FINAL PUBLISHABLE REPORT

Grant Agreement number	14SIP05
Project short name	TF-STANDARD
Project full title	Developing a Standard for Valid Methodology for the Characterisation of Functional Alloy Thin Films
Period covered	From 01.07.2015 To 30.06.2017
Coordinator	
Name, title, organisation	Dr. Cornelia Streeck, Physikalisch-Technische Bundesanstalt
Tel:	+49(0)30 3481 7157
Email:	cornelia.streeck@ptb.de

Other partners

BAM, Germany

TABLE OF CONTENTS

1 Executive summary

Introduction

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.

The Problem

Calibration standards globally maintain the reliability and reproducibility of measuring results. They provide an independent reference with respect to the location, measuring device and environment. This immanently important property is a vital prerequisite to ensure a constant and invariable quality of the producing industry and for process control. The limited number of available certified reference materials (CRMs) for thin film analysis and in parallel the growing market of novel thin film materials induces a growing gap of required calibration samples.

One example of such advanced thin films is the compound semiconductor material $Cu(In_{1-x}Ga_x)Se_2$ (shortly CIGS) which is used as absorber material for thin film solar cells. The band gap of this CIGS material can be enhanced by increasing the Gallium (Ga) to Indium (In) ratio. Thus, by tuning the in-depth elemental distribution the energy conversion efficiency of the device can be optimized. For such materials no certified reference materials are available to for instance use them as calibration samples for in-line process control, real-time investigations during film deposition, or quality management.

The Solution

A previous EURAMET project, EMRP IND07 *Metrology for the manufacturing of thin films*, developed traceable measurement techniques to determine the composition and in-depth gradient of thin film samples.

This project, 14SIP05 builds 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.

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.

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 (Copper), In (Indium), Ga (Gallium) and Se (Selenium) in $Cu(In,Ga)Se_2$ Films’.

A draft for a NWIP was prepared for a new ISO Standard covering XRF analysis of industrial thin film samples by calibration using thin film reference materials. This International Standard targets on the demand of thin film reference materials for the use in XRF analysis where up to now no CRMs are available. The International Standard describes a procedure to establish a calibration sample for a thin film XRF analysis. The aim here is it to use samples from the production process (out-of-production samples) itself for generating calibration samples. There are already several traceable characterization methods established.

2 Need for the project

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.

3 Objectives

The objectives of this project are to:

1. To 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. To 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.

4 Results

To 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.

Both partners of this project were part of the international CCQM[1] 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. The partner BAM participated with its sputtering assisted Auger Electron Spectroscopy (AES), and the partner PTB used their methodology for reference-free X-Ray Fluorescence (XRF) analysis. The final results are open access and published in the technical supplement of the journal Metrologia. Based on this key comparison an entry in the key comparison data base[2] for a certified measurement capability (CMC) was realised.
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 can be made chemically traceable. 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. The established standard operation procedures allow now for the characterization of CIGS thin-films coming from different production processes. These samples may have different elemental in-depth distributions due to variations of process-parameters during production. Despite of the existing gradient, these production-near samples can be qualified as reference-samples and can be used in the production line as well-characterised calibration standard.

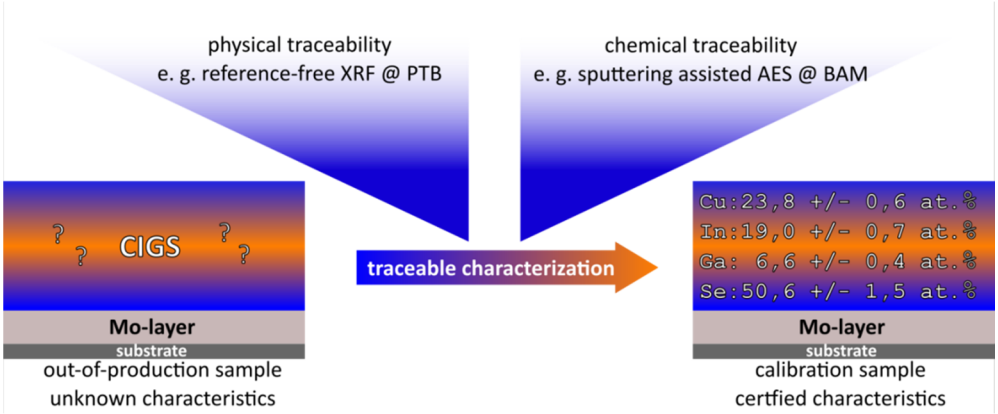

Figure 1: The scheme illustrates the certification of a typical out-of-production sample, here as an example, a CIGS-layer on a molybdenum coated substrate, to a traceable sample for calibration of methods used for in-line analysis at production facilities. The reference measurement methods can be based either on physical or chemical traceability chains.

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 analysed with respect to a certified calibration samples characterized by the SIP-partners. Three ramifications could be worked out: At first, the quantification results without any further calibration in comparison to the quantification using the certified calibration sample showed especially in the Indium concentration a significant deviation. At second, the deviations with regard to the elemental in-depth gradient showed as well a pronounced effect on the result of the Indium concentration. Thus, the analysis showed, that the influence of a large element in-depth gradient is of similar magnitude as the correction of the Indium concentration based

[1] Consultative Committee for Amount of Substance of the BIPM (Bureau International des Poids et Mesures), https://www.bipm.org/en/committees/cc/ccqm/
[2] BIPM key comparison data base KCDB, https://kcdb.bipm.org/

upon the quantification method by retracement to the certified values of the calibration sample. The third result was, that the quantified thickness of the layer using the certified calibration sample was about 20 % thinner. This means, the application of a calibration sample can help to achieve a major manufacturing cost reduction as the correct layer thickness now can be correctly measured. The non-discriminability of the first and second effect is not so relevant for the industrial production process, as the process parameter are already optimized to a moderate elemental in-depth gradient which is well reproducible. In addition, using X-Ray fluorescence analysis as monitoring method for the mass deposition of Cu, In, Ga and Se, is sufficiently sensitive to monitor fluctuations of the total layer composition. As result of the study with the primary supporter it can be stated, the application of certified calibration samples for CIGS process control is both economically beneficial and furthermore supportive to quality control assuming the process target is aimed at samples with smaller variations of the element in-depth gradient.

At the Spring Meeting of the European Material Research Society (E-MRS) this SIP was represented with an exhibition booth. With 26 parallel symposia and typically over 2000 international attendees the EMRS Spring Meeting is one of the largest conferences for recent technological developments of functional materials and which includes industry, government, academia and research laboratories. At the exhibition, which took place at 3 full conference days, around 80 international exhibitors were present. The exhibition booth was well-frequented and many flyers have been distributed.

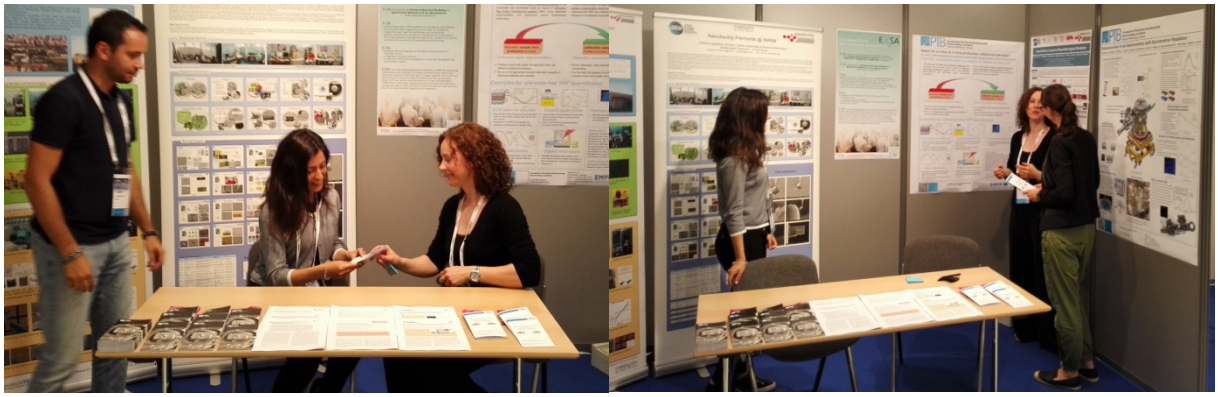

Figure 2: Exhibition booth at the E-MRS Spring Meeting in June 2017

Figure 3: Pictogram from the flyer for conferences and the exhibition booth showing the main concept for traceability for thin layer production with layer structures where no certified reference sample exist.

With these results the objective was met.

To 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.

Based on the contribution to the key comparison CCQM-K129 and the new established SOPs a new work item proposal (NWIP) to ISO TC 201 (Surface Chemical Analysis) was prepared. It was submitted to the German

mirror committee at DIN and its further progress will be continued beyond the project end. The focus of the new work item proposal (NWIP) got a more general orientation within the duration of the project. The originally intended NWIP based on the contribution to the key comparison K129 would have been limited on CIGS sample systems, which are only one example for novel and advanced thin film samples where no reference materials are available. To allow the traceable calibration also for other industrial relevant thin films, the NWIP was formulated in a more general way.

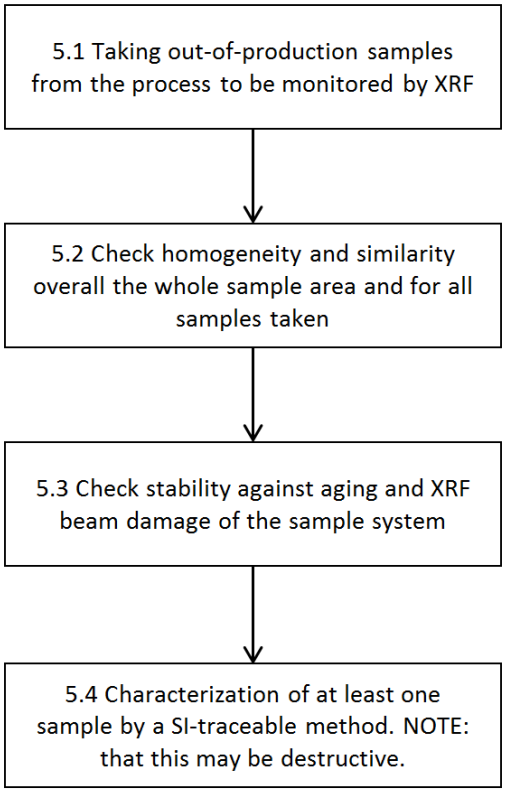

Figure 4: Flowchart of the procedure to characterize an out-of-production sample as calibration sample for XRF quantification as described in the NWIP.

5 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.

6 Contact details

Project coordinator: Cornelia Streeck (cornelia.streeck@ptb.de)

Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, DE-10587 Berlin, Germany