Publishable Summary for 16ENG03 HyMet
Hybrid metrology for thin films in energy applications

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.

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.

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 applications to support the development of new, innovative products, thereby enhancing the competitiveness of EU industry.

Progress beyond the state of the art

The complexity of thin films used in energy applications often requires the use of multiple characterisation methods for a full understanding of materials' properties and their impact on energy applications. Typically, a trial and error approach is used to build correlation between manufacturing processes, characterisation data and device performance/durability. Such inefficient process needs to be repeated for each material system and energy technology, increasing development cost and time to market.

Hybrid metrology is the concept that to meet metrology requirements of complex technology, data from multiple metrology sources must be combined or "hybridised". Hybrid data analysis of separate methods used to measure the same parameter have been demonstrated to reduce uncertainty and improve quality control of nanoscale feature dimensions that are critical for microelectronic components.

This project has extended this concept for the challenging case of combining methods that measure different (but correlated) sample parameters with a focus on developing the required metrology basis for the hybrid metrology concept. The benefits of the method were demonstrated in three different case studies with stakeholders from the energy sector. A generalised approach towards combination of multiple parameter metrology was developed.

In the area of characterisation of aging, state of the art at the time of the project relied on accelerated tests that cannot be validated for new energy products as acceleration factors are often unknown. It also relied on separate analysis of individual measurements that do not allow easy identification of the key degradation processes and their relative importance to device lifetime. This project went beyond by developing in-situ, in-operando and in-process measurement protocols that allow identification of degradation processes in novel energy technologies. These were combined with new hybrid data analysis methods to allow identification of key materials parameters that can be used to monitor early signs of degradation and simplified measurement methods.

Results

<u>Hybrid experimental methods for improved analysis of complex energy thin film material properties and their impact on the performance of energy products</u>

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. Three case studies, for photovoltaics, electrocatalysis and power electronics, were delivered demonstrating the benefits of these methods in improving the performance of energy products.

- Hybrid metrology for photovoltaics – combination of X-ray diffraction (XRD), X-ray fluorescence (XRF) and white light reflectometry (WLR) to characterise depth dependent microstructure. The project has completed installation of a hybrid setup for combined XRD, XRF and WLR measurements and evaluated the benefits of the method on industrially relevant solar cells. The absolute photon flux for high-flux metal jet X-ray source has been determined and reference calibration samples have been validated. The hybrid method allows simultaneous monitoring of important film properties such as chemical depth gradients and bandgap gradients with high time resolution (in the order of tens of seconds), opening the possibility of real time measurements and process control during film deposition. Applications extend to wider functional thin films, such as composites and metallic alloys.

- Hybrid metrology for electrocatalysts - Analysing electrocatalytic thin layers by means of multiple surface methods. The project has developed a method to determine critical parameters of mesoporous doped oxide and carbon layers that correlate with the electrochemical properties, which are critical for the performance of these materials in electrocatalysis. The method combines electron microscopy, optical spectroscopy, optical scatterometry, X-Ray scattering, and electrochemistry and has produced a large reference dataset of enduring value for advancing the properties of electrocatalytic layers. In addition, a new in situ method for combining electrochemical measurements with optical spectroscopy was demonstrated and serves as a basis for further optimisation of these materials as well as for future process quality assurance methods. 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.

<u>Data analysis, data fusion and mathematical models to implement the hybrid metrology methods</u>
The project has developed mathematical methods, data analysis and data fusion techniques to allow implementation of hybrid metrology methods. While the implementation of hybrid metrology needs to be optimised for the specific application of interest, this project has identified key steps in a general procedure to implement hybrid metrology that is proposed as a guide to facilitated uptake and implementation of hybrid metrology approaches.

Examples of advances in hybrid data analysis include:

- 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. 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. This project has developed an industry-compatible reference based approach that resulted in the development of a GIXRF/XRR data analysis software to determine depth-dependent properties of the complex thin film stacks.
- 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. This project has developed a procedure for hybrid data analysis that improves accuracy of measurements by correct calculation of the X-ray standing wave intensity at different positions within the thin film, which depend on multiple parameters, including incident energy, the angle of incidence, sample properties, such as density, layer thickness (both as mass deposition or mass per area), roughness, and optical constants of the constituent elements. Modelling tools for reliable evaluation and assessment of measured GIXRD-NEXAFS data were developed and demonstrated for determining impact of annealing post process conditions in very thin atomic layer deposited films.

<u>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.</u>
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.

- This project designed and built a Hyperspectral Coherent Fourier Scatterometer (HCFS) that extends the resolution and improves the sensitivity of Coherent Fourier Scatterometry by exploiting the diversity given by a broad spectral range. The system achieves sub-nanometre uncertainty (0.1 nm) in dimensional measurements in a spectral range from 400 nm to 900 nm.
- A method was developed to process complex thin film samples for accurate depth resolved chemical, optical and electrical measurements, by combining TOF-SIMS, optical, and scanning probe methods, achieving lateral resolution below 200 nm.

- The project also analysed the benefits and limitations of the different techniques when applied to thin film energy applications. 2D and 3D analysis of small and large area samples were performed and evaluation of translation of some of the methods from off-line laboratory measurements towards in-line industrial monitoring was performed for one technology.

Key measurement parameters for improved stability of thin film energy products and generation of new materials datasets as a function of aging

The project has developed in-situ metrology facilities that can generate realistic aging conditions in a controlled way, transfer chambers and procedures to avoid sample contamination and uncontrolled aging during transport and storage, and improve quantification and specificity 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.

- A new measurement facility for in-situ characterisation of solar cells was demonstrated combining 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.
- Two key parameters have been identified that can facilitate assessment of methods to improve stability of solar cells: lateral spatial uniformity of optoelectronic properties and charge carrier lifetime. The project used these parameters to investigate the impact of processing on solar cell efficiency and the impact of atomic layer deposition (ALD) of passivation layers to improve stability of thin film solar cells, including comparison between lab based ALD and industrial spatial ALD.

Partners have investigated novel approaches for data fusion combining imaging and electrical data to identify defects in solar cells.

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 15 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) 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”.

Publications

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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

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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.

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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.

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

<table>
<tr><td colspan="2">Project start date and duration:</td><td>01 June 2017, 42 months</td></tr>
<tr><td colspan="3">Coordinator: Fernando Araujo de Castro, NPL Tel: +44 2089 436 357 E-mail: fernando.castro@npl.co.uk
Project website address: https://www.hymet.ptb.eu/</td></tr>
<tr><td>Internal Funded Partners:
1 NPL, United Kingdom
2 BAM, Germany
3 CEA, France
4 CMI, Czech Republic
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6 VSL, Netherlands</td><td>External Funded Partners:
7 Aalto, Finland
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