Publishable Summary for 14IND01 3DMetChemIT
Advanced 3D chemical metrology for innovative technologies

Overview

European industry and manufacturing had a need for improved capability for 3D-resolved chemical composition and interfacial material properties measurement. This project advanced the measurement capability and developed trusted measurement procedures for 3D chemical imaging at the micro- and nano-scale. Prototype instrumentation is now available and accessed by industry at consortium partner organisations using the developed procedures.

Need

Prior to the start of the project there was a need for improved chemical imaging in 3D. The need was, and still is, driven by the incessant demands from consumers for innovation in high value-added manufacturing. To meet the demands, industry had increasingly turned to the use of 3D architectures, additive manufacturing and a rapidly expanding library of materials. This was equally the case for devices based on organic materials, such as smart optical films and advanced coatings, as it was for inorganic nano-layered, high-density 3D devices. In many technologies, e.g. sensors and semiconductors, the interface between organic and inorganic materials caused severe measurement issues. This created the need for beyond state-of-the-art capabilities to measure chemical composition and interfacial properties with 3D-spatial resolution.

A major issue for organic multi-layer technologies and coatings, such as light management films are inclusions leading to defects at buried interfaces. The state of the art for industrial analysis of buried interfaces at the start of the project relied on cross-sectioning with a microtome, which is often unsuccessful as it is a ‘hit and miss’ affair. 3D chemical imaging, based on ion beam etching in combination with layer-by-layer imaging was identified as a promising technique for revealing and identifying defects in 3D, but lacked the required capability for chemical identification and failed for heterogeneous devices where the ion beam etching rate varies within the material.

In the semiconductor, steel and energy storage industries, analysts are faced with challenges to measure the chemical composition of inorganic devices or heterogeneous systems containing organic/inorganic layers and interfaces. A notorious example is the need to measure dopants in next-generation semiconductor devices in 3D on the sub-nm scale. The combination of 3D-spatial resolution (< nm), mass identification (isotope selectivity) and sensitivity (<10 ppm) made atom probe tomography (APT) a major contender for these characterisation needs. However, as an emerging technology, APT had many artefacts, it completely lacked standardisation, and insights into the fundamental physics underpinning its technology were lacking.

Objectives

The overall aim of the project was to provide European industry and manufacturing with urgently needed, trusted measurement capability and standards for 3D-resolved chemical composition and interfacial material properties**.**

The project addressed the following scientific and technical objectives:

1. To develop metrology for chemical and compositional 3D imaging of organic and heterogeneous devices with high mass resolution chemical identification (>100 000) and sub-micron spatial resolution (80 nm) using mass spectrometry.
2. To develop metrology for reliable and traceable detection, identification, localisation and quantification of chemical components in the depth of organic layers to improve accuracy and achieve sub-50 nm

resolution in 3D chemical imaging by resolution enhancement resulting from the integration of topography information in the 3D reconstruction of chemical data.

3. To develop metrology for atomic resolution 3D elemental imaging techniques for inorganic devices and improvement of tomographic methods. The objective is to obtain layer thickness/quantification accuracy better than 5 % and repeatability better than 20 % in heterogeneous systems where distortions are known to occur at present.
4. To develop a metrological traceable method for quantifying element depth profiles in 3D structured nano-layered devices and 3D nano-structured reference materials with a high control of shape and size using organic domain structures ranging from 10 nm to 100 nm, to transfer traceability to online analytical instrumentation.
5. To engage with industry to facilitate the take up of the technology and measurement infrastructure developed by the project, to support the development of new, innovative products and thereby enhance the competitiveness of EU industry.

Progress beyond the state of the art

Mass spectrometry is, arguably, one of the most powerful techniques for chemical analysis. Secondary ion mass spectrometry (SIMS) combines this analytical capability with analysis of surfaces through imaging with a primary ion beam. The project led the metrological evaluation of two, at the start of the project, unique SIMS instruments.

The typical mass resolving power in SIMS analysis at the start of the project was around 10,000 achieved with a ToF mass analyser. In the project, the ability to perform chemical imaging and analysis with a mass resolving power > 300,000 was achieved using the 3D OrbiSIMS instrument. Methods for exploiting this for the analysis in buried domains were developed.

The 3D topography of samples was not captured in ToF-SIMS imaging, and for that reason 3D SIMS was only able to provide 3D characterisation for a limited set of materials. The concept of correcting 3D SIMS data based on topographic measurements had been introduced but its routine use had not been established. The project led the exploitation of the 3D TopoSIMS instrument which incorporates a scanning probe microscope in a Tof-SIMS instrument and addressed challenges that needed to be overcome for this to become routine.

Atom probe tomography (APT) offers atomic resolution 3D chemical and compositional analysis of complex inorganic structures. Prior to the project, it was known that APT reconstructions often suffer from severe inaccuracies. The project addressed two important cases and found underlying explanations and recommendations for correcting the inaccuracies.

Prior to the start of the project, no micro- and nano-structured reference materials containing different chemical domains in a characterised structure were available. The project developed three prototype reference materials and qualified these. The materials were used in the project to evaluate the 3D imaging techniques. The materials have not been made widely available at the end of the project but the developed concepts were found to be promising and laid the foundation for further materials development.

New models and fundamental parameters were determined for reference-free grazing incidence x-ray fluorescence (GIXRF) for characterisation of thin layer mass depositions in 2- and 3D nanostructures. Such a characterisation was not possible before due to the fact that the additional effects when performing GIXRF analysis of regularly ordered nanostructured samples could not be modelled.

Results

Objective 1: Metrology for chemical and compositional 3D imaging of organic and heterogeneous devices

The performance of the 3D OrbiSIMS instrument was characterised and optimised. This led to SIMS imaging of ZrO nanofibers with mass resolving power better than 300,000 and with an image resolution of 172 nm. The ability to obtain 3D SIMS and analyse buried domains with high mass-resolving power, >200,000, was demonstrated for organic multilayer model samples and, in case studies, for organic light emitting diodes. The objective to develop metrology for chemical imaging with high lateral resolution and high chemical resolution was achieved. Better lateral resolution had been targeted but the result is considered very satisfactory.

A protocol for preparing a cross section of heterogeneous organic-inorganic materials for SIMS analysis was developed. The method uses a focused ion beam for making the cross section and, importantly, a gas cluster ion beam to remove the organic material that has been damaged by the focused ion beam. A second method for preparation of a cross section in organic samples was developed. This method was shown to be useful for studying deep interfaces in multi-layer samples using high-resolution secondary ion mass spectrometry imaging. A depth of analysis of more than 50 µm was be achieved using this method. The objective of developing methods for chemical imaging of heterogeneous devices was met with the development of these procedures.

Objective 2: Metrology for reliable and traceable detection, identification, localisation and quantification of chemical components in the depth of organic layers

High lateral resolution (60 nm) images combining SPM and SIMS data to achieve true 3D representations were successfully obtained. The SIMS and the scanning probe microscopy (SPM) part of the 3D TopoSIMS instrument was thoroughly evaluated. This was key to developing reliable data acquisition protocols and accurate in situ SPM-based reconstruction schemes for ToF-SIMS data. With the availability of those and having achieved imaging with a lateral resolution very close to the ambitious target of 50 nm, the project achieved Objective 2.

Objective 3: Metrology for atomic resolution 3D elemental imaging techniques for inorganic devices and improvement of tomographic methods

A novel, ion beam-based method was developed for the preparation of site-specific APT tips from organic-inorganic systems with increased success rates in view of site-specificity and negligible damage to the region of interest. Key experimental parameters that contribute to the uncertainty budget in APT analysis were identified, and an uncertainty budget for APT was calculated. Two studies were conducted on the quantification inaccuracy in APT for boron and silicon, as well as studies on quantification in SiGe and GaN. An interlaboratory study on APT was initiated.

Part of the objective was to achieve accurate quantification in heterogeneous systems. This was achieved for Ge in Si where the statistical quantification uncertainty was below 10%, the repeatability was 1.5% and the concentration of Ge measured using APT was within 1% of the sample composition as measured using the reference method RBS.

Objective 4: A metrological traceable method for quantifying element depth profiles in 3D structured nano-layered devices and 3D nano-structured reference materials

Microscale 3D model systems incorporating organic and inorganic materials in regular patterns were fabricated and characterised with a suite of dimensional methods. At the nanoscale, nanostructured templates were fabricated using di-block copolymer (DBC) self-assembly lithography. Three DBCs with different molar masses were selected for fabrication of nano-structured templates, leading to different feature dimensions in the 16 to 30 nm range.

GIXRF experiments were performed on various types of 3D-structured samples and work was started on quantification and modelling algorithms for such nanostructured GIXRF experiments. As part of this, a new computational method for calculating the X-ray standing wave field was developed for characterisation of nano- and micro-structured films.

With the development of new micro- and nano-structured reference material prototypes and the development of a method for the traceable characterisation of these, the project fully met this important objective.

Impact

A total of 11 papers have been published in peer-reviewed journals and are open access, and a further five papers have been submitted or are in preparation. Additionally, 106 conference presentations and posters were presented over the lifetime of the project. There have also been a number of conferences, training sessions and workshops to aid the uptake of the work completed in this project.

ION-TOF have held various workshops such as the 11th DACH FIB Workshop exploring novel FIB source concepts, FIB based analytics and FIB based applications in different research fields. A workshop organised by the project consortium (EMRS/ALTECH) has also aided the uptake of methods developed in the 3DMetChemIT project, with many partners taking part to discuss techniques and disseminate results. The 79th

IUVSTA Workshop, reviewing 3D Chemical imaging and organised by NPL, INRIM and IMEC was organised in June 2017 where over 26 people across a mixed audience (industry, academia etc.) participated.

Currently there are further plans for another training workshop as a satellite event to SIMS Europe next year in Germany, to discuss methods developed in this projects.

Impact on relevant standards

In ISO TC 201 (Surface Chemical Analysis), the project has provided input to a new work item proposal on measurement of the sputtering yield in gas cluster ion sputter depth profiling of organic materials. This is the first formal step towards the development of an international standard for measuring this important parameter which will help laboratories measure the depth of interfaces in sputter depth profiles.

NPL has had input into a draft documentary standard for the interactions standards development organisation of TC 201 (surface chemical analysis) committee of the SC6 (secondary ion mass spectrometry) subcommittee in September 2017.

Impact on industrial and other user communities

The project advanced the measurement capability and provided the essential metrology for spatially resolved chemical analysis. This will have direct impact across a broad range of industry sectors, all with the need for 3D chemical metrology. These include, but are not limited to, industries dealing with semiconductors, carbon-based electronics (organic electronics, graphene), medical devices, advance manufactured multi-layered films and additive manufacturing. The metrology output is, in the first instance, targeted at these industries and measurement service providers addressing industry issues.

X-ray spectrometry fundamental parameters for Ni were determined in the project. The fundamental parameters are required for accurate quantification with x-ray fluorescence. These new values were taken up by two x-ray fluorescence instrumentation vendors.

SIMS analysis is commonly used for identification and imaging of contaminants resulting from materials processing and affecting device or material performance. A more than 10-fold improvement in mass resolution in SIMS (from 10 000-15 000 to >150 000) significantly improves the reliability of chemical identification with immediate impact for the end users that need to identify contaminants to pinpoint processing issues. This capability by autumn 2018 will be available at three partner organisations.

Impact on the metrology and scientific communities

The fundamental parameters determined for Ni will become widely available and improve accuracy in x-ray fluorescence spectrometry, a widely used technique in materials analysis.

Longer-term economic, social and environmental impacts

The improved measurement capability is projected to underpin development and manufacture in a range of industries including the semiconductor, steel and energy storage industries where analysts are faced with challenges to measure the chemical composition of inorganic devices or heterogeneous systems containing organic/inorganic layers and interfaces. This can have a great effect on performance of a product and therefore lifetime. By allowing for accurate measurements of these layers, it may be possible to identify defects more readily and remove materials that can have a detrimental effect on product lifetime or efficiency.

List of publications

1. S. Surana, T. Conard, C. Fleischmann, J. G. Tait, J. P. Bastos, E. Voroshazi, R. Havelund, M. Turbiez, P. Louette, A. Felten, C. Poleunis, A. Delcorte, W. Vandervorst*, Understanding the physico-chemical aspects in the depth profiling of polymer:fullerene layers*, J. Phys. Chem. C, 2016, 120, 28074.
2. M. Tiddia, G. Mula, E. Sechi, A. Vacca, E. Cara, N. De Leo, M. Fretto, L. Boarino, *4-Nitrobenzene grafted in porous silicon: an application to optical lithograph*. Nanoscale Research Letters, 2016 11, 436.
3. M. Dialameh, F. Ferrarese Lupi, D. Imbraguglio, F. Zanenga, A. Lamperti, D. Martella, G. Seguini, M. Perego, N. De Leo, L. Boarino, *Influence of the Block Copolymer feature size on pattern transfer into silicon,* Nanotechnology, 2017, 28, 404001.

4. P. Seah, R. Havelund, I. S. Gilmore, *SIMS of Delta Layers in Organic Materials: Amount of Substance, Secondary Ion Species, Matrix Effects, and Anomalous Structures in Argon Gas Cluster Depth Profiles*, J. Phys. Chem. C, 2016, 120, 26328.
5. R. Havelund, M. P. Seah, M. Tiddia, I. S. Gilmore, *SIMS of Organic Materials – Interface Location in Argon Gas Cluster Depth Profiles Using Negative Secondary Ions*, J. Am. Soc. Mass Spectrom., 2018, 29, 774.
6. M. Guerra, J. M. Sampaio, F. Parente, P. Indelicato, P. Honicke, M. Muller, B. Beckhoff, J. P. Marques, J. P. Santos, *Theoretical and experimental determination of K- and L-shell X-ray relaxation parameters in Ni*, Phys. Rev. A, 2018, 97, 42501.
7. F. Scholze, J. Probst, J. Eilbracht, Y. Kayser, P. Honicke, V. Soltwisch, B. Beckhoff, *Element sensitive reconstruction of nanostructured surfaces with finite elements and grazing incidence soft X-ray fluorescence*, Nanoscale, 2018,10, 6177.
8. W. Vandervorst, P. van der Heide, L. Arnoldi, M. Zhao, C. Fleischmann, D. Melkonyan, R. J. H. Morris, R. Cuduvally, *Toward accurate composition analysis of GaN and AlGaN using atom probe tomography*, J. Vac. Sci. Technol. B, 2018, 36, 03F130.
9. B. Pivac, M. Perego, G. Seguini, P. Dubček, W. Vandervorst, C. Fleischmann, T. Weimann, Y. Kayser, B. Beckhoff, P. Honicke, F. Ferrarese Lupi, M. Dialameh, N. De Leo, L. Boarino, *Development and Synchrotron-Based Characterization of Al and Cr Nanostructures as Potential Calibration Samples for 3D Analytical Techniques*, Phys. Status Solidi A, 2018, 215, 1700866.
10. T. Conard, C. Fleischmann, R. Havelund, A. Fanquet, C. Poleunis, A. Delcorte, W. Vandervorst, *Inorganic material profiling using Ar_n^+ cluster: Can we achieve high quality profiles?*, Applied Surface Science, 2018, 444, 633.
11. M. K. Passarelli, A. Pirkl, R. Moellers, D. Grinfeld, F. Kollmer, C. F. Newman, P. S. Marshall, H. Arlinghaus, R. Havelund, M. R. Alexander, A. West, S. Horning, E. Niehuis, A. Makarov, C. T. Dollery, I. S. Gilmore, *The 3D OrbiSIMS—label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power*, Nature Methods, 2017, 14, 1175. Full text available via http://europepmc.org/abstract/MED/29131162.

<table>
<tr><td colspan="2">Project start date and duration:</td><td>01 June 2015, 36 months</td></tr>
<tr><td colspan="3">Coordinator: Rasmus Havelund, NPL Tel: +44 208 943 6202 E-mail: rasmus.havelund@npl.co.uk
Project website address: http://empir.npl.co.uk/3dmetchemit/</td></tr>
<tr><td>Internal Funded Partners:
Partner 1 NPL, United Kingdom
Partner 2 CEA, France
Partner 3 CMI, Czech Republic
Partner 4 INRIM, Italy
Partner 5 PTB, Germany</td><td>External Funded Partners:
Partner 6 CNR, Italy
Partner 7 FCT-UNL, Portugal
Partner 8 IMEC, Belgium
Partner 9 UPO, Italy
Partner 10 UNOTT, United Kingdom</td><td>Unfunded Partners:
Partner 11 CPI, United Kingdom
Partner 12 ION-TOF, Germany</td></tr>
</table>