PROJECT FINAL REPORT

CP-TP 200613-2

3D NanoChemiscope

Combined SIMS-SFM Instrument for the 3-Dimensional Chemical Analysis of Nanostructures

Publishable Summary

Collaborative project targeted to SMEs
2008-09-15 to 2013-01-14

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Executive Summary

3D NanoChemiscope is a collaborative project targeted to small and medium enterprises (SMEs) which was co-funded by the Commission within the seventh framework programme. The work of the consortium was dedicated to the development of an innovative analysis tool built from a novel Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS) with substantially improved lateral resolution and sensitivity and a new metrological high resolution Scanning Force Microscope (SFM). The combination of these two techniques in a single ultra-high vacuum instrument provides complementary information on the nanoscale surface chemistry and surface morphology. Together with a layer by layer removal of material which is accomplished either by low energy atomic sputtering or large argon gas cluster sputtering and quantitatively measured by the SFM, the 3D NanoChemiscope instrument is unique for the 3-dimensional chemical characterisation of nanostructured inorganic as well as organic materials.

Project Context and Objectives

Advances in analytical instrumentation and nanometrology have been key to the remarkable progress in nanoscience and nanotechnology research over the last two decades. Detailed knowledge of the physical, chemical, mechanical, electronic, photonic and magnetic properties is needed in all phases of the development from exploratory research to concept, prototyping and finally manufacture. However, the resolution, sensitivity, accuracy and information provided by existing analytical techniques are often stretched to the limit and will not meet all future industrial demands.

The scanning probe techniques and particularly Scanning Force Microscopy in its various operation modes are widely used in nanosciences and can yield information on nanostructures with superb lateral and vertical resolution down to the atomic scale, but they lack the true chemical information which is often needed. On the other hand, all existing techniques for the chemical analysis of surfaces, interfaces and three-dimensional structures using electron, ion or photon beams have severe limitations either in lateral resolution, depth resolution or in sensitivity. An even larger gap exists for the chemical nanoanalysis of organic materials and molecular devices with high lateral resolution.

The 3D NanoChemiscope project started on 15th September 2008 with eight partners[1] from industry and public research organisations under the 7th Framework Programme of the European Commission. The goal of the project was to develop an innovative and novel combination of a new Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS) with substantially optimised lateral resolution down to ten nm and improved sensitivity, combined with a new high resolution ultra-high vacuum Scanning Force Microscope (SFM). The combination of the two techniques provides for the first time previously unavailable, complementary information on nanoscale surface chemistry and surface morphology in one instrument.

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1 **Consortium**:
ION-TOF Technologies GmbH; **Germany**
NanoScan Ltd.; **Switzerland**
Eidgenössische Materialprüf- und Forschungsanstalt (EMPA); **Switzerland**
Université Catholique de Louvain, Unité de Physico-Chimie et de Physique des Matériaux; **Belgium**
Université de Namur (FUNDP), Laboratoire Interdisciplinaire de Spectroscopie Electronique; **Belgium**
Vienna University of Technology, Institute for Chemical Technology and Analytic; **Austria**
Institute of Scientific Instruments, v.v.i., Academy of Sciences of the Czech Republic; **Czech Republic**
Netherlands Organisation for Applied Scientific Research TNO, Holst Centre; **The Netherlands**

For the analysis of ultra-thin layers and 3D nanostructures, material will be removed layer by layer in a highly controlled way by using ultra low energy sputtering and cluster sputtering techniques. The topography at the surface and at various depths will be quantitatively measured in-situ by the depth calibrated SFM while the chemical information is gathered with the ToF-SIMS.

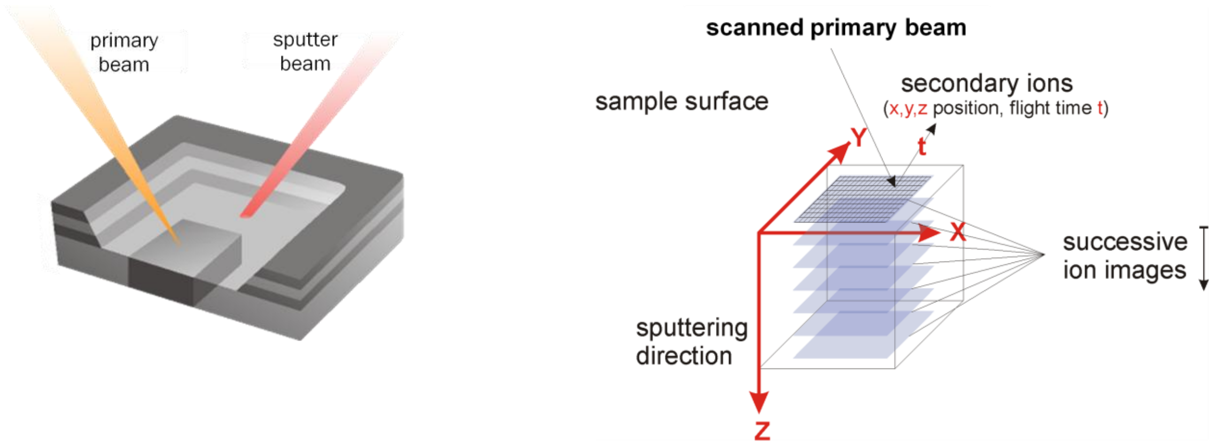


Figure: Schematic of the TOF-SIMS 3D depth profiling approach. The dual beam principle is shown on the left side. SFM measurements can be included at any time on the 3D depth profile.

This implies being able to analyse with both ToF-SIMS and SFM at the same sample location within one Ultra High Vacuum (UHV) chamber. Technically this is not simultaneously possible, but it can be achieved via a transfer system that precisely and reproducibly moves the sample between the ion guns of the ToF-SIMS and the SFM head. The development of an UHV XYZRT-stage providing the required stiffness, precision and reproducibility is one key objective of the project. For the SFM operation with a lateral resolution of less than 1 nm and a vertical spatial resolution better than 0.1 nm the gap between the tip and the sample must be stable in the same order. Because of this stringent additional requirement on the UHV XYZRT- stage, the stage has to be a constructional element of a totally new designed SFM platform. Beyond that the SFM platform comprises of a newly designed XYZ-piezo table, the SFM head and a UHV compatible device which permits the in-situ change of the SFM tip without venting the entire UHV chamber.

A combination of chemical information, provided by a ToF-SIMS measurement with topographic information from a SFM measurement requires the extension of the ToF-SIMS technique into the field of nanoscaled objects. The two major objectives to be addressed in order to reach this goal are the development of a new bismuth cluster liquid metal ion gun (Bi LMIG) delivering high mass cluster projectiles into a spot size of around ten nm and the increase of the sensitivity by a new Time-of-Flight mass analyser. Combined with novel software which is capable of calculating and displaying 3-dimensional distributions of all chemical species from the measurement data of both techniques, these instrumental developments lead to a totally new and highly innovative "3D NanoChemiscope" with broad multidisciplinary application areas. The sophisticated instrumental developments of the 3D NanoChemiscope project go along with basic research on ion-solid interactions, ionisation in SIMS and organic depth profiling.

Results and Foreground

At the end of the 3D NanoChemiscope project all major tasks have been fulfilled and the consortium was able to present a running instrument. The first measurements with the newly developed tool have shown TOF-SIMS data with a lateral resolution down to 16 nm as well as high resolution SFM data. The complementary information on the nanoscale surface chemistry and morphology of both techniques is merged using a novel software package for the calculation and display of 3-dimensional distributions of all chemical species.

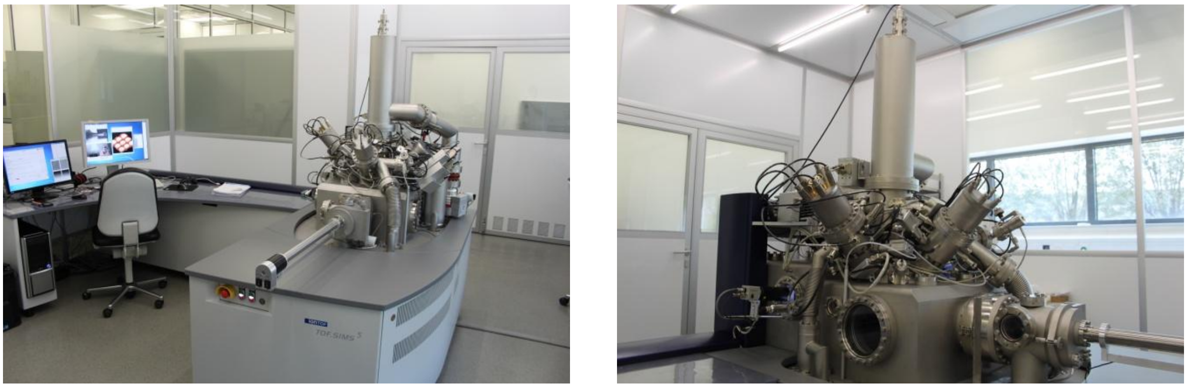


Figure: 3DNanoChemiscope - combined SIMS-SFM instrument for the 3-dimensional chemical analysis of nanostructures.

The technical requirements that had to be implemented in the combined instrument necessitated considerable deviation from the original work plan and significantly increased the complexity of the stage-SFM platform, which is the mechanical key component of the instrument.

The design had to be extended by an additional tilt- and rotary axis in order to ideally position the sample for the TOF-SIMS and SFM analysis. In the final design the XYZ-flexure scanner of the SFM no longer scans the sample but the cantilever and the sample is kept in a fixed position. This allows the required flexibility on the sample holder layout. Consequently a radically new SFM head had to be developed which could not be based on existing technology. The velocity of the piezo driven 5-axis-stage had to be increased to speed up the measurement time with the combined tool and required innovations regarding a more powerful piezo motor controller.

The high precision of the XYZRT stage enables stitching of 2D and 1D scans taken with the SFM scanner. This step is necessary in order to adapt the typical field of view of a SFM, which is of the order of some ten micrometers, to the dimensions of a TOF-SIMS sputter crater (300 x 300 µm). Surface profiling with the SFM over a distance of several hundred micrometers up to more than a millimeter in combination with high lateral and depth resolution is essential to determine the crater depth and morphology of the sample after sputtering. The additional depth and morphology information gained by the SFM is then integrated into the correct 3D reconstruction of the ToF-SIMS data.

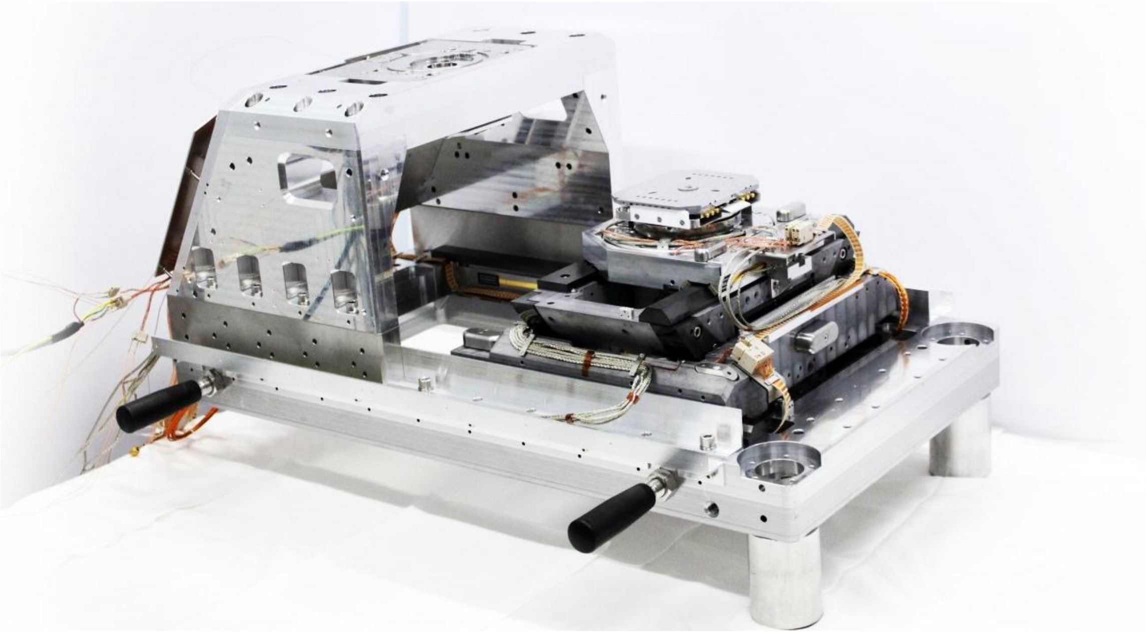


Figure: Stage-SFM platform of the combined instrument: 5-axis stage with a dome built on the Y-axis of the stage supporting the SFM scanning head.

On the TOF-SIMS side the consortium focused on the improvement of the ion probe diameter and the sensitivity of the ToF mass spectrometer. Experimental and theoretical data of the liquid metal ion source (LMIS) emission cone were the input parameters for the layout of the ion column. The new ion column is based on a two lens design which shows minimal aberrations, while de-magnifying the virtual source down to 16 nanometres. A piezo driven variable aperture controls the aperture angle in the ion column and permits adjustment of the minimum spot size and the available beam current to the analytical needs. For the required mass separation of the different Bi-clusters the ion column is equipped with a DC-mass filter.

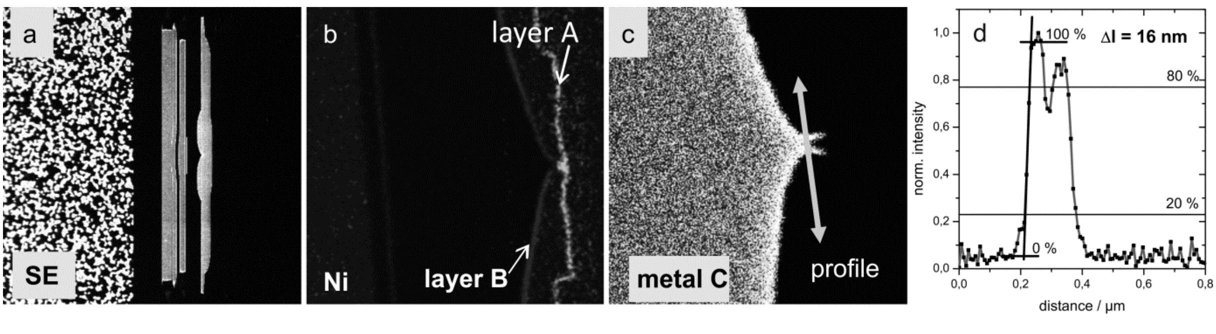


Figure: Read write (RW) head of a hard disk. (a) secondary electron overview image, 50 x 50 µm², (b) overlay of RW head layer structures 3.8 x 3.8 µm², 11 min (c) detail view of the RW head 1.9 x 1.9 µm², pixel size 7 nm, 9 min, (d) line profile over the RW head.

A major breakthrough could be achieved in the field of organic depth profiling which has always been a key issue in the 3D NanoChemiscope project. In the course of the project the application of large argon gas cluster ions for the non-destructive removal of organic material from solid surfaces was presented by scientists of the Kyoto University in Japan. The results demonstrated that depth profiling of organic polymers using an Ar gas cluster ion beam (GCIB) is possible without losing the molecular information as is typically observed for other sputter projectiles. The extremely low energy/atom of a few eV to several 10 eV of these Ar clusters seemed to be the key to avoid radiation damage and induced cross-linking. The main disadvantage of the GCIB technique presented by the Kyoto group was however the relatively poor GCIB beam quality. The consortium decided to change the original work plan and include the development of an Ar GCIB (gas cluster ion beam) ion source into the work plan. Spot size and resulting sputter crater shape as well as beam current and current stability of the newly developed GCIB ion source are outstanding and perfectly suited for 3D SIMS depth profiling of organic matter. Experimental results of the consortium on a variety of organic compounds such as polymers, OLED test structures and samples relevant to the field of organic photovoltaics suggest so far that large Ar clusters are a universal depth profiling projectile for organic matter.

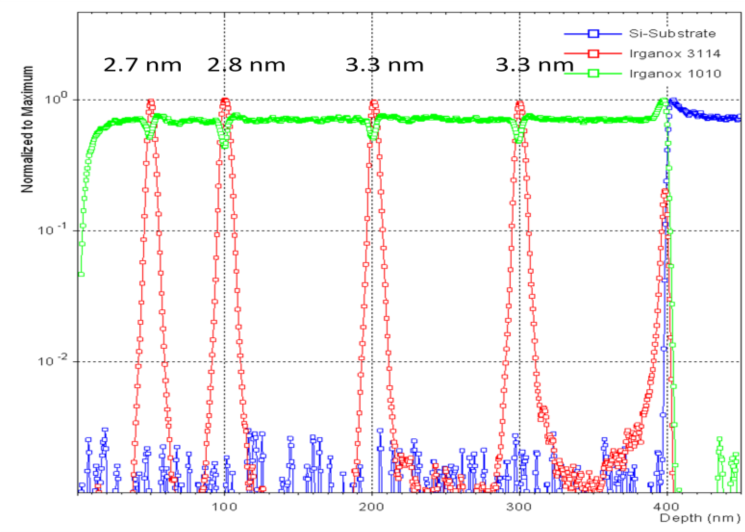
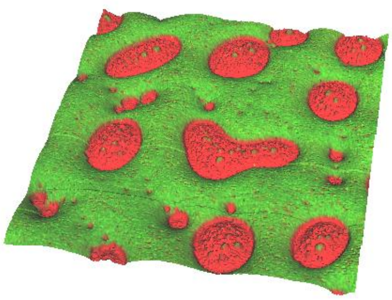


Figure: Dual beam depth profile of an Irganox 1010/3114 multilayer. Sample with courtesy of Alex Shard, National Physical Laboratory, UK. The numbers show the depth resolution on the respective delta layer (FWHM). Sputter beam: Ar_{2500} @ 2.5 keV cluster size: 2500; Analysis Beam: Bi_3 @ 15 keV.

On the software side components for the instrument control and the visualisation of combined 3D TOF-SIMS and SFM data were developed. A viewpoint correction accounts for the different viewing angle of both techniques. Carpet plots show a chemical surface image with additional height information. True 3D TOF-SIMS images are easily calculated from the in-situ acquired TOF-SIMS and SFM data. This provides a realistic 3D map of the analysed volume just with a minimum of mouse clicks.



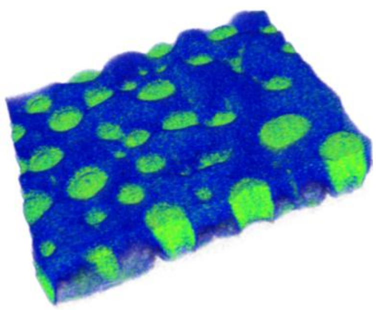


Figure: Left – Carpet plot of a polystyrene / PMMA copolymer. Right - 3D view of a polystyrene / PMMA polymer blend. FoV: 40 µm x 40 µm x 0.190 µm.

Beside the instrumental developments the consortium worked on the investigation of new methodologies for organic depth profiling and at the improvement of the SIMS sensitivity for atoms and molecules under analysis and depth profiling conditions. A set of reference materials for depth profiling, including molecular and polymeric samples, was defined. These were then circulated in the consortium and depth profiled using different methodologies including cluster projectiles such as C_{60}^{+} and large argon clusters and low energy Cs^{+} ions. Molecular dynamics simulations of Bi_n, C_{60} and Ar_n gas cluster bombardment of various targets were performed to provide the fundamental basis for new methodological developments. Finally, methods to enhance the secondary ion yield, which are based on a high pressure gas injection system, were successfully developed and implemented.

Potential Impact

The 3D NanoChemiscope provides a completely new combined tool, and introduces important improvements to both Scanning Force Microscopy and Time of Flight Secondary Ion Mass Spectrometry. Both techniques are already established tools in industrial quality control, research and development. However, the combination of ToF-SIMS with SFM allows chemical analysis with precise, lateral, depth and topographic information for thin film and 3D analysis on the nanoscale in one instrument. A completely new methodology has become available for the sputter profiling of all kinds of organic materials with low chemical damage, high sensitivity and excellent depth resolution. Presently, no instrument employing this or any other analysis technique exists that could offer comparable information, in particular for organic thin films and organic nanostructures, with similar versatility. This combined instrument will be commercialised by ION-TOF in collaboration with NanoScan.

This project will strongly support the development of new nanotechnology-based products, industrial processes and the tailoring of their properties and reliability. Considerable progress in local chemical analysis regarding resolution, sensitivity, molecular information in the ten nm range in combination with morphological information will enable and support the development of new nanotechnology-based products and processes. This holds for R&D as well as for process and product control in important areas of nanosciences and nanotechnologies such as nanoelectronics, photonics, molecular electronics, nanomaterials and nanomedicine. In all these areas, the reliable and quantitative analytical characterisation supplying chemical and molecular information with high lateral and in-depth resolution is mandatory for future developments and commercial exploitation. The project has united leading European researchers to develop this completely new and innovative instrument. It also represents a direct competitive advantage to the involved European parties. The new metrology tool will first become available to researchers in Europe and the European industry and is likely to refine standardisation.

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