Publishable Summary for 17SIP07 Adlab-XMet
Advancing laboratory based X-ray metrology techniques

Overview

Adlab-XMet aimed at the dissemination and exploitation of the EMRP NEW01 TReND project results. In particular, the project focused on promoting the characterised organic and inorganic material systems (e.g. atomic layer depositions of Al_2O_3 or ion implants) produced in TReND and sharing the knowledge obtained on reliable TXRF (Total reflection X-Ray Fluorescence analysis), GIXRF (Grazing Incidence X-Ray Fluorescence analysis) and XRR (X-Ray Reflectometry) based characterisation of such materials. In addition, this project developed a novel, fast and automatable alignment strategy for the laboratory tools used by Bruker Nano GmbH, the primary supporter of this project.

Need

Many applications of TXRF and GIXRF are used for contamination analysis, elemental depth profiling, nanoparticle, and thin layer characterisation, as well as related existing quantification. Consequently, well characterised, and appropriate reference materials are required for calibration to ensure that the results are reliable and quantitative. Specific instrumental parameters such as the effective solid angle of detection are crucial when extending towards GIXRF, thus enabling depth-resolved elemental analysis. Although, calibration standards such as dried droplet samples exist, these standards often suffer from inhomogeneous and partially unknown elemental distributions which severely degrade the reliability of the quantification.

For the continuation towards GIXRF analysis, the droplet standards are no longer suitable as their inhomogeneities may result in a non-interpretable GIXRF fluorescence profile. Therefore, there was a clear need for well-defined calibration samples which do not suffer from such drawbacks. The Primary supporter, Bruker, intended on using parts of the well-characterised organic and inorganic material systems from the EMRP NEW01 TReND project; to gain a better understanding of laboratory capabilities; based on TXRF, GIXRF and XRR instruments. This was achieved by comparing experimental data from these instruments with the synchrotron radiation-based data obtained from the TReND project, allowing for a reliable determination of relevant parameters of the laboratory tools. In-depth knowledge on such instrumental parameters is a key aspect for the modelling of experimental data that enables a significantly widened applicability of the laboratory-based instruments.

In addition, further dissemination of the more conceptual and theoretical findings from the TReND project activities with respect to TXRF, GIXRF and XRR was crucial for laboratory tools. This included the transfer and adoption of an advanced and fast alignment procedure, which provides reliable control of relevant instrumental parameters of the primary supporter's lab tools.

Objectives

The overall aim of the project was the dissemination and exploitation of the project results from EMRP project NEW01 TReND. The specific objectives of the project were the following:

1. To provide novel and more reliable calibration methods for laboratory TXRF and GIXRF instruments, which will be established with the use of the well characterised (with respect to their lateral homogeneity and their in-depth elemental distributions) calibration samples from the EMRP project NEW01 TReND.
2. To transfer and disseminate the developed alignment and optimisation procedures to the laboratory X Ray instrumentation for TXRF, GIXRF and XRR (X-Ray Reflectometry) in order to eventually make this knowledge available to users of these equipment.

Results

To provide novel and more reliable calibration methods for laboratory TXRF and GIXRF instruments (Objective 1)

Key project results have been summarized in a peer-reviewed paper “Towards a calibration of laboratory setups for grazing incidence and total-reflection X-ray fluorescence analysis” which was published during the project. It also includes the detailed process of pre-characterising samples using PTB’s calibrated instrumentation to character the laboratory instrument in the BESSYII laboratory. Using a forward modelling of the experimentally determined grazing incidence X-ray fluorescence (GIXRF) emission from the sample as well as its reflectivity, a model for the composition of the sample was derived. Employing the same model, the incident angular dependent fluorescence emission to be expected for the specific excitation conditions on the laboratory instrument could also be calculated. By comparing this calculated dataset to actual experiments and a geometrical model for the geometry of the fluorescence detector on the laboratory instrument, the effective solid angle as a function of the incident angle has been characterized. In addition, the employed characterization technique led to the derivation of the incident photon flux on the laboratory instrument.

All in all, these parameters enabled the project partners to achieve quantitative GIXRF depth profiling on the laboratory instrument without requiring any other reference or calibration sample. Given that this was not possible before, it is a significant enhancement of the experimental capabilities that the instrument can now offer to end-users. For demonstration and validation purposes, this has also been showcased in the publication by performing GIXRF based quantitative depth-profiling of two different low energy ion implants into silicon and comparing both the derive depth profile as well as the quantified total implant doses to results obtained using PTB’s reference-free GIXRF technique. The good agreement found, demonstrates the feasibility of the newly obtained experimental capabilities for the Bruker T-Star instrument therefore this objective has been fully met.

To transfer and disseminate the developed alignment and optimisation procedures to the laboratory X Ray instrumentation for TXRF, GIXRF and XRR (Objective 2)

The main project results with respect to objective 1 take into account the successful optimization of the existing sample alignment strategy for the Bruker T-Star instrument. The alignment strategy has been extended and improved by incorporating sample alignment strategies developed at PTB on the one hand side and by automizing it in order to provide a fast, reproduceable, reliable and convenient sample alignment to the end-user. The new alignment procedure was assessed with respect to these features and significant improvement with respect to speed and reproducibility has been found along with the evaluation of the long-term stability of the alignment. Furthermore, the geometrical model created for the fluorescence detector which considers calculation for its solid angle of detection along with the strategy developed for the characterization of the instrument, are key project results. As they can be applied to other types of laboratory-based instruments for TXRF and GIXRF without having to redevelop major parts, it is expected that many more instruments can be characterized using the project results developed here. In fact, a first cooperation with another Bruker subsidiary as well as an end-user of the Bruker T-Star instrument is already in being negotiated respectively. Thus, the objective has been met.

Impact

The project has published three papers in peer-revied scientific journals. The publications are related to the reference-free GIXRF-XRR technique (which is used for pre-characterization of the calibration samples), the determination of the solid angle of detection on the demonstrator tool from the Primary Supporter Bruker and the project results that were applied to industrially relevant multilayer samples in conjunction with TU Berlin. In addition, several presentations at scientific conferences were given including one at the European PRORA Conference in November 2019 and at the #EXSA2021 conference in June 2021. A poster presentation was given at the ALTECH symposium of the EMRS spring conference in 2021. In addition, two internal presentations were given in company seminars that were held at BRU and Bruker AXS. Furthermore, a training session on GIXRF basics was provided to new PhD students in February 2020. Both the main project results as well as work closely related to this project were presented to ISO (TC 201) and DIN (NA 062-08-16 AA) technical working groups dealing with surface analysis.

The main impact of the project was the successful characterization of the TXRF and GIXRF laboratory instrument of the primary supporter Bruker (and other Bruker subsidiaries). Using well-characterized calibration samples as well as a geometrical model of the detection geometry we could successfully determine the necessary instrumental parameters to determine the effective solid angle function. In addition, the characterization procedure provided an insight also into other parameters of the instrument which are relevant for enabling quantitative analysis. This transfer of PTB's SI traceable and reference-free X-ray spectrometry approach to the laboratory instrument establishes possibilities for high-accuracy quantitative measurements, e.g., for nanolayer or sub-monolayer elemental depositions. This technology transfer from the project will be a benefit also to the users of the characterized laboratory instruments and through their role in current and future EMPIR JRPs (e.g.19ENV08 AEROMETII) in which both synchrotron radiation based as well as laboratory based applications of TXRF, GIXRF and XRR methodologies are a crucial part for the main project objectives. In addition, a very recent collaboration was initiated as a follow-up on a project presentation given at #EXSA2021 - Virtual Conference on X-ray Spectrometry in June 2021. Here, the TU Clausthal, which is a user of a Bruker T-Star instrument expressed interest in performing the characterisation of the effective solid angle for their instrument. This will be performed after the duration of the project.The developed techniques and procedures were also developed in a way that they are transferable also to other laboratory tools of the same product series as the demonstrator used in the project. Moreover, both the well-characterized samples and the developed procedures are adoptable for similar instruments from other vendors or even custom build instruments. Depending on the actual detector geometries, minor adoptions are necessary, however. Several activities within other EU-funded projects to perform this transfer to instruments from Bruker as well as other vendors are currently ongoing and will continue even after the project duration.

The X-ray metrology techniques addressed in the project are very relevant for various applications in the semiconductor industry, material sciences, environmental research and health related research. The reliability of quantitative analyses depends on the calibration procedure which may suffer from inappropriate calibration specimens such as no homogeneously dried droplet standards. An improvement of the calibration strategies is already a field of several research activities. In addition, the transfer and application of the alignment procedures as well as the determination of the instrumental parameters will significantly broaden the scope of application fields for the TXRF and GIXRF techniques. As these are key parameters for performing a reliable experiment and allow for a meaningful modelling, this proposal paves the way for a successful application of GIXRF-based depth profiling for analytical nanometrology offering potential uptake by the ISO TC201 (surface analysis) SC10 committee on XRR and XRF. This will increase the characterisation possibilities from a simple quantification of the amount of substance to a sensitive and quantitative characterisation of the elemental distribution, which is crucial for many applications, e.g. dopant depth profiling.

List of publications

1. P. Hönicke, B. Detlefs, E. Nolot, Y. Kayser, U. Mühle, B. Pollakowski, B. Beckhoff, Reference-free grazing incidence X-ray fluorescence and reflectometry as a methodology for independent validation of X-ray reflectometry on ultrathin layer stacks and a depth-dependent characterization, J. Vac. Sci. Technol. A (2019) 37, 041502 https://arxiv.org/abs/1903.01196 , https://doi.org/10.1116/1.5094891
2. V. Szwedowski-Rammert, P. Hönicke, M. Wu, U. Waldschläger, A. Gross, J. Baumann, G. Goetzke, F. Delmotte, E. Meltchakov, B. Kanngießer, P. Jonnard, I. Mantouvalou, Laboratory grazing-incidence X-ray fluorescence spectroscopy as an analytical tool for the investigation of sub-nanometer {CrSc} multilayer water window optics, Spectrochim. Acta, Part B (2020) **174**, 105995, https://arxiv.org/abs/2006.12198, doi:10.1016/j.sab.2020.105995
3. P. Hönicke, U. Waldschläger, T. Wiesner, M. Krämer, B. Beckhoff, Towards a calibration of laboratory setups for grazing incidence and total-reflection X-ray fluorescence analysis, Spectrochim. Acta, Part B (2020) **174**, 106009, https://arxiv.org/abs/2003.05192, DOI:10.1016/j.sab.2020.106009

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

Project start date and duration:	1 June 2018, 36 months	
Coordinator: Philipp Hönicke, PTB Tel: +49 30 3481 7174 E-mail: Philipp.hoenicke@ptb.de Project website address: https://www.researchgate.net/project/Advancing-laboratory-based-X-ray-metrology-techniques		
Primary Supporter: Ullrich Waldschläger, Bruker		
Internal Funded Partners: 1. PTB, Germany	External Funded Partners:	Unfunded Partners: 2. Bruker, Germany