general applicability of the advanced metrology developed, facilitate uptake of results by equipment manufacturers, device manufacturers and end-users and generate demonstrable impact within the project lifetime. They were further disseminated via webinars, conference presentations and papers.

- Accelerated time to market of more cost-efficient technologies will be enabled by the development of failure mechanism identification and production quality (both in process and post process). The project has been working closely with manufacturers and are characterising industrially relevant samples in end-user defined conditions to accelerate uptake of knowledge.

- New calibration facilities, new reference samples and innovative new measurement methods will be generated to support the EU energy community. Several companies already benefited from access to the new measurement services, new technical consultancy and knowhow developed by this project.

- Instrument manufacturers will benefit from validation of experimental methods and standardisation activities that will strengthen the reputation and acceptance of the new measurement technologies.

Impact on the metrology and scientific communities

The hybrid metrology approach developed in this project provides a new paradigm in metrology in Europe where single metrology areas previously developed separately will be merged to deliver better support for the energy sector. This concept drives collaboration and open innovation to the benefit of multiple stakeholders and is central to the increasing challenge of developing metrology for complex systems. Results from the project have been disseminated through 44 conference/workshop presentation, delivery of 14 training events as well as 17 peer-reviewed publications. The consortium has also organised a successful Autumn Physics School on Metrology for Thin Film Materials during the 2018 European Optical Society Biennial Meeting, a workshop on metrology and standardisation for scanning probe microscopy (June 2019, UK), and a Hands-on training workshop on advanced characterisation of solar cells (Sep 2019, Finland) that were focused on disseminating project results to the next generation of scientists and engineers. In 2019, the consortium has also organised special technical sections during the following conferences: SPM Workshop in Lednice, Czech Republic, ECASIA 2019 in Dresden, Germany, and a workshop on Advanced Optical Measurements and Imaging in Berlin, Germany. In 2020, a virtual workshop on International initiative on x-ray fundamental parameters was organised and a Webinar series on the importance of hybrid metrology for energy applications was delivered to present case studies from the HyMET project. These were focused on end-users from both metrology, academia and industry communities.

Impact on relevant standards

This project had direct impact in pre-standardisation (leading an interlaboratory study through VAMAS), in a pilot study within CCQM and on the development of standards within DIN and ISO. It also produced 2 best practice guides and recommendation documents to support future standardisation activities. Partners of this consortium were very active in pre-normative standards in VAMAS and standardisation activities in DIN and ISO. Traceability is established through the Surface Analysis Working Group (SAWG) of CCQM at the BIPM. The experience of all the partners and an international network has ensured that standards developed are suited to the needs of industry, based on the best science and inter-operability of procedures evaluated through interlaboratory studies.

The project partners provided input to 5 documentary standards and presented consortium research results and activities in several working group and standards committee (ISO, DIN and VAMAS). In particular this project contributed significantly to DIN50989-1 Ellipsometry Part 1 and Part 2 which is now being extended to progress as an ISO document, has approved a New Work Item for standardisation related to porous thin film characterisation and led Project 4 of TWA42 of VAMAS.

Longer-term economic, social and environmental impacts

- This project addresses two of the eight pillars of the European Energy Security strategy: "further developing energy technologies" and "moderating energy demand". By accelerating adoption of cost-effective and energy saving energy technologies it will contribute to the implementation of EU directives on Energy Efficiency, Energy Performance of Buildings, indication by labelling and standard product information of the consumption of energy and other resources by energy-related products and Renewable Energy. This is expected to reduce requirement of energy imports that currently amount to €350 billion per year.

- Substantial contribution to the pre-commercial developments of thin film energy material based products is expected. This project addresses the more accurate measurements of parameters that are relevant for product production optimisation, improvement of designs, and the quantification of ageing processes. Understanding of correlation between materials composition and electronic structure should accelerate development of high-performance energy devices, increase efficiency and reduce costs by replacement of expensive material combinations by cheaper ones.

The outputs of this project will also support the following potential longer-term impacts:

- Lower cost, reliable power electronics devices will increase adoption providing huge energy savings: motor-driven appliances (2/3 of all electric power consumption in industry)[12] can be made 40 % more efficient, lighting up to 75 % more efficient (equivalent to more than 10 % electrical energy consumption saving worldwide) and consumer electronics (e.g. computers) up to 30 % more efficient.

- The US Dept of Energy calculated that for an average household producing 1000 KWh of electricity by solar power, over 28 year device lifetime, would avoid conventional electrical-plant emissions of more than half a ton of SO_2, and third of a ton of NOx and 100 tons of CO_2. The International Energy Roadmap for photovoltaic energy projected that accelerated use of PV would result in emission reduction of more than 2Gt of CO_2 per year by 2050.

- According to the European commission document "Europe2020, A European strategy for smart, sustainable and inclusive growth", 2010, page 13:

    "Meeting the EU's objective of 20 % of renewable sources of energy alone has the potential to create more than 600 000 jobs in the EU. Adding the 20 % target on energy efficiency, it is well over 1 million new jobs that are at stake".

6   List of publications

1) [Assessing Optical and Electrical Properties of Highly Active IrOx Catalysts for the Electrochemical Oxygen Evolution Reaction via Spectroscopic Ellipsometry](#), René Sachse, Mika Pflüger, Juan-Jesús Velasco-Vélez, Mario Sahre, Jörg Radnik, Michael Bernicke, Denis Bernsmeier, Vasile-Dan Hodoroaba, Michael Krumrey, Peter Strasser, Ralph Kraehnert, and Andreas Hertwig, ACS Catalysis **2020** 10 (23), 14210-14223.

2) [AlOx surface passivation of black silicon by spatial ALD: Stability under light soaking and damp heat exposure](#), Heikkinen, I.T.S., Koutsourakis, G., Virtanen, S., Yli-Koski, M., Wood, S., Vähänissi, V. (Aalto University, Espoo, Finland), Salmi, E., Castro, F.A. and Savin, H., Journal of Vacuum Science & Technology A **2020** 38 (2) 022401. Green OA: http://eprintspublications.npl.co.uk/8722/

3) Stability of the Surface Passivation Properties of Atomic Layer Deposited Aluminum Oxide in Damp Heat Conditions, I. T. S. Heikkinen, G. Koutsourakis, S Wood, V. Vähänissi, F. A. Castro, H. Savin, AIP Conference Proceedings, **2019**, 2147, 050003.

4) Analysis of elemental composition and porosity of mesoporous iridium-titanium mixed oxide thin films for energy application by SEM/EDS, René Sachse, Vasile-Dan Hodoroaba, Andreas Hertwig, L. Kotil, R. Kraehnert, Microscopy and Microanalysis 25, Supplement S2, **2019** 1770-1771.

5) Photon flux determination of a liquid-metal jet X-ray source by means of photon scattering, Malte Wansleben, Claudia Zech, Cornelia Streeck, Jan Weser, Christoph Genzel, Burkhard Beckhoff and Roland Mainz, Journal of Analytical Atomic Spectrometry, **2019**, 34, 1497-1502. https://arxiv.org/abs/1903.06024

6) Time-resolved photoluminescence on double graded Cu(In,Ga)Se2 – Impact of front surface recombination and its temperature dependence, T. P. Weiss, R. Carron, M. H. Wolter, J. Löckinger, E. Avancini, S. Siebentritt, S. Buecheler, A. N. Tiwari, Science and Technology of Advanced Materials, **2018**, 20, Issue 1, 313-323.

7) Bulk and surface recombination properties in thin film semiconductors with different surface treatments from time-resolved photoluminescence, T. P. Weiss, B. Bissig, T. Feurer, R. Carron, S. Buecheler, A. N. Tiwari, Scientific Reports, **2019,** 9, 5385

8) Role of Radial Charges on the Angular Momentum of Electromagnetic Fields: Spin-3/2 Light, O. El Gawhary, T. Van Mechelen, H. P. Urbach, Physical Review Letters, **2018**, 121, 123202.

9) Assessing the validity of transient photovoltage measurements and analysis for organic solar cells, S. Wood, J.C. Blakesley, F.A. Castro, Physical Review Applied **2018**, 10, 024038.

10) Analysis of Mesoporous Iridium Oxide Thin Films by the Combined Methodical Approach SEM/EDS/STRATAGem, R. Sachsé, A. Hertwig, R. Kraehnert, V.-D. Hodoroaba, Microscopy and Microanalysis, **2018**, 24, 762-763.

11) Accurate experimental determination of Gallium K- and L3-shell XRF fundamental parameters, R. Unterumsberger, P. Hönicke, J.L. Colaux, C. Jeynes, M. Wansleben, M. Müller, B. Beckhoff, Journal of Analytical Atomic Spectrometry, **2018**, 33, 1003-1013.

12) In situ contactless thermal characterisation and imaging of encapsulated photovoltaic devices using phosphor thermometry, Y. Cao, G. Koutsourakis, G. J. M. Sutton, J. W. E. Kneller, S. Wood, J. C. Blakesley, F. A. Castro, Progress in Photovoltaics: Research and Applications. **2019**, 27, 673-681.

13) Nanoscale 3D characterisation of soft organic material using conductive scanning probe tomography, Ravi Chandra Chintala, Sebastian Wood, James. C. Blakesley, Paola Favia, Umberto Celano, Kristof Paredis, Wilfried Vandervorst, Fernando. A. Castro, AIP Advances, **2019**, 9, 025105.

14) Colloidal bimetallic platinum–ruthenium nanoparticles in ordered mesoporous carbon films as highly active electrocatalysts for the hydrogen evolution reaction René Sachse, Denis Bernsmeier, Roman Schmack, Ines Häusler, Andreas Hertwig, Katrin Kraffert, Jörg Nissen and Ralph Kraehnert: Catal. Sci. Technol., **2020**,10, 2057-2068

15) Challenges and opportunities for an efficiency boost of next generation Cu(In,Ga)Se2 solar cells: prospects for a paradigm shift, Mario Ochoa, Stephan Buecheler, Ayodhya N. Tiwari, Romain Carron: Energy Environ. Sci., **2020**,13, 2047-2055

16) [ALD-ZnMgO and absorber surface modifications to substitute CdS buffer layers in co-evaporated CIGSe solar cells](#), Ramis Hertwig, Shiro Nishiwaki, Mario Ochoa, Shih-Chi Yang, Thomas Feurer, Evgeniia Gilshtein, Ayodhya N. Tiwari, Romain Carron: EPJ Photovoltaics. **2020**, 11, 12

17) [Insights from Transient Absorption Spectroscopy into Electron Dynamics Along the Ga-Gradient in Cu(In,Ga)Se2 Solar Cells](#), Yu-Han Chang, Romain Carron, Mario Ochoa, Carlota Bozal-Ginesta, Ayodhya N. Tiwari, James R. Durrant, and Ludmilla Steier, Adv. Energy Mater. **2021**, 11, 200344

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

References

[1] Sachse R. et al., *ACS Catalysis*, 10 (2020) 14210–14223

[2] DAMA UK. (2013). The Six Primary Dimensions for Data Quality Assessment. Available from https://www.whitepapers.em360tech.com/wp-content/files_mf/1407250286DAMAUKDQDimensionsWhitePaperR37.pdf

[3] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML. Evaluation of measurement data - Guide to the expression of uncertainty in measurement, Joint Committee for Guides in Metrology, JCGM 100:2008, 2008.

[4] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML. Evaluation of measurement data – Supplement 1 to the Guide to the expression of uncertainty in measurement - Propagation of distributions using a Monte Carlo method, Joint Committee for Guides in Metrology, JCGM 101:2008, 2008.

[5] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML. Evaluation of measurement data Supplement 2 to the Guide to the expression of uncertainty in measurement Extension to any number of output quantities, Joint Committee for Guides in Metrology, JCGM 102:2011, 2011.

[6] Li J. et al., *npj Quant. Mater.,* 2 (2017) 56

[7] Atamanuk K. et al., *Beilstein J. Nanotechnol.,* 9 (2018) 1802-1808.

[8] Ma J.-Y. et al., *ACS Appl. Mater. Interfaces,* 11 (2019) 21627-21633.

[9] Vickerman J. C. and Briggs D., TOF-SIMS: Materials Analysis by Mass Spectrometry. IM Publications, 2013, Chichester, UK: IM Publications, 2013.

[10] Lin W. Et al., *Adv. Mater. Interfaces,* 4 (2017) 1600673.

[11] R. A. Zubarev and A. Makarov, "Orbitrap Mass Spectrometry," *Anal. Chem.,* 85 (2013) 5288-5296.

[12] Chirilă A. *et al.*, Nature Materials 10 (2011) 857

[13] Repins I. L. *et al.*, Rev. Sci. Instrum. 86 (2015) 013907

[14] Kuciauskas D. *et al.*, Appl. Phys. Lett. 102 (2013) 173902

[15] Kanevce A. *et al.*, J. Appl. Phys. 118 (2015) 045709

[16] "IEC 60904-7:2019 Photovoltaic devices. Computation of the spectral mismatch correction for measurements of photovoltaic devices." IEC, 2019.