

FINAL PUBLISHABLE REPORT

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1 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.

2 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.

3 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:

- 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.
- 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.

4 Results

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

Key project results with respect to project objective 1 have been summarized in in a peer-reviewed paper "Towards a calibration of laboratory setups for grazing incidence and total-reflection X-ray fluorescence analysis" which was drafted and 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. For this purpose, GIXRF and X-ray reflectometry experiments have been performed on the sample. By performing a combined forward modelling of the experimentally determined GIXRF-XRR dataset, a quantitative model for the depth dependent composition of the sample has been derived. The model for the sample composition and structure can now be used to calculate the samples angular GIXRF response for excitation photon energy in an absolute manner. Thus, the expected GIXRF signals for both Ni and Si on the Bruker instrument, where a Mo-Ka X-ray tube is used, can be calculated.

Employing this dataset as well as actual experimental data of this sample measured on the Bruker tool, one can determine the geometrical parameters describing the incident angle dependent effective solid angle of detection, the incident photon flux on the tool as well as the overall detection efficiency of the instrument for Ni and Si fluorescence radiation. Both the calculated and the experimental data, normalized to these instrumental parameters must match according to the Sherman equation and were thus successfully determined by performing a parameter optimization for the various geometrical and instrumental parameters.

Once they are known, these parameters allow to perform quantitative GIXRF depth profiling on the laboratory instrument on unknown samples without requiring any other reference or calibration sample. As this was not possible before it is a significant enhancement of the experimental capabilities the instrument can offer to end-users. For demonstration and validation purposes, this has also been demonstrated 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 and shows that the respective objective was fully achieved.

Furthermore, the demonstrated characterization of the tool also allows to implement any changes to the detection geometry without having to repeat the characterization procedure. This is realized by simply changing the corresponding parameter and a recalculation of the effective solid angle. Thus, if e.g. the distance between the fluorescence detector and the sample surface is changed, this can be taken into account by changing the corresponding parameter in the developed geometrical model for the solid angle function.

The stability of this characterization procedure with respect to time-dependent changes of the respective instrumental parameters, especially the incident flux, was also investigated as far as possible within the framework of this project. This was performed by repeating the characterization procedure multiple times over the duration of the project to detect possible drifts of certain parameters. As expected, the geometrical parameters did not change and for the incident photon flux, a guidance on how often the characterization should be repeated could be derived.

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 of sample, exciting radiation beam and detector towards each other plays a crucial role in any grazing incidence X-ray fluorescence (GIXRF) measurement. Only if the centre of the incident beam, the centre of rotation for the axis realizing the incident angle as well as the centre of the field of view of the detector are all pointing to the same crossing point, then reliable measurements can be performed.

With this in mind, PTB together with Bruker have improved the alignment strategy by incorporating sample alignment strategies which were developed at PTB. Also, it has been extended further through atomization of processes in order to provide a fast, reproduceable, reliable and convenient sample alignment for 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. In addition, long-term stability of the alignment has been evaluated as far as the project duration allowed. Thus, the objective has been met.

General project results

Current and future end-users of the Bruker T-Star instrument will be able to use the good practice guide, which was a deliverable in the project. The purpose of this guide is to summarize the findings of the project related to the overall operation of the Bruker T-Star instrument for grazing incidence X-ray fluorescence and explain

how the calibration procedure should be performed for reliable results, if new Bruker T-Star customers wish to perform GIXRF experiments.

Furthermore, the developed geometrical model for the employed fluorescence detector used for the calculation of its solid angle of detection as well as the developed strategy for the characterization of the instrument are considered as significant project results. Since both developments can be applied to other types and models of laboratory-based instruments for TXRF and GIXRF without having to redevelop major parts. This is currently already being performed in the framework of the EU ECSEL project MADEin4, the EMPIR project AEROMETII and other bilateral activities between PTB and other end users. Specifically, in the MADEin4 project, the procedure is being transferred to two different types of instruments, namely a TXRF machine for 200 mm and 300 mm Si wafers as well as a custom build instrument at an Italian research institute. The other mentioned activities consist of applying the procedure to Bruker T-Star instruments in their customer's laboratories. Additionally, it is expected that many more instruments can be characterized by using the project results developed here.

5 Impact

The project has published three papers in peer-reviewed 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.

6 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](https://doi.org/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](https://doi.org/10.1016/j.sab.2020.106009)

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