Final Publishable JRP Summary Report for IND07 Thin Films Metrology for the manufacturing of thin films

Overview

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

Need for the project

The manufacturing of thin films is of key importance as it underpins a significant number of industries where Europe holds a leadership position. Of strategic importance for the EU are high value thin films used in the optoelectronics industry, such as plastic and printed electronics, displays and lighting, memory storage devices and solar cells. A major challenge is control of consistency in thin film processing. The next generation of thin film optoelectronic devices use non-traditional materials (organic, inorganic and composites) and take advantage of low-cost, high-volume production such as continuous and roll-to-roll processing which have the potential to markedly reduce production costs and to provide a step change in the energy, sensor, display and lighting sectors. During scaling up it is crucial to measure optical and optoelectronic properties of the thin films and whole devices across their length and breadth in order to assess product quality and identify variability of individual processing stages. The lack of appropriate metrology for large area measurements can lead to the production of out-of-specification films, wasted production runs and increased costs.

Advanced thin film devices are based on complex structured multilayered architectures, which are strongly influenced by processing history and conditions (layer deposition is often sequential and materials' properties are highly dependent on microstructure). Unfortunately high resolution measurements of their microstructure in 3D is a challenge and new non-destructive measurement procedures and reference materials need to be developed. Furthermore, the combination of inaccurate models and non-traceable measurement methods leads to a wide variation in reported materials parameters (e.g. X-ray fundamental parameters, electronic charge mobility of organic semiconductors…), even when comparing nominally the same material and processing conditions. This is also the case for thermal properties of thin films where values obtained in bulk materials can differ by up to 100x when compared to values obtained for the same material processed as a thin film. Such changes are partially related to the effect of microstructure changes and therefore demonstrate the need for the development of a multi-method approach to thin film metrology. Finally, once these thin films are produced, they often need to be encapsulated to avoid exposure to air and moisture and increase product lifetime. Novel optoelectronic devices require very high quality thin film barrier layers but the cost of these can be phohibitive. Therefore it is crucial to develop traceable and accurate measurements of the water vapour transmission rate through these thin films at extremely high resolution. In such way, end users would be able to choose the lowest cost barrier that meets their specification. The lack of reliable measurement methods and measurement strategies for process quality control for large area manufacturing and device performance evaluation undermine confidence in the area and slow down market penetration.

Scientific and technical objectives

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

The key scientific and technical objectives were:

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

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

Results

This project has achieved all its objectives and has delivered significant technical and scientific breakthroughs that are already having direct impact in European industry.

Some of the key achievements were:

1. *Development of traceable measurements and validation of measurement methods for materials and thin film properties (thermal transport properties, charge carrier mobility, atomic fundamental parameters relevant for thin film characterisation)*
   - A novel facility for traceable measurement of thermal conductivity in thin films for temperatures up to 1000 ^{o}C based on modulated photothermal radiometry has been developed and validated and it is now available to support thin films microelectronics industry. Measurements of temperature dependent thermal conductivity have already provided a device manufacturer with insight into the development of thin film phase change memory devices.
   - A validated new protocol for charge carrier mobility characterisation of thin film of organic semiconductors has been developed, reducing uncertainty in analysis from 300 % to 20 %. The protocol has been made available free of charge to stakeholders. Discussions with different working groups will take this work a step closer to standardisation.
   - The accurate determination of fundamental atomic parameters, using x-ray spectrometry, has been carried out for a series of key elements with significant potential in the development of thin film photovoltaics (e.g. Cu, Zn, Ni, In). Substantial development of X-ray spectrometry (XRS) to characterise elemental composition and impurity concentration of complex thin films produced has also been achieved. Both the mass deposition and the stoichiometry have been determined successfully using a new protocol for angular dependent grazing incidence X-ray fluorescence (GIXRF). Reduction of the uncertainty of atomic fundamental parameters will have an immediate positive impact on the accuracy of all X-Ray based measurements and will be quickly disseminated through ongoing collaboration with the International Atomic Energy Agency.
2. *Traceable, accurate measurement of water vapour transmission rate through barrier layers to low levels*
   - This project has developed a facility for traceable and accurate measurements of water vapour transmission rate through barrier layers. This approach is a significant advance beyond existing methods and provides accuracy and traceability with a detection limit below 5×10^{-5} g/m^2/day. It is capable of stable and repeatable operation with an estimated relative expanded uncertainty of approximately ± 2 % for measurements above 1×10^{-2} g/m^2/day. There is a trade-off between price and performance of these barriers, therefore precise

characterisation of the minimum required level of performance will allow significant cost savings for industry, reducing product price and opening new addressable markets.

3. *Development of microstructure characterisation (morphology) by non-destructive and contact-less measurements*

    - The project developed a GIXRF spectroscopy method for the depth profiling of complex thin films, including significant development in accurate data analysis. A thin film device manufacturer learned valuable insights about the temperature-limitations of Si/ZnO thin film solar cells through high resolution measurements of speciation where temperatures above 1000 °C were shown to promote the formation of new chemical compounds within about 10 nm of the interface.

    - A new ultra high vacuum(UHV) chamber for hard X-ray experiments has been installed and tested in the synchrotron beamline at the SOLEIL facility in France. The instrument includes a 7-axis manipulator for an independent alignment of the samples and enables various analytical techniques based on energy dispersive X-ray detectors such as reference-free X-ray fluorescence analysis (XRF), total-reflection XRF, grazing-incidence XRF in addition to optional X-ray reflectometry (XRR) measurements. This enables the measurement of i) probe surface contamination, ii) layer composition and thickness, iii) depth profile of matrix elements or implants and iv) species of nanolayers, nanoparticles or buried interfaces for samples up to 100 mm x 100 mm in size.

4. *Characterisation and development of reference materials and transfer standards relevant to production*

    - We designed, produced and validated a novel 2D sub-micron calibration sample for spatially resolved Raman measurements with dimensions traceable to the metre. A patent application covering the calibration sample has been filed. This was developed in response to the lack of appropriate calibration samples and it allows successful µ-Raman measurements on samples with known size below 400 nm. Different companies have requested access to the prototype calibration samples and discussions about commercial exploitation are ongoing.

    - A procedure was developed to produce industrially relevant reference samples for in-line monitoring for quality control of complex multicomponent thin films, using Raman Spectroscopy. The use of these samples allows monitoring of relative concentrations or different elemental compositions, which is crucial to reliable thin film photovoltaic performance.

    - A reference material and an optimised method for its production have been developed as a reference for unusually thick layers of dielectric thin films. This material is already in use by a manufacturer of reflectometric thin film measurement devices that collaborated with this project. A key target community for this technology are test laboratories measuring critical thicknesses of barrier layers, varnishes and protective layers in the photovoltaic industry.

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

    - This project has designed and produced of a novel compact ellipsometry head for mapping of optical parameters over up to 0.5 m x 1 m. This was combined with the development and validation of fast and accurate data analysis software.

    - A prototype multielectrode system for photo-electrochemical imaging of thin films was designed and produced. A procedure for 2-electrode measurement and combination with photoexcitation for photoelectrochemical imaging has been demonstrated. This has the advantage of requiring simple and cheaper electronics when compared to traditional 4-electrode measurements.

    - A new protocol for accurate photocurrent mapping of challenging 3rd generation solar cells has been developed and validated. The project demonstrated that poor choice of measurement parameters can lead to false results, which can have direct impact in R&D

costs when scaling up solar cell production. The new method has been used to characterise samples from industrial stakeholder and helped them identify issues in the manufacturing process.

- A new digital reflectometry setup and new analysis software has been developed and is available to support the thin film optics industry.

6. *Development of traceable optical measurements for inhomogeneous thin films*

    - A combined ellipsometry and reflectometry metrology approach was used to validate data analysis models to take into account the effect of inhomogeneity in the thin film.
    - A procedure for traceable 2D µ-Raman measurements on samples with known size below 400 nm have been successfully developed. The method was successfully applied to complex thin film solar cells where knowledge of phase dimensions and composition is both important and challenging.

Actual and potential impact

Dissemination

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

Two 1-day workshops attracting over 50 attendees from industry and academia were held in the first and second year of the project. These workshops have successfully disseminated the multi-method approach to thin film analysis developed in this project to different targeted communities (e.g. optical, X-ray, Raman spectroscopy). Some of the stakeholders became project collaborators and as a result were the first to utilise results from the project to improve their competitiveness.

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

Impact on standardisation

The consortium worked closely with standardisation bodies and has disseminated results to different working groups, as listed below.

In the metrology community

- BIPM CCQM SAWG (Bureau International des Poids et Mesures (BIPM), Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology, (CCQM) Working Group on Surface Analysis (SAWG)) - Participation in the pilot study P-140 that addressed the characterisation of Copper indium gallium (di)selenide (CIGS) systems with matrix element depth profiles which was one of the key systems of interest in this project.
- Versailles Project on Advanced Materials and Standards (VAMAS), Technical Working Area (TWA) 36: Organic Electronics - Establishment of a new working item and responsability for an interlaboratory study on charge mobility. NPL was appointed as chair of the TWA36 and will continue leading work in this area towards international agreed procedures.

In the industrial community

- Working Group "Encapsulation" of the Organic and Printed Electronics Association. The goal of this industry working group is to generate data for best practice in characterisation of encapsulation layers and support the development process of standards (usually within IEC). Participation in international intercomparison of water vapour transmission rate measurements and dissemination of project results. Results from this intercomparison have been included in a publication in Review of Scientific Instruments. A follow up activity has been performed outside this project and the new results were published in Organic Electronics in 2014.

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

Industrial impact

The uptake and early impact of the work by the thin films industry started before the end of the project as described in the sections above. New calibration samples and methodology developed in this project are already in use by the manufacturers of thin films characterisation instrumentation. This disseminates measurement traceability across the value chain, targeting in particular test laboratories measuring critical thicknesses of barrier layers and protective layers in the semiconductor industry. Other equipment manufacturers have evaluated prototype calibration samples developed by this project. For some of the samples developed discussions about commercial exploitation are ongoing. Additionally, thin film manufacturer companies have already benefited from the new measurement procedures by obtaining key insight into how processing/manufacturing steps affect the performance and quality of their thin film products, including advanced barrier layers and photovoltaic devices.

The traceable facilities and equipment design developed in this project are being commercially exploited by NMIs to support industry development of cost-effective thin film devices. Partnerships between project partners and stakeholders, such as equipment manufacturers, have been established to further exploit the project results. These include IP protection, commercialisation of reference samples and input into standardisation bodies. As an example, reduction of the uncertainty of atomic fundamental parameters will have an immediate positive impact in the accuracy of all X-Ray based measurements and will be quickly disseminated to industry through the project collaboration with the International Atomic Energy Agency.

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

Finally, in the longer term, the measurement tools developed by this project will underpin the improved quality control in thin film manufacturing and enable the production of the technologies necessary for Europe to meet the new directive targets on the use of energy efficient devices and renewable energy. Through reduction of time-to-market and production costs, it will reinforce the leadership position of Europe in the creation of thin film and flexible or printable electronics tailored to meet key societal and economic needs.

List of publications

- P. J. Brewer, B. Goody, Y. Kumar, M. J. T. Milton, "Accurate measurements of water vapor transmission through high-performance barrier layers", Rev. Sci. Instrum. 83, 075118 (2012).
- P. Petrik, B. Pollakowski, S. Zakel, T. Gumprecht, B. Beckhoff, M. Lemberger, Z. Labadi, Z. Baji, M. Jank, and A. Nutsch, "Characterization of ZnO structures by optical and X-ray methods", Applied Surface Science, 281, 123 (2013).
- P. Petrik, T. Gumprecht, A. Nutsch, G. Roeder, M. Lemberger, G. Juhasz, O. Polgar, C. Major, P. Kozma, M. Janosov, B. Fodor, E. Agocs, M. Fried, "Comparative measurements on atomic layer deposited Al_2O_3 thin films using ex situ table top and mapping ellipsometry, as well as X-ray and VUV reflectometry", Thin Solid Films 541, 131 (2013).
- P. Petrik, "Optical thin film metrology for optoelectronics", Journal of Physics, Conference series, 398, 012002 (2012).
- T. Gumprecht, P. Petrik, G. Roeder, M. Schellenberger, L. Pfitzner, B. Pollakowski and B. Beckhoff "Characterization of Thin ZnO Films by Vacuum Ultra-Violet Reflectometry". MRS Proceedings, 1494, pp 65-70. doi:10.1557/opl.2012.1677 (2013).
- C. Becker, M. Pagels, C. Zachäus, B. Pollakowski, B. Beckhoff, B. Kanngießer, and B. Rech, "Chemical speciation at buried interfaces in high-temperature processed polycrystalline silicon thin-film solar cells on ZnO:Al", J. Appl. Phys. 113, 1089 (2013).
- D. Rosu, P. Petrik, G. Rattmann, M. Schellenberger, U. Beck, A. Hertwig, "Optical characterisation of patterned thin films", Thin Solid Films, 571(3), 601–604 (2014).
- C. Streeck, S. Brunken, M. Gerlach, C. Herzog, P. Hönicke, C.A. Kaufmann, C. Becker, J. Lubeck, B. Pollakowski, R. Unterumsberger, A. Weber, B. Beckhoff, B. Kanngießer, H.-W. Schock, and R. Mainz, "Grazing-incidence x-ray fluorescence analysis for non-destructive determination of In and Ga depth profiles in Cu(In,Ga)Se2 absorber films", Appl. Phys. Lett. 11, 113904 (2013).
- A. Cappella, J.-L. Battaglia, V. Schick, A. Kusiak, A. Lamperti, C. Wiemer and B. Hay, "High temperature thermal conductivity of amorphous Al2O3 thin films grown by low temperature ALD", Advanced Engineering Materials, 15,1046 (2013).
- S. Wood, J. S. Kim, D. T. James, W. C. Tsoi, C. E. Murphy, and J.-S. Kim, "Understanding the relationship between molecular order and charge transport properties in conjugated polymer based organic blend photovoltaic devices", The Journal of Chemical Physics, 139, 064901 (2013).
- O. E. Gawhary, A. J. L. Adam, and H. P. Urbach, "Nonexistence of pure s- and p-polarized surface waves at the interface between a perfect dielectric and a real metal", Phys. Rev. A, 89, 023834 (2014)
- I. Juric, E. Tutis, "Traps and transients: dark injection spectroscopy in organics and the tail of density of states", Organic Electronics, 15, 23901 (2013).
- N. Fleurence, B. Hay, G. Davée, A. Cappella and E. Foulon, "Thermal conductivity measurements of thin films at high temperature by modulated photothermal radiometry at LNE", Physica Status Solidi (c), 212 (3), 535 (2015).
- S. Pourjamal, H. Mäntynen, P. Jaanson, D.M. Rosu, A. Hertwig, F. Manoocheri and E. Ikonen, "Characterization of thin film thickness", Metrologia, 51 S302 (2014).
- R. Koops, P. Sonin, M. v. Veghel, O. El Gawhary, "A compact new-concept ellipsometer for accurate large scale thin films measurements", Journal of Optics 16, 065701 (2014).
- J. C. Blakesley, F.A. Castro, W. Kylberg, G.F.A. Dibb, C. Silva, J.S. Kim, "Towards reliable charge-mobility benchmark measurements for organic semiconductors", Organic Electronics, 15, 1263 (2014).
- S. Zakel, B. Pollakowski, C. Streeck, S. Wundrack, A. Weber, S.Brunken, R. Mainz, B. Beckhoff and R. Stosch, "Quantitative Raman spectrometry and x-ray fluorescence analysis as non-destructive methods for spatially resolved chemical characterization of Cu(In,Ga)Se2 absorber films", Applied Spectroscopy, accepted.

- Y. Ménesguen, M. Gerlach, B. Pollakowski, R. Unterumsberger and M.-C. Lépy, “High accuracy experimental determination of copper and zinc mass attenuation coefficients for photons in the 100 eV to 30 keV energy range”, Physical Review A, submitted.

JRP start date and duration:	01 August 2011, 36 months
JRP-Coordinator: Dr. Fernando Araujo de Castro, NPL, Tel+44 20 8943 6357 E-mail: fernando.castro@npl.co.uk JRP website address: http://projects.npl.co.uk/optoelectronic_films/	
JRP-Partners:	
JRP-Partner 1 NPL, United Kingdom	JRP-Partner 7 PTB, Germany
JRP-Partner 2 Aalto, Finland	JRP-Partner 8 VSL, Netherlands
JRP-Partner 3 BAM, Germany	JRP-Partner 9 Inmetro, Brazil
JRP-Partner 4 CEA, France	JRP-Partner 10 PANalytical, Netherlands
JRP-Partner 5 CMI, Czech Republic	JRP-Partner 11 SolarPrint, Ireland
JRP-Partner 6 LNE, France	JRP-Partner 12 Total, France
REG1-Researcher (associated Home Organisation):	Alfons Weber/Stephan Brunken,* Germany (HZB, Germany)
REG2-Researcher (associated Home Organisation):	Peter PETRIK, Hungary (FhG, Germany)
REG3-Researcher (associated Home Organisation):	Jong-Soo Kim, Republic of Korea (IC, UK)
REG4-Researcher (associated Home Organisation):	H. Paul Urbach, Netherlands (TU Delft, Netherlands)
REG5-Institution (associated Home Organisation):	Wolfgang Malzer, Germany (TUB, Germany)
RMG1-Researcher (associated Employing Organisation)	Ivan JURIĆ, Croatia Institut za Fiziku, Croatia

* Alfons Weber was the REG1-Researcher from 1 December 2011 to 31 July 2012. Stephan Brunken was the successor of Alfons Weber as from 1 August 2012.

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union