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

Overview

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

Need

“Faster”, “smarter” and “cheaper” demands from consumers are driving innovation in high value-added manufacturing. To meet the demands, industry is increasingly using 3D architectures, additive manufacturing and a rapidly expanding library of materials. This is equally the case for devices based on organic materials, such as smart optical films and advanced coatings, as it is for inorganic Nano-layered, high-density 3D devices. In many technologies, e.g. sensors and semiconductors, the interface between organic and inorganic materials causes severe measurement issues. This creates a need for beyond the 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 defects such as particulates or voids at buried interfaces. The current state-of-the-art for industrial analysis of buried interfaces relies on cross-sectioning using a microtome to cut thin layers for use with microscopy. This is often unsuccessful as the probability of hitting the defects and exposing them is low. However, 3D chemical imaging, based on ion beam etching in combination with layer-by-layer imaging, holds the potential for revealing and identifying defects in 3D, but it currently lacks the required capability for chemical identification and fails for the analysis of heterogeneous devices where the ion beam etching rate varies within the samples.

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, i.e. elements that are inserted into a semiconductor in very low concentrations to alter its electrical or optical properties, 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) makes atom probe tomography (APT) a major contender to meet this characterisation need. However, as an emerging technology and it currently lacks standardisation and insight into the fundamental physics underpinning its technology.

Objectives

The project addresses 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 lateral resolution in 3D chemical imaging.
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.

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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

3D chemical imaging

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 will push SIMS imaging beyond the state of the art by addressing the most critical analytical shortcomings using two unique SIMS instruments:

1. The 3D nanoSIMS instrument is a hybrid SIMS instrument incorporating a time-of-flight mass analyser and an Orbitrap HF mass analyser. The Orbitrap HF mass analyser brings an order of magnitude improvement over the current state of the art in mass scale resolving power and accuracy which currently limit the ability to identify chemical components.
2. The 3D TopoSIMS combines SIMS with atomic force microscopy (AFM) allowing *in situ* nano scale topography measurement. This allows fusion of chemical data from Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) with high resolution topography images from AFM measurements in order to provide reliable 3D imaging and, corrections for artefacts caused by the 3D topography of the analysed surface.

This project will also establish the metrology needed for laser-assisted APT which offers atomic resolution 3D chemical and compositional analysis of complex inorganic 3D hetero-structures. APT is considered absolute in terms of composition assessment, but inaccurate compositions are obtained when experimental conditions are not well chosen; and APT data reconstruction and analysis evaluation routines currently lack validation and standardisation.

Reference materials and metrological traceability

The project will develop novel nano- and micro-scale reference materials. These are required within the project to benchmark the experimental techniques and push them beyond their current limitations in terms of spatial resolution, sensitivity and reliability.

The traceability of reference-free grazing incidence x-ray fluorescence (GIXRF) is well-established for the determination of thin layer mass depositions. However, inorder to enable traceable measurements in 3D structured and heterogeneous materials the codes and algorithms needed for X-ray standing wave (XSW) field calculations need to be capable of modelling the local X-ray intensities in such 3D structures. Within this project, numerical codes will be used to calculate XSW intensities in 3D structured materials.

Results

To meet the five technical objectives, the project has:

1. Achieved 3D SIMS imaging and depth profiling of model samples with mass resolving power of 240000. The excellent mass resolving power has been shown to permit the separation of different secondary ion signals that cannot be distinguished using conventional mass analysers. The ability to record depth profiles from multilayers of organic compounds with depth resolutions better than 8 nm has been demonstrated.

2. Obtained 3D SIMS images of organic-inorganic multilayer samples, integrating topography information (ToF-SIMS/SPM). The preliminary results emphasize the potential for accurate high resolution spatial reconstruction of 3D SIMS images using the combination of the two techniques.

3. Investigated the reproducibility and accuracy of compositional analysis using APT on a model system of SiGe alloy embedded in a narrow SiO_2 matrix. These early results permit a study of the role of the SiO_2 thickness during APT analysis (non-hemispherical tip shape evolution and ion trajectory aberrations) and its effect on the chemical composition analysis.

4. Produced nano- and micro-structured reference material prototypes using block copolymers and lithographic methods, performed initial GIXRF measurements on 3D-structured materials and started the development of numerical codes to support GIXRF traceable quantification of substance mass in nano-structured layered devices.

5. The project consortium has held meetings with industry stakeholders to inform about project plans and discuss the potential impact and opportunities to collaborate in the framework of the project.

Impact

The project partners have disseminated project plans and progress in more than 10 presentations at international conferences and workshops. The partners have contributed to the organisation of several meetings, including a Royal Society workshop, and submitted successful proposals to organise a conference session at the European Materials Research Society 2017 and an IUVSTA workshop on 3D chemical imaging.

Impact on relevant standards

The project progress and engagement will be reported at ISO TC 201, VAMAS and CCQM-SAWG meetings. Pre-normative standardisation work in the project includes an inter-laboratory study for atom probe tomography and a CCQM pilot study on ‘the amount of substance in a buried layer. The project has provided expert input to a new work item for total-reflexion x-ray fluorescence in ISO TC201.

Impact on industrial and other user communities

The project will advance the measurement capability and provide 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.

SIMS analysis is commonly used for identification and imaging of contaminants resulting from materials processing and affecting device or material performance. The 10 fold improvement in mass resolution in SIMS (from 10 000-15 000 to >150 000) provided by the Orbitrap HF analyser of the 3D nanoSIMS instrument significantly improves the reliability of chemical identification with immediate impact for the end users that need to identify contaminants to pinpoint processing issues. The project further aims to establish methods for predicting the recorded ion signal dependence on the concentration based on the chemical structure of the analysed materials. This will be a step change in quantitative analysis and be widely applicable.

APT is increasingly being used for 3D chemical analysis of nanoscale semiconductor architectures such as FinFETs. This project will establish both methods for sample preparation and determine the uncertainty in APT. This will improve the efficiency and reliability of the technique to provide increasingly valuable information in the development of new semiconductor technology but also other technologies such as Nano-engineered steel materials.

The project will also develops reference samples for 3D chemical analysis. Analysts will benefit from the availability of these as a quality assurance tool, offering improved reliability and credibility. Likewise, analysis instrument vendors will benefit from the availability of reference samples for benchmarking of methods and, in turn, advancing measurement capability.

A significant part of the metrology developed in this project enables 3D chemical analysis of materials and devices that currently cannot be analysed. The industrial communities will benefit from these developments, giving important insights to processing and advanced engineering issues. Overall, the project is expected to have impact across a broad range of industries reflecting the wide-ranging needs for 3D chemical metrology.

Impact on the metrological and scientific communities

The 3D nanoSIMS is revolutionary and is at least two leaps ahead of current technology. The scientific community will intermediately benefit from the potential for studying secondary ion energetics using the two mass analysers together, which will contribute to an understanding of the underlying processes in secondary ion mass spectrometry. If the two mass analyser hybrid instrument concept establishes itself as the next generation of SIMS instruments, the scientific community will benefit from the procedures for optimal operation developed in the project.

Procedures, good practice guides and reference samples for FIB-SIMS, SIMS in combination with AFM, APT and traceable GIXRF chemical characterisation will be developed throughout the project and disseminated to the wider metrological and scientific communities. The production and availability of standard methods and reference materials will increase reliability and robustness of the analytical methods.

At present there is a major gap in European metrology and standardisation for APT. This project is the first European initiative to address this critical gap. The project will lead a VAMAS inter laboratory study, which will be the first of its kind and will establish a metrological framework and bring together the community to stimulate metrology developments and drive advances in APT.

Project start date and duration:	01 June 2015, 36 months	
Coordinator: Fiona Moriarty, NPL Tel: +44 208 943 6792 E-mail: fiona.moriarty@npl.co.uk Project website address: http://empir.npl.co.uk/3dmetchemit/		
Internal Funded Partners: Partner 1 NPL, UK Partner 2 CEA, France Partner 3 CMI, Czech Republic Partner 4 INRIM, Italy Partner 5 PTB, Germany	External Funded Partners: Partner 6 CNR, Italy Partner 7 FCT-UNL, Portugal Partner 8 IMEC, Belgium Partner 9 PMO, Italy Partner 10 UNOTT, UK	Unfunded Partners: Partner 11 CPI, UK Partner 12 ION-TOF, Germany