Final Publishable JRP Summary for NEW01 TReND
Traceable characterisation of nanostructured devices

Overview

This project has developed essential metrology for the chemical and electrical characterisation of novel materials and devices used in the micro and nano-electronic industry. The improvements in analytical capability gives the industry a set of reliable analytical methods to directly measure properties that determine device performance. This will underpin innovation of next generation electronics, provide valuable information for the optimisation of device manufacture and strengthen quality control.

Need for the project

The micro and nano electronic world is experiencing a revolution in tackling the new challenges in terms of miniaturisation, power consumption, power density and processing speed. Novel inorganic semiconductor materials (Ge, InGaAs, GaN, SiC, and high-k dielectric materials) and novel 3D-architectures (Multiple Gates FETs, Nanowire T-FETs, etc.) with feature sizes < 30 nm are replacing traditional silicon devices. There is now a critical need for metrology to give traceable and quantitative chemical composition measurement of new inorganic electronic materials in complex 3D-architectures with buried interfaces and with nanometre depth resolution to enable the effective design and manufacture of such devices.

Concurrent with these developments is the emergence of electronics based on organic semiconductors, made of small organic molecules or conductive polymers arranged in ordered assemblies. This is an important new knowledge-based, high innovation and high value (multibillion €) sector for the EU. Unfortunately, the techniques developed for the inorganic semiconductor industry do not directly apply and there is an urgent need for methods to give 3D nanoscale chemical and electrical imaging. For organic electronic materials, the state of the art for chemical imaging at the outset of the project, 3D SIMS with C_{60} sputtering, failed completely and no methods were available for 3D nanoscale electrical measurements where a resolution better than 30 nm is needed. The challenges are for metrology at the nanoscale and it is clear that no single technique can provide all the answers required by industry. Whilst a single technique may offer repeatable high precision results, the accuracy (closeness to a true value) of all techniques is limited. This causes major difficulties in manufacturing and research and development since a complete nanoscale picture cannot be reliably assembled. The solution is traceability of the nanoscale measurements and availability of nanostructured reference materials.

Scientific and technical objectives

The aim of the project was to develop traceable measurement and characterisation of physical and chemical properties for the next generation of nano-structured electronic devices incorporating inorganic semiconductors or organic semiconductors with sub 30 nm dimensions using novel 3D architectures. The project had three high-level technical objectives.

1. Improvement of non-destructive methods for the characterisation of inorganic nanolayers and buried interfaces, by chemical depth-profiling of nanolayers (up to 200 nm) with trace level sensitivity.
2. Development of essential metrology to enable 3D nanoscale chemical imaging of organic electronic materials using new massive argon cluster sputtering combined with secondary ion mass spectrometry (SIMS).
3. Development of a novel method for 3D nano scale electrical characterisation of organic electronic materials (with resolution better than 30 nm) and nanostructured self-assembled reference materials for the metrological studies of the techniques.

EMRP
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Results

Improvement of non-destructive methods for the characterisation of inorganic nanolayers and buried interfaces, by chemical depth-profiling of nanolayers (up to 200 nm) with trace level sensitivity

An aim of the project was to reduce the relative uncertainties of analytical methods for the determination of surface contaminations, layer compositions and buried interface compositions of novel inorganic semiconductor materials. The non-destructive analytical methods of interest were Total Reflection X-Ray Fluorescence (TXRF) and Grazing Incidence X-Ray Fluorescence (GIXRF) analysis. In order to achieve reduced uncertainties, the partners optimised these analytical methods for the characterisation of nanolayered materials used in the development of nanoelectronic devices. Both the reliability and traceability of the applied methods were improved significantly, bringing relative uncertainties below 10 %. In particular, the accuracy of the x-ray standing wave field calculations was improved and validated.

The most successful example of an improved analysis of novel materials used in semiconductor devices was the GIXRF characterization of the high-k dielectric nanolayers that are increasingly used in and crucial for the continued minituarisation of electronic devices. This was enabled by the strong cooperation of PTB and the two researchers at IMEC and CEA. The results were published in the special issue on “High-k Materials and Devices 2014” of the peer-reviewed open-access journal Materials.

Development of essential metrology to enable 3D nanoscale chemical imaging of organic electronic materials using secondary ion mass spectrometry with new massive argon cluster sputtering.

The project has studied the effects of key parameters for argon cluster sputtering for depth profiling and 3D imaging of organic electronics materials and devices using secondary ion mass spectrometry (SIMS). The studies have led to an extensive description of argon cluster sputtering including a popular universal equation for the sputtered volume per ion dependence on the argon cluster energy, cluster size and incidence angle. The description provides a valuable basis for selecting appropriate experimental parameters for a given type of sample. The project has also established recommendations to reduce ion beam and electron beam damage effects in 3D imaging and sputter depth profiling to improve reliability of the analysis.

Quantitative analysis by SIMS is generally limited by the so-called matrix effect leading to a non-linear relationship between the analyte concentration and the secondary ion signal intensity. The project has made systematic studies of the matrix effect in SIMS in the active layers of organic photovoltaic devices and demonstrated quantitative analysis of such samples based on the analysis of reference samples with known composition. Building on this, the project has used model systems with carefully constructed mixed organic layers to establish a method for measuring the matrix effect in SIMS and a parameter to quantify the effect. In an inter-laboratory study conducted under the project, it was shown that matrix effects are remarkably consistent between instruments. Importantly, it was demonstrated, using a simple normalization method, that virtually all participants in the study could have obtained excellent estimates of the composition. Another important outcome of the study was that matrix effects affect the apparent position of an interface in depth profiles.

The many outcomes provide a solid metrological foundation for optimal argon cluster sputter depth profiling of organic electronic materials, and organic materials in general, with minimal chemical degradation, depth resolutions close to 5 nm at 400 nm depth and with a lateral resolution better than 0.5 µm. The objective of developing the essential metrology for argon cluster sputtering has firmly been achieved.

Development of a novel method for 3D nano scale electrical characterisation of organic electronic materials (with resolution better than 30 nm) and nanostructured self-assembled reference materials for the metrological studies of the techniques.

This project has demonstrated a novel method for 3D electrical characterisation of organic semiconductor nanostructures with resolution below 30 nm. The approach is based on the use of atomic force microscopy (AFM) and photoconductive AFM (PC-AFM) to map the local electrical and photo-electrical properties of organic semiconductor nanostructures. The project focused on two steps to achieve the objective, a) development of a reliable 2D mapping method, and b) development of a novel simulation tool to extract 3D nano-electrical information from the measurement data.

The project tackled the main sources of uncertainty in PC-AFM by developing a reliable measurement protocol and putting in place engineering control actions to minimise these sources of uncertainty. That included the use of high quality nitrogen gas and calibrated mass flow controllers to avoid sample degradation without inducing mechanical noise; temperature stabilisation; laser spatial homogeneity and laser power stability; and good definition of sample-probe contact area.

In order to build a better understanding of the results from such analyses, a complete computational model was developed and demonstrated. The model can be used to estimate resolution and topography related artefacts that are sources of large uncertainties in AFM-based electrical experiments. The modelling tools give a better understanding of the 3D information contained in the experimental 2D images obtained by PC-AFM measurements and will allow future work on new methods to directly measure 3D information.

Actual and potential impact

The project has delivered a high scientific output. To obtain a long term sustainable impact in the scientific community the communication channels of written manuscripts, presentations and training at conferences were chosen. The key data of the project are the following:

- 20 publications in the public domain and another 6 publications anticipated
- 66 conference presentations and posters
- 12 training sessions

The consortium organised several special sessions and workshops including a highly succesful European Materials Research Society Symposium continuing the ALTECH conference series. In total 160 contributions were presented, including 11 invited presentations, 87 contributed oral presentations and 69 poster presentations.

Throughout the project, the partners engaged in pre-normative and standardisation activities in VAMAS (Versailles Project on Advanced Materials and Standards) and under ISO, as well as the national bodies DIN (Germany) and BSI (UK). Based on results from the project, NPL led the discussion on a standard for sputter depth profiling of organic materials at the ISO/TC201 (Surface Analysis) meeting in Berlin, September 2014. The development of a standard was encouraged by the committee.

The improved capability of reference-free GIXRF to quantify low mass depositions of a high variety of elements, including high-k dielectic materials on various substrate materials, is the prerequisite for (fundamental) studies aiming at a detailed understanding of deposition processes, reaction mechanisms and origins of growth inhibition in nanoelectronics manufacture. In addition to its fundamental importance, the reference-free quantification method is also of high relevance in process technology and layer engineering, where quantification of various materials is performed on a routine basis relying on calibration standards. The reference-free GIXRF method allows for the qualification of calibration standards used for laboratory equipment or to perform a reliable quantification of unconventional materials. This quantification approach reduces the dependency on appropriate reference materials, which are rarely available for nanolayered systems and enables the qualification of calibration standards for inline TXRF analysis.

Argon cluster sources have become highly popular. Today, more than half of new SIMS and x-ray photoelectron spectroscopy instruments are sold with an argon cluster source. An estimated >200 are now in operation worldwide in industry and academia and several measurement service providers offer depth profiling of organic electronic devices. Companies in the organic electronics industry regularly make use of these to assess layer and interface chemistry, for example to locate and identify contaminants that compromise device performance. The rapid uptake of argon cluster sources creates an increased need for robust measurement procedures. The outputs of the project comprise a timely response to this need. Analysts can now rely on the extensive body of work generated in the project that will help them select appropriate analytical conditions for optimal analytical capability and reliability. The immediate uptake of the results is evident from the project's 10 scientific publications in this area having been cited more than 80 times in the scientific literature in total as at February 2016. To accelerate the uptake of the outputs in industry, a follow-on project has been established in the EURAMET EMPIR programme to convey the results into an international standard for argon cluster depth profiling. The development of this standard was encouraged by stakeholders from industry and the metrology community. Its availibility is envisaged to ensure reliable chemical depth profiling to underpin and accelerate innovation in the organic electronics industry, contributing to economic growth and development of environmentally friendly and low cost technologies.

The universal equation for cluster sputtering has led to a new route to clean graphene surfaces to prepare the graphene for chemical modification and incorporation into novel electronic devices (Tyler et al, J Phys Chem C, 2015). This research shows that polymer residues left from the transfer process in single layer graphene production may be sputtered away using argon clusters whilst leaving the graphene virtually undamaged. With the great potential graphene-technologies hold, in particular due to the extraordinary electric properties, this could have important commercial application and is especially useful since it is already compatible with the current 300 mm semiconductor production standard.

Advanced software has been developed in this project to allow simulation of the impact of nanoscale 3D morphology on the measurement of electrical properties with resolution below 30 nm. This will support the development of nanoscale electrical measurements to directly assess key properties for organic photovoltaic devices and so underpin growth in the nanoelectronics industry.

Our research has also had far greater impact in fields previously not envisaged in this research. For example, the pharmaceutical industry has taken up the results of our research to use 3D SIMS imaging to measure the drug disposition in tissue and cells. This has led to ION-TOF GmbH (member of this consortium) and Thermo Scientific (not in this consortium) to invest in building a revolutionary new instrument - the 3D nanoSIMS (see press release http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging). Sir Colin Dollery adviser to the GlaxoSmithKline Chairman of Research and Development comments: "GlaxoSmithKline scientists are looking forward to the opportunities the new equipment will provide to explore in detail the sites of action of novel drug molecules within single cells. Designing drugs that are specific for molecular targets is part of drug development but knowing that they reach their target molecule in the right amount at the right place in the right cells is only just beginning to be attainable in intact cells within tissues. This ability will be a great opportunity."

List of publications

1. Sputtering Yields for Gold Using Argon Gas Cluster Ion Beams. L. Yang, M. P. Seah, and I. S. Gilmore, J Phys Chem C, 2012, 116, 23735-23741

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3. Universal Equation for Argon Gas Cluster Sputtering Yields. M.P. Seah, J. Phys. Chem. C, 2013, 117 (24), 12622–12632.

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