Publishable Summary for 14SIP05 TF-STANDARD
Developing a Standard for Valid Methodology for the Characterisation of Functional Alloy Thin Films

Overview

Thin film materials possess novel properties, which make them ideal for use in solid state lighting and solar panels. Precise analysis of the composition and structural properties of the films is crucial to their development and exploitation, as it greatly affects their performance. Many industries, including instrument manufacturers such as Helmut Fischer GmbH, need access to appropriate calibration samples and reference materials to enable them to make precise and reliable analysis of thin films for process control and quality management. EMRP project IND07 developed traceable measurement techniques to determine the composition and in-depth gradient of thin film samples.

This project built on these results to provide thin film calibration samples and standard industry operating procedures for traceable measurements of composition through an inhomogeneous film.

The project also generated a New Work Item Proposal (NWIP) for ISO/TC 201 (Surface Chemical Analysis) for the use of thin film reference materials for X-Ray Fluorescence (XRF) analysis for the characterisation of functional alloy thin films where up to now no Certified Reference Materials were available.

Need

A thin film is a layer of material ranging from fractions of a nanometre to several micrometres in thickness. Several technologies which have the potential to help reduce energy consumption, for example power electronics, solid state lighting and solar panels, use advanced thin films. The physical and chemical properties of the thin film material change the effectiveness of the device performance; therefore the composition, interface properties and thickness of complex thin films has to be precisely controlled during manufacture. Reliable analysis of these properties is key to their development and production. Current methods rely on a few particular calibration samples or reference materials, and the results show significant discrepancies. Industry requires traceable depth profiling techniques for different calibration samples, which can be used in the laboratory or inline process control. In order to minimise uncertainty, these calibration samples currently have to be similar to the samples being measured. However, new reference measurement techniques could be developed which can be characterised with different inhomogeneities, or from different applications to the calibration samples. This will support both process control and quality management in the production process.

A key output of EMRP project IND07 Thin Films was a SI traceable measurement procedure based on reference free X-Ray Fluorescence (XRF) analysis of Cu(In,Ga)Se_2 (CIGS, or copper indium gallium selenide) thin films, commonly used as an absorber layer for thin-film solar cells. This enabled the composition of thin film samples with non-homogeneous elemental in-depth distribution to be analysed, but the project highlighted the lack of appropriate calibration samples and reference materials. Therefore this project was needed to provide CIGS thin film calibration samples and complementary traceable analytical methods for looking at the in-depth profile in order to take account of inhomogeneities. Sputter-assisted Auger Electron Spectrometry (AES) was also included within this project.

International standards provide a means of documenting conformance to quality management systems. Surface-analysis service laboratories are under pressure to improve their efficiency and reduce the cost of their analyses; and the analytical results obtained by one surface analyst should be compatible with those obtained by other surface analysts when the same specimen is used. ISO/TC 201 (Surface Chemical Analysis) standards provide procedures for surface analysts to improve the reliability and efficiency of their services and to ensure compatibility and accuracy. This project contributed to an ISO/TC 201 standard on valid methodology for the characterisation of functional alloy thin films (where an alloy is a mixture of metals or metals and another element).

This need is supported by the primary supporter, Helmut Fischer GmbH, one of the world leading companies in manufacturing instruments for quantitative X-ray fluorescence (XRF) analysis including coating composition and thickness, and supplier of appropriate Certified Reference Materials. Presently these materials are restricted to single elements or homogenous alloy films. The project aimed to establish traceable methods to provide calibration samples of advanced multi-elemental, non-homogenous thin films, so that the primary supporter can expand their commercial Certified Reference Material products and services based on a certification of traceability.

Objectives

The objectives of this project were to:

1. Provide well-characterised advanced thin film CIGS samples, with a non-homogenous element in-depth distribution, and develop standard operating procedures (SOPs) for traceable depth profiling techniques to support advanced thin film material production by enhanced process control procedures.
2. Prepare and submit a NWIP to ISO TC 201 (Surface Chemical Analysis) for a new standard on valid methodology for the characterisation of functional alloy thin films.

Results

Provide well-characterised advanced thin film CIGS samples

In order to establish traceable measurement methods for providing thin film calibration samples of CIGS material for both techniques, two standard operation procedures were developed. Reference-free XRF at PTB is a physically traceable method which allows for the determination of the composition and film thickness of a thin film layer without any further need of a calibration sample or reference material. Sputter-assisted AES at BAM is a chemically traceable method. Here the measurement is based on a similar reference material and careful calibration. Both techniques enable the traceable determination of the composition of a CIGS thin film. In addition, reference free XRF allows the thickness of the layer to be quantified. These standard operating procedures enable CIGS thin-films from different production processes and of varying content to be characterised. Standards can be calibrated and then used as references in the production line.

Both techniques were part of the international CCQM (Consultative Committee for Amount of Substance of the BIPM (Bureau International des Poids et Mesures), key comparison on the “Measurement of mole fractions of Cu, In, Ga and Se in Cu(In,Ga)Se_2 films”. CCQM is the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology, and part of BIPM. The objective of this comparison was to compare the measurements of mole fractions of Cu, In, Ga and Se in a thin CIGS film. Based on this key comparison an entry in the key comparison data base for a certified measurement capability (CMC) was realised.

CIGS samples prepared in different ways can have quite different elemental in-depth distributions, which can affect the production process control. To have CIGS samples qualified by a reference methodology which takes any variation of composition into account enables a more reliable manufacturing process. An extended study on CIGS thin film samples for calibration procedures in XRF was performed with the primary supporter of this project. CIGS thin-film samples with different elemental in-depth gradients and mole-fractions were compared with certified calibration samples characterised by the SIP-partners. This showed:

1. Measurements using the certified calibration sample, in comparison to those without, showed a significant deviation especially in the Indium concentration.
2. Deviations of elemental in-depth gradient were shown to have a pronounced effect on the measurement of the Indium concentration, of a similar magnitude as the correction of the Indium concentration based upon the measurement using certified values of the calibration sample.
3. The measured thickness of the layer using the certified calibration sample was about 20 % thinner than the measurement without the sample. This correct measuring of the layer thickness can help to achieve a major manufacturing cost reduction.

The extended study with the primary supporter shows that the use of certified calibration samples for CIGS process control is both economically beneficial and useful for quality control, assuming the process target is aimed at samples with smaller variations of the element in-depth gradient.

Prepare and submit a NWIP to ISO TC 201 (Surface Chemical Analysis)

A new work item proposal (NWIP) to ISO TC 201 (Surface Chemical Analysis) was prepared. This was based on the contribution to the key comparison CCQM-K129 and the new standard operating procedures developed in objective 1. It was submitted to the German mirror committee at DIN (mirror committees are responsible for developing the national position on international standards) and it is expected to be progressed to the ISO committee covering valid methodology of characterisation of functional alloy thin films, although this will be after the project has finished.

The planned NWIP, based on the contribution to the key comparison K129, would have been limited to CIGS samples, which are only one example of novel and advanced thin film samples where no reference materials are available. To allow the traceable calibration for other thin films used in industry, the NWIP was formulated more generally, allowing the procedure to be used on other materials.

Impact

Dissemination of results

Results of the project were presented at five conferences, and an article entitled 'CCQM K-129 Measurement of mole fractions of Cu, In, Ga and Se in Cu(In,Ga)Se_2 Films Final Report' was published in the journal *Metrologia.* A second article was submitted to the trade journal *Spectroscopy Europe* with the title 'Qualifying calibration samples for advanced thin film materials characterisation'.

A training workshop was given to employees of Helmut Fischer GmBH, the primary supporter, to introduce the capabilities and the benefits of the reference-free methodology to characterise CIGS samples.

An additional training course for industrial stakeholders with the title 'Advanced characterisation of thin layered energy materials by X-ray spectrometry' was attended by around 80 attendees.

Impact on standards

The project consortium worked with technical committee ISO TC-201 Surface Chemical Analysis to provide input to new international standard 'Quantitative XRF analysis of industrial thin film samples by calibration using thin film reference materials'.

The project results contributed to BIPM CCQM Working Group on surface and other micro/nano analysis, and were included in the report of the results of the CCQM K-129 key comparison 'Measurement of Mole Fractions of Cu, In, Ga and Se in Cu(In,Ga)Se_2 Films'.

Participation of this project in the BIPM key comparison resulted in an entry in the BIPM Calibration and Measurement Capabilities Key Comparison database (a public website containing information about institutes offering internationally recognised measurements) for amount of substance of Cu, In, Ga, Se in Cu, In, Ga, Se alloy (microcrystalline thin- film).

Actual impact

This project has enabled primary supporter Helmut Fischer GmbH to be provided with a CIGS calibration sample and other CIGS samples with varying compositions. The company used the data set for an extended study on the measurement improvements for the characterisation of functional alloy thin films based on the Certified Reference Materials provided. The primary supporter can in principle now offer their improved measurement and calibration capability to customers interested in monitoring the production of CIGS thin films.

A new standard operating procedure was implemented at PTB for the determination of the mass deposition of layers and their mole fractions by reference-free XRF which includes explicitly the characterisation of CIGS thin films. PTB can now offer a service for traceable characterisation of CIGS samples with an in-depth gradient.

A new standard operating procedure was implemented at BAM for the measurement of Mole Fractions of Cu, In, Ga and Se in Cu(In,Ga)Se_2 Films using sputter-assisted AES. This has resulted in a new service available to customers.

Potential impact

The draft ISO standard, likely to be published in the next two years, will support industrial manufacturers in the precise characterisation of thin films thus reducing manufacturing costs and opening new markets in thin film material production for application with non-homogeneous material.

Since many applications of thin films are associated with renewable energies, low cost high efficiency products based on advanced thin films will also bring a positive environmental effect from energy saving and reduced CO_2 production.

<table>
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