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NANOBEAMS

Nanoanalysis using finely focused ion and electron beams

Network of Excellence

Priority 3 - NMP

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Table of Contents

1.	Introduction.....	3
1.1.	Project Partners	3
1.2.	Contact	4
1.3.	Summary of project objectives.....	4
2.	Project Execution.....	5
2.1.	Work performed and end result.....	5
2.1.1.	Collaboration towards improved instrumentation	5
2.1.2.	Emission and ion formation processes in SIMS	11
2.1.3.	SIMS on organic and biological samples	17
2.1.4.	Contribution to standards	17
2.1.5.	Contribution to the dissemination of knowledge.....	19
2.1.6.	Project impact on industry and research sector	20
2.2.	Conclusion	21
3.	Dissemination and use	22
3.1.	Publications and presentations	22
3.1.1.	Full list of joint publications.....	22
3.1.2.	Presentations.....	24
3.1.3.	Selection of Poster presentations.....	26
3.1.4.	Abstracts:.....	26
3.2.	Exploitable knowledge and its use.....	28
3.3.	Dissemination of knowledge.....	29
4.	Further References	33

1. Introduction

The Nanobeams Network of Excellence (NoE) started on January 1st, 2005 and ran for a total of 48 months, funded by the European Commission under the “Nanotechnology and nanosciences, knowledge-based multifunctional materials and new production processes and devices” (NMP) component of the Sixth Framework Program (FP6). The NoE concentrated on analytical techniques using focussed ion and electron beams in order to develop analytical techniques and instruments matching future requirements for the analysis of nanomaterials. The three complementary techniques included in the NoE are listed below:

- Secondary Ion Mass Spectrometry (SIMS) and Laser-Secondary Neutrals Mass Spectrometry (Laser-SNMS);
- Auger Electron Spectrometry (AES);
- Transmission Electron Spectroscopy (TEM);

SIMS uses a focused beam of ions (primary ions) to sputter a material and produce a localized ion emission characteristic of the composition of the material itself (secondary ions). Typical primary ions are Cs⁺, Ga⁺ and O₂⁺. The secondary ions emitted by the specimen are analyzed by mass spectrometry (magnetic sector quadrupoles or time of flight analyzers). Modern spectrometers provide transmissions in the range of 50% at high mass resolution ($M/\Delta M = 5000$). The SIMS technique can be divided into two distinct types of instruments: dynamic SIMS (D-SIMS) which is a depth profiling and nano/micro volume analysis tool, and static SIMS (S-SIMS), essentially ToF-SIMS, which is specifically for the analysis of the surface monolayer and molecular adsorbates. The SIMS technique offers ppm-ppb sensitivity for the consumption of $<10^{-13}$ cm³ of material, and has the potential to determine the composition of even extremely small volumes – down to 1 nm³ containing approximately 50 atoms. Hence, SIMS is an obvious choice for probing the chemical composition of the sample on the 10 nm scale. When a primary ion impinges on a solid surface, it deposits its energy (several keV) into a subsurface volume in an area of less than 10 nm in diameter around the point of impact. The dissipation and recoil of the deposited energy leads to the desorption and ionization of elements, small clusters and even intact molecules. As a result, the chemical information obtained through mass analysis of the ions generated by a single primary ion is by definition “real” nanoscale analysis.

High-resolution Auger Electron Spectroscopy (AES) may be used to perform an analysis of the first 20 nm of a sample making use of the Auger process. The range of elements that may be analyzed by AES lies between lithium and uranium. AES has the advantage over SIMS that it is a quantitative technique. However, in order for it to discover an element, the latter must be present by at least a percentage of 1.

Transmission Electron Microscopy (TEM) is a powerful technique with extremely high resolutions at the atomic scale. The disadvantage of this technique is, however, that samples need to be very thin for analysis. Therefore this demands a high level of expertise in sample preparation, and the preparation of such samples is very time consuming. TEM is the method of choice for obtaining crystallographic information with very high spatial resolution.

1.1. Project Partners

The Nanobeams NoE was composed of manufacturers of scientific instruments, as well as the leading research laboratories in the field. Overall, it involved 80 researchers and 40 PhD students. The total budget for the NoE was approximately €30 million. The contractors are listed here-underneath:

- CRP-GL: Centre de Recherche Public - Gabriel Lippmann¹, “Département Sciences et Analyse des Matériaux” (SAM) and the “Département Informatique, Systèmes et Collaborations” (ISC), Luxembourg (<http://www.lippman.lu/>);

¹ CRP-GL is also known as the CRP-Gabriel Lippmann

- IPM: Physikalisches Institut, Westfälischen Wilhelms-Universität Münster, Germany (<http://www.uni-muenster.de/Physik.PI/Arlinghaus/>);
- PCPM: Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Belgium (<http://www.pcpm.ucl.ac.be/>);
- LISE: Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix de Namur, Belgium (<http://www.fundp.ac.be/facultes/sciences/departements/physique/recherche/centres/lise/>);
- GFE: Gemeinschaftslabor für Elektronenmikroskopie, RWTH-Aachen, Germany (<http://www.gfe.rwth-aachen.de/>);
- OXMAT: SIMS Group, Department of Materials, Chancellor, Masters and Scholars of the University of Oxford, United Kingdom (<http://www.materials.ox.ac.uk/>);
- MITAC: Universiteit Antwerpen, Micro-Trace Analysis Centre, Belgium (http://www.ua.ac.be/main.aspx?c=*SCHEIKUN&n=12187&ct=007985&e=t16924);
- BioSIMS: Laboratoire et Assemblages Moléculaires: Modélisation et Imagerie SIMS, Université de Rouen, France (<http://www.univ-rouen.fr/>);
- CAMECA: Cameca S.A.S., France (<http://www.cameca.com/>);
- ION-TOF: Ion-TOF GmbH, R&D Lab, Germany (<http://www.ion-tof.com/>);
- TE: Thermo Electron Corporation, now Thermo Scientific(up to December 2006), Great Britain (<http://www.thermo.com/>);
- OP: Orsay Physics, France (<http://www.orsayphysics.com>).

1.2. Contact

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1.3. Summary of project objectives

The main activities of the different partners in the Nanobeams NoE were instrumental development, the coordination of fundamental research, the application of advanced analysis techniques to nanomaterials, the coordination of manufacturers, the organization of an annual European workshop and training sessions on the different instruments.

The project's objectives were the following:

- To improve SIMS for providing lateral resolutions down to 10 nm and a depth resolution of 1 nm;
- To develop new techniques for the measurement and analysis of nanostructured materials;
- To use these techniques for nanoscopic analysis and nano-metrology;
- To contribute to the development of Standards. This would also involve the definition of important parameters with regard to measurement systems;
- To disseminate knowledge via:
 - The implementation of a European PhD School on “Nanoanalysis using finely focused ion and electron beams”;
 - The organization of an annual European workshop;
 - The creation of two working groups for users in biology and materials science at a European level;
 - The organisation of various user training sessions on SIMS, TEM and XPS aimed at improving the skills of the machine operators.

2. Project Execution

2.1. *Work performed and end result*

Throughout the project period, the Nanobeams partners worked hard to achieve the aims set forth in the project. The partners collaborated by contributing novel ideas, which resulted in the submission of new research projects. In this respect, a number of feasibility studies were carried out and pilot ideas were developed.

2.1.1. Collaboration towards improved instrumentation

Throughout the project duration, the Network partners and especially WP3 partners have collaborated with the aim of developing more efficient instrumentation. This can be seen from the number of collaborative research project-proposals submitted in the frame of the Nanobeams NoE at a National or a European level. Section 2.1.1.1 of this report presents the efforts of the Nanobeams NoE to collaborate in various research projects in order to further improve their instruments.

Furthermore, the Nanobeams NoE partners have been involved in measuring the lateral and depth-resolutions of their state-of-the-art SIMS instruments on a range of different samples. The measurement procedures and results are shown in section 2.1.1.2 of this report.

2.1.1.1. Submitted project proposals

Introduction

Over the duration of the project, several project-proposals have been submitted for future funding, with a high success rate. 2 out of the 4 project-proposals were accepted, and so the Nanobeams NoE partners have had the opportunity for practical progress towards their aim of developing more efficient instrumentation. This has been underpinned with a number of feasibility studies.

In the frame of the „*Negative Ion Sources*“ project, stable prototype negative ion sources have been developed. These are in the phase of being tested. We have deliberately delayed submission of a number of journal papers on this work in order not to compromise a possible patent application on these sources.

In the frame of the “*3D-NanoChemiscope*” project, which started in September 2008 involving several Nanobeams partners, a new instrument combining SFM and TOF-SIMS will be developed. In this way, a resolution of less than 10 nm will be achieved by the end of the project in 2012. This is clear evidence that the NoE partners will continue active collaboration in this field of research after the end of the Nanobeams NoE.

The “*Negative Ion Sources*” project proposal, whose objective it is to develop high brightness negative ion sources, was submitted to the Luxembourgish “Fonds National de la Recherche” in the frame of the “Innovative materials and nanotechnology (NANO)” program in June 2005. This project-proposal included 3 NoE partners and 4 external partners and started in April 2006 for a duration of 30 months after acceptance by the FNR.

The German SIMS manufacturer ION-TOF and several network partners worked on the development of advanced ion sources in order to improve both the lateral and depth resolutions. Using Bi_3^+ multi-atomic guns the lateral resolution could be drastically improved from approximately 200 nm down to 40 nm (cf. section 2.1.1.2). These practical improvements in performance are already incorporated in commercial ToF-SIMS apparatus in the marketplace, and are thus adding to the ability of the EU to compete for market shares in this significant sales area.

Project-proposal objectives

“Negative Ion Sources” objectives

One major problem, which needed tackling at the beginning of the NOE, concerned the analysis of electropositive elements (which are detected as positive secondary ions in SIMS). To analyze these species with a good sensitivity, a primary ion beam of electronegative species is needed. Most SIMS instruments are as a consequence equipped with a duoplasmatron type ion source which can be run with an oxygen gas feeding in order to produce O_2^+ or O^- ion beams. These duoplasmatron ion sources unfortunately have an important handicap: their brightness is low and, as a consequence, the ion beam delivered by this source is quite broad and cannot be focussed down to a spot small enough to allow imaging applications with a good lateral resolution (cf. table 1).

This disadvantage becomes even more apparent on the CRP-Gabriel Lippmann’s NanoSIMS50 instrument. This instrument, which has known an enormous success since its installation in Luxembourg, is dedicated to ion imaging with a lateral resolution as good as 50 nm. However, this lateral resolution can only be reached when the Cs^+ primary ion source is in use (thus while detecting negative secondary ions), as the duoplasmatron source also available on the instrument cannot offer O^- spot sizes compatible with the required experimental resolution. As a consequence, the potential of the NanoSIMS50 (an instrument offered by an EU company with no effective competitor in the marketplace) cannot be fully exploited for positive secondary ions.

Up to the start of the project, only a few attempts had been made to introduce primary ions with electronegative species other than oxygen. Moreover, the consortium was been aware of any current projects trying to develop such negative ion sources. As a result, the partners introduced a project aimed at optimizing SIMS analysis with high sensitivity of electropositive elements by introducing new primary ion guns based on electronegative species (primarily on the NanoSIMS50, but also on the other instruments of the CRP-Gabriel Lippmann). The research work performed in the framework of this project consists both in a combined fundamental/analytical study of SIMS using negative primary ions and the development of sources producing such negative ions.

“3D NanoChemiscope” objectives

The objective of this “*Combined SIMS-SFM Instrument for the 3-dimensional chemical analysis of nanostructures*” project is to develop an innovative and novel combination of a new TOF-SIMS with substantially improved lateral resolution and sensitivity, combined with a new metrological high resolution SFM (Scanning Force Microscope). The two techniques provide complementary information on nanoscale surface chemistry and surface morphology. In combination with a layer by layer removal of material using low energy sputtering, quantitatively measured by SFM, this combined ultra-high vacuum (UHV) instrument will be unique for the 3-dimensional chemical characterization of nanostructured inorganic as well as organic materials with down to at least 10 nm lateral resolution and down to 1 nm in depth resolution. Combined with novel software for the calculation and display of 3-dimensional distributions of all chemical species, this leads to a totally new instrument – the 3D NanoChemiscope.

2.1.1.2. Measurement of SIMS lateral and depth resolutions

Introduction

This section will give an overview of the progress achieved by the NoE partners in the optimization of their instruments in order to reach better lateral and depth resolutions over the past four years. At first, the determination of the lateral and depth resolutions is discussed in sections 2.2.2 and 2.2.3. Then, the progress and results of the various NoE partners within this area is described (section 2.2.4).

Determination of lateral resolution

The diameter of the ion probe depends on the brightness of the ion source and on the optical properties of the column used to focus the ion beam on the sample. The brightness B of an ion source is defined as follows:

$$B = \frac{I}{S \cdot \Omega},$$

where I is the ion current, S the ion emitting surface and Ω the solid angle in which ions are emitted. High brightness ion sources thus allow the producing of very finely focussed probes while keeping a sufficient current for correct secondary ion intensities. Table 1 shows an overview of the characteristics of those ion sources, that are the most commonly used in SIMS. This table shows that the highest brightness can be reached with liquid metal ion sources (operating with field emission ionization).

	electron impact	duoplasmatron	surface ionization	liquid metal
species	Ar, Xe, O ₂ , SF ₆ , C ₆₀ ...	Ar, Xe, O ₂ , ...	Cs	Ga, In, Au _n , Bi _n
size of source	1 mm	200 μm	10 μm	3 nm (virtual)
ion energy	0.1 - 20 keV	0.1 - 10 keV	0.3 - 20 keV	2 - 30 keV
beam current	1 - 1000 μA	1 - 1000 mA	10 μA – 100 mA	1 - 1000 μA
brightness	1 A sr ⁻¹ cm ⁻²	10 ² A sr ⁻¹ cm ⁻²	10 ³ A sr ⁻¹ cm ⁻²	10 ⁷ A sr ⁻¹ cm ⁻²
energy dispersion	1 - 10 eV	5 - 20 eV	0,2 - 0,5 eV	5 – 50 eV

Table 1: Main characteristics of the ion sources, which are the most commonly used in SIMS

The determination of the lateral resolution of a SIMS instrument uses a conventional method based on imaging and performing a linescan of sharp edges of a test sample. The lateral resolution is defined as the separation of 16-84% contours in a plot of intensity of the elemental or molecular signal (see figure 1).

In the past, various SIMS users have used their own reference materials. More recently, a specifically developed Certified Reference Material (CRM) has been developed by the German Certification Authority Bundesanstalt für Materialforschung, BAM. This sample is constituted from polished cross-sections of a AlGaAs-InGaAs-GaAs layer stack. These layers form a complex stripe pattern at the surface whose gratings range from finely graded periods of 2 nm to 600 nm [20,21].

Determination of depth resolution

The depth resolution of a SIMS instrument can be determined by performing a depth-profile on a bulk sample including a so-called delta layer. There are several methods for determining the depth resolution: Usually, depth resolution cannot be better than surface roughness:

- According to [22], the “depth resolution corresponds to the distance (depth range) over which a 16% to 84% (or 84% to 16%) change in signal is measured” when profiling through an interface of two media. This definition was introduced by [23-25] and later adopted by IUPAC and the ASTM E-42 committee [26].
- According to [27], “depth resolution is measured in terms of the decay length, the distance over which the signal falls by a factor e , the natural log base. It is also sometimes described in nm/decade as this is easy to estimate from a graph since SIMS depth profiles are presented, almost universally, with a logarithmic concentration axis due to their high dynamic range.”

In general, depth resolution depends on several factors, one of the most important of which is surface roughness, which generally increases as depth profiling proceeds.

Progress and end result

Taking into account that the instruments were continuously improved in the frame of these collaborative projects as well as the feasibility studies performed by various Nanobeams NoE partners over the time span of the Nanobeams NoE, considerable progress has been achieved in the improvement of the lateral resolution in static and dynamic SIMS. Thus, OXMAT achieved a resolution of 29 nm when measuring a PMMA film following the optimization of their CAMECA NanoSIMS50 instrument’s parameters (see figure 1).

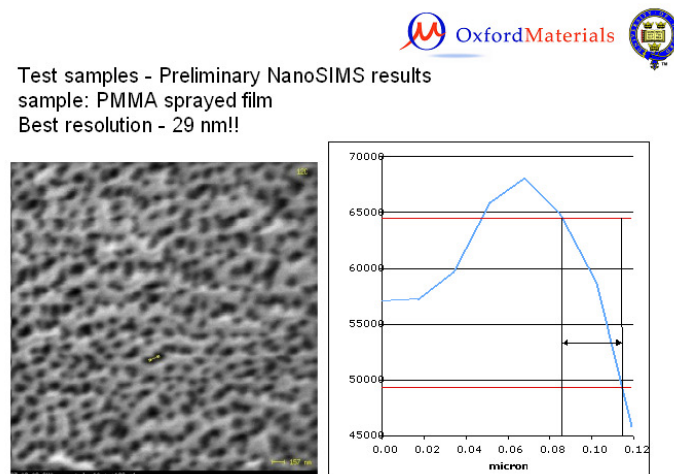


Figure 1: Measurement of lateral resolution using a PMMA sprayed film. The measurement of the distance corresponding to a 84-16% intensity variation shows a lateral resolution of 29 nm on OXMAT’s NanoSIMS50 instrument using a cesium ion gun.

In the frame of the “*NanoBioMaps*” project, which was integrated into the Nanobeams NoE and involves the German SIMS manufacturer ION-TOF and IPM (University of Münster), ION-TOF performed a number of measurements using their recently developed Bi_3^{++} cluster ion gun on their TOF-SIMS IV instrument [21]. As shown in table 1 above, Bi_3 ion sources are high brightness liquid ion metal sources. Such sources allow the production of very finely focussed probes as explained above. As can be deduced from figure 2, the German manufacturer determined the lateral resolution of their instrument using the recently developed CRM BAM-L200 as a sample. The result was that using a Bi_3^{++} cluster ion gun, the lateral resolution on their TOF-SIMS IV instrument was 40 nm. Before the development of such cluster ion guns, the lateral resolution for TOF-SIMS was in the range of 100 nm or above. This is a very significant improvement in a key performance metric over the duration of the NoE.

In order to achieve better depth resolutions, it is important to lower the impact energy, E , of the primary ion beam. As chromatic aberrations are inversely proportional to E , the lowering of the energy would drastically degrade the focus of the primary ion beam on conventional SIMS instruments. In order to overcome this problem, the SC-Ultra instrument has been specifically developed by the French SIMS manufacturer CAMECA. Unlike other SIMS instruments, this instrument uses a “Floating Low energy Ion Gun” (FLIG). As can be seen in the example of figure 2, the column is held at a high potential (e.g. 7500 V), even though the impact energy is kept low. This innovative concept allows for chromatic aberrations to be kept at a minimum and for the impact energy also to be kept low. As a consequence, the decay length within the target material is small, and high depth resolutions can be achieved.

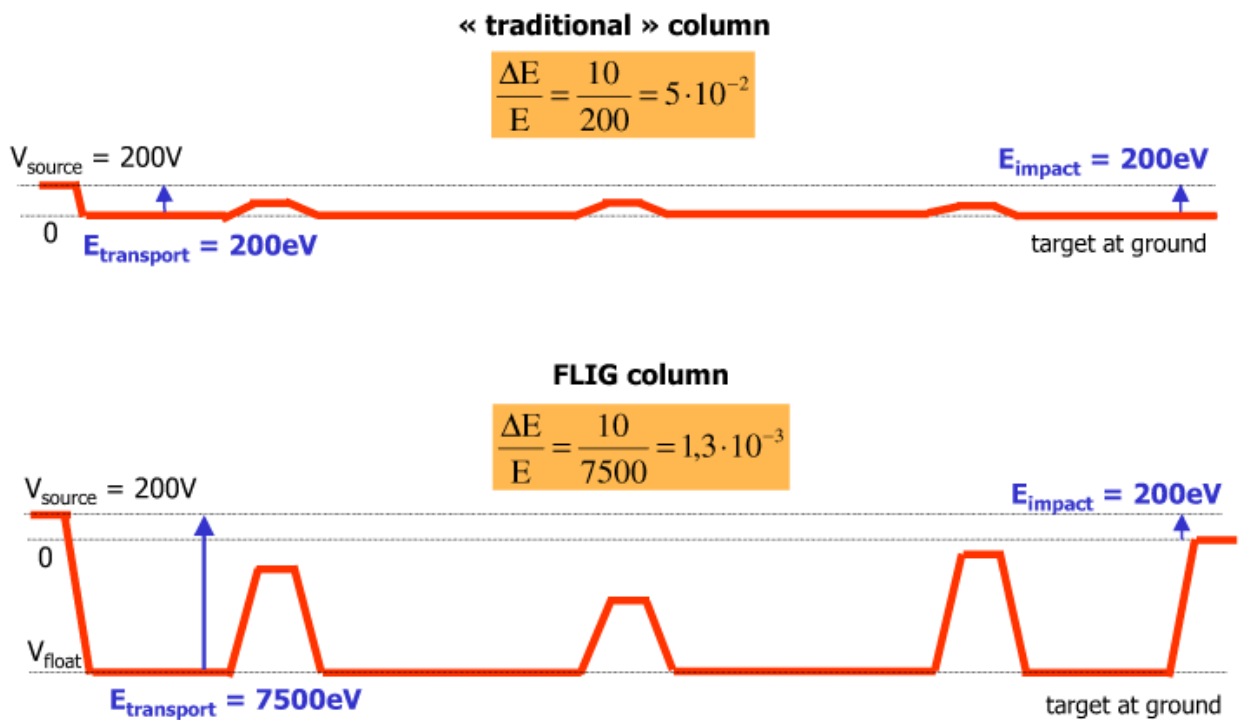


Figure 2 : The above figure depicts both the traditional and the recently developed FLIG column. Both of these columns include electromagnetic lenses, which are used for focussing the beam. In traditional columns, where the column itself is at ground and the ion source is held at a potential V_{source} , the impact energy is equal to the transport energy $E_{\text{transport}}$. In FLIG columns, the column is held at a negative potential V_{float} . This means that the transport energy of the ion beam is increased. As the beam passes a grounded electrode just before the impact on the sample, the impact energy is different from the transport energy. Using FLIG columns, aberrations can be kept at a minimum without increasing E_{impact} .

Using their recently developed SC-Ultra SIMS instrument, the NoE partner Cameca, the world leader in the manufacturing of dynamic SIMS instruments, performed a number of depth resolution studies on a Si sample including a boron delta layer. The depth resolution was determined according to the definition given in subsection entitled “Determination of depth resolution”. It was found that the distance over which a 16% to 84% (or 84% to 16%) change in signal is measured is less than 1 nm. Using the method suggested by [27], the

depth resolution corresponds to 0.75 nm/decade. The analysis was performed using an ultra-low energy sputtering O_2^+ ion beam of 150 eV. Whereas in 2005, the depth resolution on such samples was still around several nanometers, the latter has now been improved to less than 1 nm. Thus, it can be concluded that the Nanobeams consortium has also achieved a significant improvement in SIMS depth resolution during the project period.

2.1.1.3. Improvement of the sensitivity of SIMS

The effective application of fine incident beams to accurate nano-analysis is not only dependent on the focussing of the beam but also on the sensitivity of the instrument. The amount of material analyzed in a very tiny area (such as $10 \times 10 \text{ nm}^2$) is very limited and a high sensitivity is required to have reasonable counting statistics. Similarly, an image with good contrast can only be obtained if a very high signal is produced, which means a higher sputtering yield and a higher ionization yield. Therefore, improving lateral resolution is intimately linked to improving sensitivity. Hence, an important aim of the Nanobeams NoE was to turn innovative ideas and concepts related to improving the sensitivity and the resolution into instrumental prototypes. This required the collaboration of laboratories specialized in different fields. Thus, the Nanobeams NoE submitted several project-proposals at national and European levels in order to fulfil these objectives. The Nanobeams consortium worked in particular on one very successful project named “**Storing Matter**”. This project is described below.

The “Storing Matter” project

This project aimed to decouple the sputtering of the specimen from the subsequent analysis step in order to enable higher sensitivity than with usual SIMS techniques. By the end of the project in June 2006, a prototype instrument had been fully assembled at the CRP-Gabriel Lippmann. Experimental studies showed that the Sputtering Storing Matter Instrument (SSMI) was a highly sensitive technique, which allowed improved quantification and thus was expected to reduce the importance of the well-known matrix effect. Indeed this effect is one of the issues in accurate quantitative analysis with the SIMS technique. By reducing this issue, more accurate nano-measurements can be performed. Indeed, the sensitivity achieved in the project is even higher than the benchmark fixed at the initial stage. During the SIMS XVI conference in Japan in September 2007, several oral presentations regarding the new instrument were given [13-15]. Thus, the project was successfully completed. One picture of the prototype instrument is shown in figure 3. In 2008, the project partners decided to continue collaborating in order to apply the storing matter concept to polymers.



Figure 3: The Storing Matter prototype at the CRP-Gabriel Lippmann.

2.1.1.4. Submission of further projects

Over the project duration, the consortium also submitted other projects for funding of direct relevance to the NoE. One of these was the “**Nano²hybrids**” project, which was funded in the frame of the FP6 STREP program. “**Nano²hybrids**” (FP6-2004-NMP-TI-4-033311), and which started in October 2006 involving the CRP-Gabriel Lippmann, LISE and PCPM. This new project concerns the “Interface design of metal nanocluster-carbon nanotube hybrids via control of structural and chemical defects in a plasma discharge”. It was of strong relevance to the NoE as it concentrates on the further development of novel nanostructured materials for functional applications, and reliable analysis protocols for these materials will be very important.

Furthermore, the Nanobeams NoE launched several projects in the area of Biology. Tacking into account the improved resolution of SIMS as well as the improved sensitivity, SIMS has become more and more useful in Biology. In the ANR-funded research project “**1cell-nanoproteomics**”, the partners BioSIMS and OP aim at analyzing the single cell proteome by nano-electrophoric devices (NEDs) using the CAMECA NanoSIMS 50. The project started in March 2007 and will finish in 2011.

One further project-proposal aiming at using SIMS in biology was submitted under FP7’s Health theme in December 2008.

2.1.2. Emission and ion formation processes in SIMS

Introduction

As one of the Nanobeams NoE’s goals was to improve our knowledge regarding emission and ion formation processes in SIMS with special emphasis on the detection of large molecular fragments, the objective was to increase the sensitivity of the method thanks to better control of the physical parameters influencing the secondary ion yield and specifically by the use of laser beams to ionize sputtered neutrals (Laser-SNMS). This increase in sensitivity is especially needed when looking at nanostructures where the amount of material available for the analysis and imaging is rather limited (especially when static conditions are required for molecular surface characterization). Moreover, a better understanding of the basic processes involved will allow us to improve significantly the quantitative interpretation of SIMS data.

The specific tasks were to increase sensitivity, by considering either the emission processes (sputtering) or the ion formation mechanisms. As an example, to enhance the secondary yield of molecular fragments by the use of cluster and molecular primary ion beams instead of atomic beams, to improve the ionization of the emitted particles by different methods of cationization/ anionization or to efficiently ionize sputtered neutrals by laser photo-ionization processes. In order to gain insights about these basic mechanisms, the procedure consisted in comparing the experimental results with predictions of the theoretical models. The experimental information mainly consists in the secondary ion yield, energy and angular distribution dependence as well as on the experimental parameters such as the primary ion nature, energy and impact angle.

Thus, it was planned to perform molecular dynamics simulations using realistic interaction potentials with the goal of obtaining theoretical information concerning the sputtering processes. With regard to the charge formation process, different models were to be tested. As an example, the PCPM group proposed a model to explain the efficient cationization of organic molecules by complexation with substrate metal atoms to form ions. This model is based on an associative ionization mechanism consisting in the recombination of an excited molecule and a metal atom above the surface and the subsequent decay of the complex via the emission of an electron, locking the system in the ionized state. Electronic structure calculations were required to study the stability of the ionized complexes formed during the emission process.

The activity was thus divided into different pilot projects:

Pilot project 1: Ion formation of molecules from mono- and multilayers

Pilot project 2: Molecular ion yield enhancement induced by metal cluster deposition

Pilot project 3: Use of cesium for enhancement of ionization probabilities and quantification

Pilot project 4: Laser-SNMS project

Activities related to pilot project 1 :

In this activity, IPM and ION-TOF collaborated in improving our understanding of mechanisms of molecular ion yield enhancement induced by metal clusters bombardment on organic surfaces. The objective was to optimize parameters for detecting hybridized DNA fragments using different primary ions, including monatomic ions, as well as cluster metal ions. In this study, important new results have been obtained, for example it was found that cluster primary ions resulted in a significantly increased yield of DNA-correlated fragments (e.g. PO_3^-), enabling higher signal intensities and better secondary ion efficiencies [10,28].

For the monatomic primary ions Ne^+ , Ar^+ , Ga^+ , Kr^+ , and Xe^+ , a continuous increase with increasing projectile mass can be observed. Compared with Ar^+ , the use of polyatomic primary ions SF_3^+ and SF_5^+ for example, led to a significant increase in the PO_3^- secondary ion yield by about a factor of 250. Compared to all the “classical” primary ions studied, SF_3^+ and SF_5^+ do not only result in the highest PO_3^- secondary ion yields, due to their polyatomic nature, but also give the best values for the secondary ion efficiency (not shown) and therefore, in general, provide a high sensitive method for detection of hybridized DNA on biosensor chips.

In order to further investigate the influence of the ion energy on the secondary ion emission of PO_3^- , an evaluation of yields, disappearance cross sections and efficiencies as a function of different primary ion energies was carried out using Bi_3^+ as an exemplar primary ion projectile. In general, within the energy range from 10 to 50 keV only a minor energy dependence is observed. With increasing energy, the secondary ion yield increases by about a factor of 2.5 and the disappearance cross-section by about a factor of 3.5. As a result from this behaviour, the secondary ion efficiency decreases down to two-thirds of the value at 10 keV.

The variation of the secondary ion yields of PO_3^- as a function of Bi primary ion species was also investigated. In general, the highest relative increase of values is observed by changing from monatomic Bi^+ to polyatomic Bi_2^+ primary ions, which amounts to approximately an order of magnitude. With increasing cluster sizes, continuous enhancements can be observed, although the enhancement factors saturate for high cluster sizes.

In general, a similar development can be found for the disappearance cross-section and secondary ion efficiency of PO_3^- , displayed in the middle and right-hand graph. Nevertheless, the enhancement factors of the disappearance cross-section and, due to the combined influence of yield and disappearance cross-section, the secondary ion efficiency shows smaller enhancement factors [10].

Changing the substrate material from silicon to gold, an additional yield enhancement for PO_3^- was observed which was highest for monatomic primary ions (more than a decade) and smallest for polyatomic primary ions (factor 2-4).

It was found that a change from monatomic to polyatomic primary ions leads to an increase in secondary ion yield of about two orders of magnitude, whereas there are smaller differences in between Bi_3^+ , Bi_2^+ , Bi_3^+ and Bi_5^+ . The data also indicates that there is a kind of saturation of the secondary ion yield with increasing cluster size. An increase in the primary ion energy resulted only in small changes of secondary ion yield and efficiency, especially in the energy range from 20 keV to 50 keV. In conclusion, the data clearly shows that it should be possible to take advantage of a simplified low-energy cluster Liquid Metal Ion Gun (LMIG) supplying doubly charged Bi_3^{++} primary ions in future analysis and thus providing optimal bombardment conditions.

The results were presented on the SIMS XV and ECASIA'07 conferences and two joint publications were published [6,10].

Pilot projects 1 & 2: Ion formation of molecules from mono- and thicker layers and molecular ion yield enhancement induced by metal cluster deposition

Thin layer samples (about one monolayer in thickness) and thick layer samples (at least 10 nm thickness) were prepared for pilot project 1. Most of them were additionally used for pilot project 2, where the effect of metal deposition was investigated. Therefore, these results are shown together. Mainly gold was used for metallization.

Hundreds of samples were prepared by various partners:

- Polyethylene, polypropylene and Irganox 1010 ($M_w = 1177$ u) (PCPM, LISE)
- A thick layer of plasma polymerized polystyrene (LISE)
- Polystyrene with different molecular weight ($M_w = 500$ u, 1800 u and 10,000 u) as thin and thick layer samples (PCPM, LISE)
- Polymer samples containing different dyes (molecular weight of about 500 u) as thin and thick layer samples (MiTAC, LISE)
- Triacotane (molecular weight of about 422 u) prepared on silicon, gold and silver as thin layer samples (PCPM)

Most samples were analyzed by more than one partner (IPM, PCPM, MiTAC) using all the different primary ion species available within the project. Additionally, LISE did electron microscope measurements on selected samples.

Many of the results obtained in pilot project 2 show the same trends, regardless of which samples were analyzed and regardless of the choice of secondary fragment ions (cf. figure 4) or secondary ions of the whole molecules.

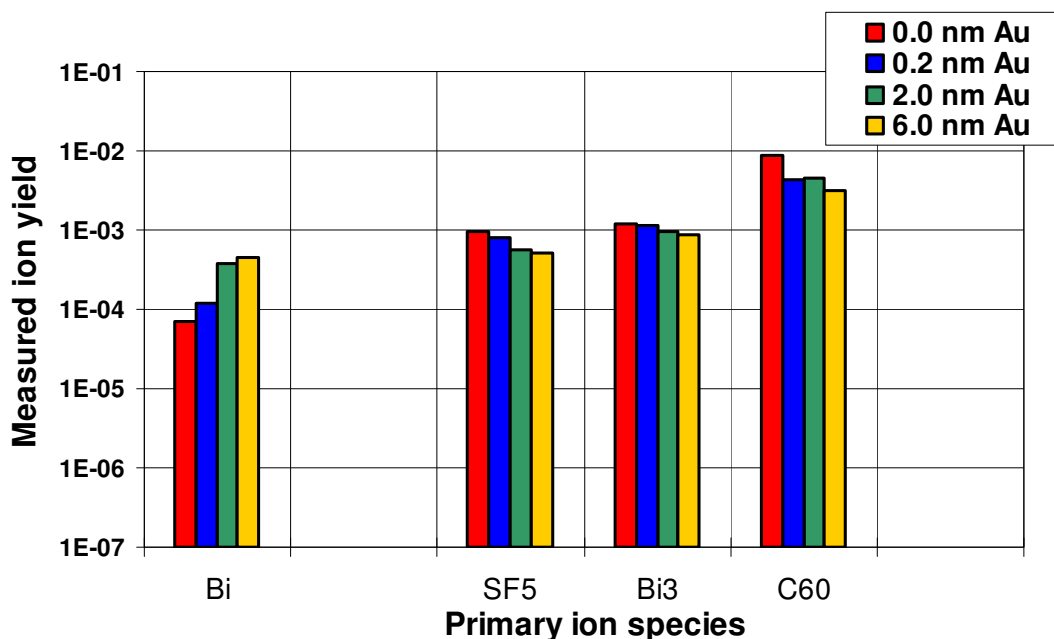


Figure 4: Secondary ion yield of a characteristic polystyrene fragment ion ($C_8H_5^+$) obtained from pristine and gold-covered samples using monatomic (Bi^+) and polyatomic primary ion bombardment (SF_5^+ , Bi_3^+ , C_{60}^+)

Due to the results obtained in this work-package, it concludes that some of the known methods to enhance the yield (thin layer/monolayer preparation, polyatomic instead of monatomic primary ion bombardment, metallization with gold) depend mainly on the same mechanism: They all help to deposit more energy near the sample surface. Therefore, when combining these methods, the yield increase is often much smaller than the sum of the single yield increases of each method. Sometimes even a yield decrease is observed. Many

results obtained in pilot projects 1 and 2 can be explained by arguments involving changes in energy deposition [7-9,11,17].

However, results from additional experiments, in which silver was used for metallization and gold and silver were used as substrate material, do not fit into the previous observations. Secondary ion yields of quasi-molecular and cationized ions obtained from these samples with C_{60}^+ and Ga^+ bombardment [11]. The yield obtained with Ga^+ from the sample with gold deposition is higher than the yield obtained from the sample with a gold substrate. This cannot be explained by the assumptions and arguments made above. Additionally, it cannot be explained why the yields of the cationized molecules are higher when using monatomic instead of polyatomic primary ions. Results obtained in pilot project 2 were presented at various conferences like ECASIA'07, SIMS XVI (Japan) and SIMS Europe 2008. Five joint publications were published on this subject [7-9,11,17]. The investigation of different metals' influence in metal-assisted SIMS will be carried on beyond the end of the Nanobeams NoE.

Pilot project 3 : Use of cesium for enhancement of ionization probabilities and quantification

Pilot project 3 dealt with ionization processes of secondary ions and clusters. These processes were studied by LISE and the CRP-Gabriel Lippmann. Thus, scientists from both institutions shared the available equipment in order to address, in a joint fundamental study, the improvement in SIMS quantification when depositing Cs at the surface.

When using the neutral cesium deposition system on a prototype SIMS instrument available at the CRP-Gabriel Lippmann, in conjunction with a simultaneous primary ion bombardment, a significant increase of the useful yields of negative secondary ions, and thus of the analysis sensitivity compared to traditional Cs^+ primary ion bombardment, is obtained. In this case, the overall useful yield qualitatively agrees with the predictions of the electron-tunnelling model. At maximal cesium surface concentrations, quantitative analyses become possible for elements with high electron affinities. For other elements, a significant increase of the analysis sensitivity is achieved.

Combining the knowledge gained on various samples using AES measurements and simulations, the two partners were able to convert the raw data, obtained from analyses using the Cs/Xe co-sputtering ToF-SIMS analysis mode, to positive and negative ionization probabilities of Cs and Si with respect to the decreasing work function. It was found that the negative Cs and Si signals increase exponentially with the Cs coverage, whereas the positive signals decrease. The data were interpreted by means of the electron-tunnelling model. During the Nanobeams project, this aforementioned technique was successfully applied to typical SIMS applications like depth profiling and the results were presented in a joint publication [16].

Pilot project 4 : Laser-SNMS

The quantification of the elemental composition of a sample surface by mass spectrometric analysis of secondary particles sputtered from solid surfaces under primary ion bombardment is limited by the fact that the flux of secondary particles of a certain element consists of both atomic particles and different kinds of molecules containing the respective element. Furthermore, some of these secondary particles are positively or negatively charged whereas the rest are neutral. These different kinds of secondary particles cannot be detected in a mass spectrometric analysis with identical probability. In contrast to the secondary ions, which can be analyzed directly (SIMS), neutral particles have to be ionized before mass separation, e.g. by the interaction with photons of a laser beam (Laser-SNMS). Depending on the photon energy, a desorbed atom can be post-ionized resonantly or non-resonantly. For sputtered molecules photo-ionization is possible as well, but – as a competitive process – also photo-fragmentation. Such photo-fragmentation processes can result in the generation of smaller fragments, which can be charged or neutral, including fragmentation into monatomic neutrals and ions (figure 5). As the composition of the flux of secondary particles depends on the chemical matrix of the respective element in the surface, changing flux compositions complicate quantitative interpretations of SIMS and Laser-SNMS data, because signal intensities obtained for the particular element

can depend strongly on the chemical matrix and do not always correlate with the elemental distribution on the surface.

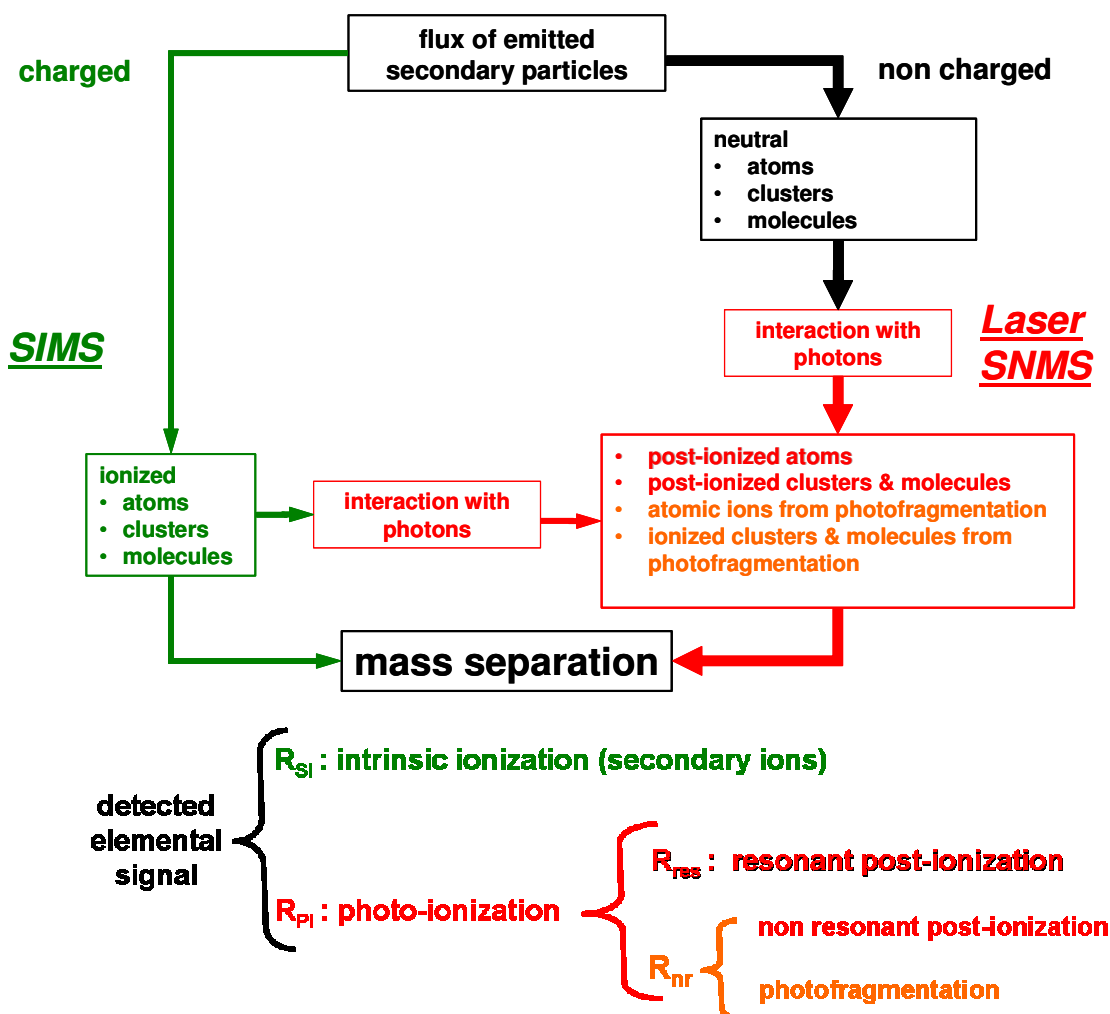


Figure 5 : Schematic diagram of the distribution of the sputtered particle flux (top) and the resulting composition of the detected elemental signal in resonant Laser-SNMS (bottom).

As a step closer towards quantitative elemental analysis using Laser-SNMS techniques, the aim was to develop a method to distinguish between different ion formation processes and to determine the influence of these processes on the total number of detected monatomic ions of a certain element. The knowledge about the composition of the detected ion yield can be used for characterizing the composition of the flux of secondary particles sputtered from different surfaces. To explain the origin of diverse fractions of differently generated ions contributing to the total yield of all monatomic ions of a certain element, a vector/matrix-formalism was developed, which describes the physical processes of sputtering, ion formation, mass separation and detection in Laser-SNMS.

In the framework of the method developed, based on this theoretic formalism, changes in the secondary flux contribution of the respective element were observed by comparing the detected monatomic ion yield obtained in specifically aligned (SIMS and) Laser-SNMS experiments. These were performed via systematic variations of certain laser parameters, ensuring that the sputter conditions and the chemical situation of the surface were kept strictly constant. The yields resulting from these experiments were used to calculate characteristic numbers to compare the flux composition from different surfaces. In particular, these characteristic numbers were utilized to indicate changes between the monatomic and the molecular part of the flux of secondary particles.

For these experimental investigations, two different laser systems were applied: a dye laser system and a 193 nm excimer laser. The dye laser system, with two separately tuneable beams, can be used to excite

resonant ionization processes of atomic neutrals, element and state selectively. In contrast, the excimer laser offers high non-resonant post-ionization and photo-fragmentation probabilities.

The potential of the method was demonstrated for the elements boron, iron and gadolinium by investigating the changes in the flux composition of secondary particles sputtered from metallic surfaces, as a function of the oxygen concentration at the surface. Exemplary analyses of various kinds of surfaces show that there is, in principle, no restriction on a general applicability of the presented method.

Laser-SNMS experiments using the dye laser system tuned for resonant post-ionization of atomic neutrals showed striking yield differences between clean and oxidized surfaces, which could not be explained by differences in surface stoichiometry or changes in sputter yield. Analyses of the composition of the detected ion yields, with the help of characteristic numbers, depicting the different influence of photo-fragmentation processes, indicate that the yield differences were mainly caused by a significant enhancement of the molecular fraction (oxides and clusters) and a tremendous reduction of the number of monatomic neutrals in the flux of secondary particles.

As the degree of photo-fragmentation depends strongly on the laser system applied, the percentage of ions generated by photo-fragmentation processes, of the yield of all monatomic ions (generated as result of the interaction of the sputtered particles with photons of the excimer laser beam) was estimated by a comparison between the yields obtained in Laser-SNMS experiments using the two different laser systems.

Furthermore, the combination of both laser systems in the same Laser-SNMS experiment was used to establish another ion formation process: the dye laser induced resonant post-ionization of atomic neutrals resulting from excimer laser induced photo-fragmentation of molecules. To examine such “pre-fragmentation” processes, the timing of the extraction voltage and the laser pulses was optimized for a separate extraction of the secondary ions and those ions generated as a result of excimer and dye laser irradiation, wherein the excimer laser pulse reaches the interaction volume before the arrival of the dye laser pulse. Applying this timing scheme, three different ion yields of the same element were recorded simultaneously in each analysis cycle. As the excimer laser induced ion signal and the dye laser induced ion signal were separated and simultaneously recorded, the influence of excimer laser irradiation on dye laser ion yield could be investigated and quantified.

Determination of the influence of pre-fragmentation on the dye laser signal allowed further quantitative estimations about changes in the flux composition and about the state of charge of the atomic products resulting from photo-fragmentation processes. Furthermore, pre-fragmentation might be an interesting way to enhance trace element signals, especially from surfaces characterized by a high molecular fraction in the flux of secondary particles.

Finally, combined Laser-SNMS depth profiles and images, obtained with both laser systems, were measured to demonstrate how the simultaneous detection of the three differently originated ion signals of the same element can be used to get additional information about the composition of the flux of sputtered particles. In this respect the presented method can be very helpful to prevent misleading interpretations of SIMS or Laser-SNMS data. Detailed information can be found in Guido Vering’s doctoral thesis (Münster (IPM), 2008).

Furthermore, experiments were carried out to compare the ionization efficiency of sputtered atoms using single photon ionization (SPI) and multiphoton ionization (MPI). It could be shown that with SPI (laser wavelength: 157 nm, photon energy: 7.9 eV) higher copper intensities can be obtained than with MPI (laser wavelength: 193 nm, photon energy: 6.4 eV).

For MPI the laser power density has to be increased by at least two orders of magnitude to get comparable count rates. These laser power densities can only be achieved by focusing the laser beam to a very small spot size. This reduces significantly the interaction volume between the laser beam and the sputtered particle cloud, thus reducing the amount of ionizable atoms.

SPI can also be used for efficiently post-ionizing sputtered molecules. For example, atmospheric aerosol particles collected on an aluminium foil were imaged with TOF-SIMS and Laser-SNMS [29]. Only in the case of Laser-SNMS in combination with a laser beam using photons with a wavelength of 157 nm, the

lateral distribution of polycyclic aromatic hydrocarbons (PAHs) could be determined. This can be explained by the fact that for some PAHs, SPI is possible because the photon energy of 157 nm radiation exceeds the first ionization potential (for example 7.43 eV in the case of pyrene). This will lead to higher yields in ionization processes while multiphoton ionization of molecules causes significant fragmentation. Detailed information can be found in Steffen Dambach's doctoral thesis (Münster (IPM), 2009).

A further decrease of fragmentation losses, although utilizing MPI processes, is expected by using fs-laser. In preliminary experiments, the effect of different laser radiation (ns-pulse laser, 157 nm and fs-pulse laser, 800 nm) on anthracene molecules released to gas phase on photo-ionization and photo-fragmentation was investigated. It was found that photo-ionization with fs-pulse laser generates less small fragments and the intact molecular ion signal shows the highest intensity compared to ns-pulse laser photo-ionization. This might be explained by the fact that with fs-pulses the number of photons needed for ionization in MPI can be absorbed within a shorter period compared to transition times known for fragmentation processes after photo-excitation. Therefore, less fragmentation processes can occur compared to MPI utilizing ns-pulse lasers, where fragmentation or ionization after preceding excitation are competing processes.

Also, a comparison between fs-laser-SMNS and TOF-SIMS spectra of tryptophan spin-coated on silicon showed that with fs-laser-SMNS much higher intensities of the two major tryptophan fragments could be obtained than with TOF-SIMS [28].

2.1.3. SIMS on organic and biological samples

As the Nanobeams NoE also wished to further promote SIMS for biological applications, the consortium also performed a number of round robin experiments on biological samples such as fixed cells and mixtures of isotopically labelled proteins. Furthermore, a number of PS-dPMMA samples were investigated using ToF-SIMS and NanoSIMS50 since polymer blends and biological samples show similar responses to SIMS analysis.

With respect to the biological samples, good progress in relation to aspects like the preparation and manipulation of biological specimens (cryofixation, use of different materials for supporting the sample), the systematic study of the behaviour of biological material bombarded with the primary ions (influence of sample heterogeneity, matrix effects, differential sputtering, insulating property of the sample, depth-profiling etc.), the study of formation of molecular ions (analytical potential of molecular emission) and the evaluation of methods of multi-isotope labelling (isotope recombination) was also made. From the results, it can be said that single amino acids can be detected. Further details about these activities can be found in two joint publications [3,18]. A further publication resulting from these activities has been submitted and is planned to be published in 2009.

With respect to the PS-PMMA measurements, one joint paper was written with four NoE partners contributing [5]

2.1.4. Contribution to standards

With the aim of improving the consistency of chemical measurements on the nanoscopic level with SIMS, the NoE partners LISE, IPM, MiTAC, PCPM and the CRP-Gabriel Lippmann made several measurements on a number of sample batches using static SIMS in order to develop adequate protocols to ensure a maximum of consistency between the results from different instruments in different laboratories. Bringing together the available competences within the network, the consortium members aimed at increasing the reliability of quantitative SIMS results and delineating the limitations of the experimental methodology. In this way, the results obtained in the frame of the Nanobeams NoE can play an essential role in the implementation of European standardization and conformity assessment procedures for a wide range of high-technology products.

S-SIMS has the unique capability to detect and quantify the molecular composition of the upper monolayer at the surface of solids with high sensitivity and an information depth of essentially one monolayer. S-SIMS is “powerful” because it probes directly and selectively the information that is relevant for the interaction of a material with its environment, because the outer surface layer is the interface at which all interactions occur and therefore its composition often determines a major fraction of the material’s behaviour in a given application. S-SIMS is “vulnerable” because the analysis of specific molecular information from only the upper monolayer with high lateral and depth resolution is unique in the field of molecular chemical analysis. No other method can deliver similar information. This also implies that the common procedures for sample preparation and handling (storage, transport) are no longer robust, i.e. they are often not calibrated sufficiently well to check for possible alterations of the chemical composition. For instance, the deposition of gaseous contaminants that stick to the solid’s outer surface becomes a problem when the method gives only information on the top monolayer. The objectives of this activity could most effectively be fulfilled by means of round-robin experiments. Four batches of test samples were circulated during the course of the project in order to assess the reproducibility in quantification and spatial resolution of the ToF-SIMS technique, to five different laboratories, using different ion sources with the aim of quantifying the concentration on a blue dye mixed with an IR dye in a matrix described in figure 6.

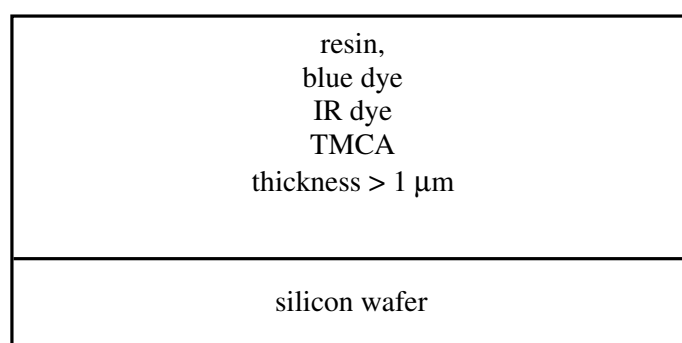


Figure 6 : The dye/polymer system.

The IR dye concentration was kept constant, as an internal standard, and the concentration of the blue dye was varied. Each participant was required to measure the intensities of molecular fragments related to the blue dye normalized by the intensities of the internal standard, versus the known concentration of the blue dye. This yielded calibration curves, which should be simply linear. A sample of unknown concentration was also distributed to all partners, who were asked to give an estimate of the blue dye concentration using the calibration curves.

Although the first round robin yielded mixed results, with some groups delivering an acceptable calibration curve and others were unable to do any quantification, owing to severe surface contamination with PDMS. The relative failure of this round robin forced the different partners to compare their different analysis protocols and to define a common analysis protocol in all laboratories. In a second batch of samples, all partners could produce good calibration curves, following the new procedure. An important outcome in this activity to standardize the analysis protocol, was that a reproducibility of about 10% could be reached. However, it appears that the best quantification accuracy is obtained when using the traditional “old” monatomic Ga^+ beams, which is quite surprising and not clearly understood. With the generalization of cluster beams, the poor quantification accuracy is an issue that should be addressed in further detail by the ToF-SIMS community.

Using this standardized analysis protocol, a last batch of samples was analyzed with the aim of determining the lateral resolution of the S-SIMS instrumentation available in the various labs. In this last batch, the nanofibres were aligned and laid flatly on the substrate. Sharp molecular images of the fibres were obtained with Bi_3^+ , with an excellent lateral resolution of 100 nm. The molecular signal was still high enough with Ga^+ to be able to visualize the fibres, but the low contrast was detrimental for the lateral resolution, limited to 200 nm at the best.

2.1.5. Contribution to the dissemination of knowledge

During the Nanobeams NoE, all project partners have been involved in dissemination of knowledge activities. The exact dates of these events are listed in section 3.3.

2.1.5.5. User schools and workshops

During the course of the Nanobeams NoE, the partners organized 4 workshops, of which one was organized in conjunction to the ECASIA conference. Furthermore, the world-leading SIMS manufacturers CAMECA and ION-TOF organized **15 user training sessions** on state-of-the-art instrumentation. Orsay Physics and Thermo Electron Cooperation organized one advanced training session each on their state-of-the-art Gallium sources and state-of-the-art high-resolution Auger Electron Spectroscopy respectively.

Moreover, due to the high demand from the nano-analysis community, the Nanobeams partners GFE, and BioSIMS organized one TEM and SPM academy respectively. Three further XPS academies were organized at LISE. These user schools, given by world-renowned experts in their field, were very successful and helped increase the knowledge amongst its user community (approx. 110 participants overall).

2.1.5.6. Exchange of personnel

During the Nanobeams project, the exchange of personnel was considered to be important for promoting the exchange of ideas between students and staff from the different institutions. These exchanges had the advantage that the collaboration in the various activities was much more effective.

Thus, for instance, several students from MiTAC visited IPM several times in order to analyze samples with organic compounds with different primary ion species and parameters. Furthermore, a researcher from PCPM visited IPM in order to measure triacontane samples within the frame of pilot project 2. Students from LISE visited the CRP-Gabriel Lippmann twice in order to analyze surface concentrations of caesium using AES. Researchers from OXMAT visited IPM in 2006 for high sensitivity experiments on frozen hydrated plant samples, and a different group of workers from OXMAT visited ION-TOF in 2008 to use the high resolution Bi source on the S-SIMS equipment for high sensitivity studies of steel and other metallic samples. 3 students theses were co-directed by 2 different NoE institutions, 2 at the CRP-GL and PCPM and 1 at the CRP-GL and LISE.

As a result of these exchanges, several joint papers could be published.

2.1.5.7. A European PhD School

As mentioned above, one of the aims of the Nanobeams NoE was the creation of a European PhD School in the area of “*Nanoanalysis using focused electron and ion beams*”. In order to reach this objective, the Nanobeams NoE created a scientific committee, the core-group, at the start of the project, which was responsible of the creation of the school as well as the overview the scientific content of the latter. The core-group was composed of the following members:

- Prof. Henri-Noël Migeon, CRP- Gabriel Lippmann
- Prof. Partick Bertrand, Université Catholique de Louvain
- Prof. Gradimir Misevic, Université de Rouen
- Prof. Joachim Mayer, RWTH-Aachen
- Prof. Susanne Siebentritt, Université du Luxembourg
- Prof. Alfred Benninghoven, Westfälische Wilhelms-Universität Münster

The European PhD School was organized such that the student finished a full cycle within 2 years. Each cycle consisted of four Teaching Weeks, the first being an overview week, and one Analysis Week. Upon fulfilling the full cycle, the student will receive a certificate as well as credit points from the University of Luxembourg. In this school, renowned professors and researchers from the Nanobeams NoE partner laboratories gave courses on the topics of SIMS, Laser-SNMS, AES and TEM. These are complemented by practical sessions on these instruments. With an average of 15 PhD students participating the various sessions, the PhD school was a real success. During the course of the project, four cycles of the European PhD School were started at CRP-Gabriel Lippmann in Belvaux (L). During this period, students that registered for the first and second cycles completed the fourth 'teaching week' and were the first to have completed the European PhD School (80 participants and 21 certificates of completion were obtained during that period).

In order to smooth the integration of this European PhD School into the University of Luxembourg's curriculum, Prof. S. Siebentritt from the University of Luxembourg was integrated into the core-group. Furthermore, the involved NoE partners have signed letters of support and thus engaged in supporting the European PhD School after the end of the Nanobeams NoE. At the beginning of the fourth project year, the core-group decided to integrate the first 'teaching week' of European PhD School organized in November 2008 into the university's curriculum. By the end of the project, a convention between the University of Luxembourg and the CRP-Gabriel Lippmann was signed engaging both partners to continue the European PhD School after the end of the Nanobeams NoE.

Thus, the European PhD School will continue to exist after the Nanobeams NoE and is an example of the strong intention of the NoE partners to continue to collaborate. The fact that the school has been integrated into the University of Luxembourg's curriculum is also an added value for the development of the Luxembourgish research sector.

All events related to the European PhD School on "Nano-analysis using finely focussed ion and electron beams" are listed in section 3.3 "Dissemination of knowledge".

2.1.6. Project impact on industry and research sector

Taking into account that the Nanobeams partners have been engaged in several projects including the world-leading SIMS manufacturers (i.e. CAMECA and ION-TOF), the Nanobeams NoE has had an enormous impact on its research sector, as well as industry. Thus, the outcome of the various research projects integrated within Nanobeams will enable the SIMS manufacturers to continue developing improved and efficient instrumentation and to keep the lead in the area of nano-analysis.

Thanks to the Nanobeams NoE, the development of a new technique combining SFM and ToF-SIMS is already underway. Being coordinated by the world leader for ToF-SIMS, this project will give the project partners the opportunity to submit further patents and to commercialize a new product.

During the course of the project, a prototype for performing quantitative analysis nano-analysis was developed (patent pending). The outcome of this project was presented at several conferences. Using the knowledge and experience gained within the Nanobeams NoE, the CRP-GABRIEL LIPPMANN is able to use this instrument for analysis.

The creation of the European PhD School on the topic of "Nano-analysis using finely focussed ion and electron beams" will have a large impact on the research sector of nano-analysis. Being the outcome of the collaboration between the Nanobeams partners as well as the University of Luxembourg, this PhD school is now integrated in the university's curriculum. Taking into account that the university was only created in 2003, the PhD school will also give a boost to the further development of the Luxembourgish research sector and as a consequence to the Luxembourgish economy.

The various user schools organized by the world-leader in SIMS and high-resolution Auger Spectroscopy as well as the advanced training courses on state-of-the-art TEM, XPS and SPM instrumentation gave the

opportunity to the user community to further improve their skills. Furthermore, the industry had the opportunity to present their latest state-of-the-art instrumentation to a large number of future customers in the research community.

2.2. Conclusion

Even though the objective for reaching a lateral resolution in SIMS was not fully achieved, the Nanobeams NoE has overall fulfilled its objectives. Technical progress has been made in several areas of key importance in the development of reliable techniques and methodologies for high resolution chemical analysis of a wide range of sample types, these have been widely reported in the scientific literature and to appropriate international audiences at major conferences, and some of these technical advances have led to improvements in commercial instrumentation. These outcomes all contribute to the international perception of the high quality of the science base in the EU, and to the competitiveness of EU industry in technical instrumentation.

3. Dissemination and use

This section provides a publishable summary of each exploitable result of the Nanobeams NoE.

3.1. Publications and presentations

3.1.1. Full list of joint publications

During the project period, the following joint publications have been submitted or published:

[1] Multitechnique characterization of thin films of immiscible polymer systems : PS-b-PMMA diblock copolymers and PS-PMMA symmetric blends

L. Kailas^a, B. Nysten^a, J.-N. Audinot^b, H.-N. Migeon^b, P. Bertrand^a

^aUniversité Catholique de Louvain, ^bCentre de Recherche Public – Gabriel Lippmann,
Surface and Interface Analysis 37 (2005) 435-443

[2] Surface segregational behaviour studied as an effect of thickness by SIMS and AFM in annealed PS-PMMA blend and block copolymer thin films

L. Kailas^a, J.-N. Audinot^b, H.-N. Migeon^b, P. Bertrand^a

^aUniversité Catholique de Louvain, ^bCentre de Recherche Public – Gabriel Lippmann,
Composite Interfaces, Vol.13, No.4-6 (2006) 423-439

[3] Method for macromolecular colocalization using atomic recombination in dynamic SIMS

G. Legent^{1,4}, A. Delaune^{1,2,4}, V. Norris^{1,4,5}, A. Delcorte^{3,4}, D. Gibouin^{1,4}, F. Lefebvre^{1,4}, G. Misevic^{1,4,5}, M. Thellier^{1,4,5} and C. Ripoll^{1,4,5*}, 2008.

¹ Laboratoire “Assemblages moléculaires: modélisation, et imagerie SIMS” (AMMIS), Faculté des Sciences de l’Université de Rouen, 76821 Mont Saint Aignan Cedex, France;

² UPRES EA 2123, Faculté de Médecine-Pharmacie de l’Université de Rouen, Boulevard Gambetta, 76000 Rouen, France;

³ PCPM, Université Catholique de Louvain, 1 Croix du Sud, B1348 Louvain-la-Neuve, Belgium;

⁴ “Nanobeams” European Network of Excellence;

⁵ Epigenomics Programme, Genopole®, 91000 Evry, France.

Journal of Phys. Chem. B 112 (2008), pp. 5534-5546, doi : 10.1021/jp7100489.

[4] Investigation of Laminated Fabric Cages Used in Rolling Bearings by ToF-SIMS

U. Gunst^a, W.- R. Zabel, N. Valle^b, H.- N. Migeon^b, G. Poll and H. F. Arlinghaus^a

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

Tribology International (2009), submitted and accepted

[5] Nanoscale characterization of PS-PMMA thin film blends

K.-H. Lau^a, K.L. Moore^a, M. Schröder^a, J.-N Audinot^b, H.-G Cramer^c, D. Rading^c, B. Boschmans^e, R. De Mondt^e, L. Van Vaeck^e, D.G Bucknall^d, E. Niehuis^c, H.-N Migeon^b, C.R.M. Grovenor^a

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^bDépartement Science et Analyse des Matériaux (SAM), Centre de Recherche Public - Gabriel Lippmann, 41, rue du Brill, L-4422 Belvaux, Luxembourg

^cION-TOF GmbH, Heisenberg Str. 15, D-48149 Münster, Germany,

^dSchool of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA30332-0295, USA

^eDept. of Chemistry, University of Antwerp (CDE), Universiteitsplein 1, 2610 Wilrijk, Belgium
Surface and Interface Analysis (2009), submitted

[6] Mass spectrometric characterization of DNA microarrays as a function of primary ion species

S. Hellweg^a, A. Jacob^b, J.D. Hoheisel^b, Thomas Grehl^c, and Heinrich F. Arlinghaus^a

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^b ION-TOF GmbH, Münster, Germany

Appl. Surf. Sci., 252 (2006), 6742-6745, doi:10.1016/j.apsusc.2006.02.281

[7] Metal-Assisted Secondary Ion Mass Spectrometry Using Atomic (Ga⁺, In⁺) and Fullerene Projectiles

A. Delcorte^{*†}, S. Yunus[†], N. Wehbe[†], N. Nieuwjaer[†], C. Poleunis[†], A. Felten[‡], L. Houssiau[‡], J.-J. Pireaux[‡], and P. Bertrand[†]

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[‡] LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Published in: *Anal. Chem.*, 79 (10), 3673 -3689, 2007, doi: 10.1021/ac062406l

[8] Molecular Ion Yield Enhancement Induced by Gold Deposition in Static Secondary Ion Mass Spectrometry

Wehbe, N. [†]; Delcorte, A. [†]; Heile, A. [‡]; Arlinghaus, H. [‡]; Bertrand, P. [†]

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[‡] IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

Applied Surface Science, 255 (2008), 824-827 (proceedings SIMS XVI conference), doi:10.1016/j.apsusc.2008.05.068

[9] Investigation of Methods to Enhance the Secondary Ion Yields in TOF-SIMS of Organic Samples

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, P. Van Royen^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

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^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

Surface and Interface Analysis, (proceedings ECASIA'07 conference), doi: 10.1002/sia.2810

[10] Influence of Different Primary Ion Species on the Secondary Ion Emission from PNA/DNA Biosensor Surfaces

Sebastian Hellweg^a, Andreas Heile^a, Thomas Grehl^b, and Heinrich F. Arlinghaus^a

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b ION-TOF GmbH, Münster, Germany

Surf. Interface Anal., 40 (2008), 198-201 (proceedings ECASIA'07 conference), doi: 10.1002/sia.2684

[11] Effects of Metal Nanoparticles on the Secondary Ion Yields of a Model Alkane Molecule upon Atomic and Polyatomic Projectiles in Secondary Ion Mass Spectrometry

N. Wehbe^a, A. Heile^b, H. F. Arlinghaus^b, P. Bertrand^a and A. Delcorte^a

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^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

Anal. Chem., 80 (2008), 6235-6244 doi: 10.1021/ac800568y

[12] Ion yield improvement for S-SIMS by use of polyatomic primary ions

Roel De Mondt^{*a}, Luc Van Vaeck^a, Andreas Heile^b, Heinrich F. Arlinghaus^b, Nicolas Nieuwjaer^c, Arnaud Delcorte^c, Patrick Bertrand^c, Jens Lenaerts^d, Frank Vangaever^d

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Rapid Communications in Mass Spectrometry (2008), Vol. 22 Issue 10, 1481-1496, doi: 10.1002/rcm.3533

[13] Storing Matter: A new quantitative and sensitive surface analysis technique

T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, G. Slodzian^c, H.-N. Migeon^a

^a Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

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Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.109

[14] The Storing Matter technique: application to inorganic samples

P. Philipp^a, F. Lacour^a, T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, G. Slodzian^c, H.-N. Migeon^a

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^b LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.075

[15] The Storing Matter technique: preliminary results on PS and PVC

P. Philipp^a, B. Douhard^b, F. Lacour^a, T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, H.-N. Migeon^a

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^b LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.070

[16] On the understanding of positive and negative ionization processes during ToF-SIMS depth profiling by co-sputtering Cesium and Xenon

J. Brison^c, J. Guillot^b, B. Douhard^a, R. Vitchev^d, H.-N. Migeon^b, L. Houssiau^a

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Nucl. Instr. Meth. Phys. Res. B, available online December, 2008, doi:10.1016/j.nimb.2008.11.026

[17] Metal-Assisted SIMS and Cluster Ion Bombardment for Ion Yield Enhancement

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, L. Van Vaeck^d, H. F. Arlinghaus^a

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^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

Appl. Surf. Sci., 255 (2008), 941-943 (proceedings SIMS XVI conference), doi:10.1016/j.apsusc.2008.05.007

[18] Biological sample preparation for chemical microscopy by dynamic mode Secondary Ion Mass Spectrometry (SIMS)

Gradimir N. Misevic^{1*}, Bernard Rasser², Vic Norris¹, Cédric Dérue¹, David Gibouin¹, Fabrice Lefebvre¹, Marie-Claire Verdus¹, Anthony Delaune¹, Guillaume Legent¹ and Camille Ripoll¹

¹ AMMIS, University of Rouen, France,

² Orsay Physics, Fuveau, France

Published in February 2009 in:

Methods in Molecular Biology, Extracellular Matrix Protocols (second edition), Humana Press.

In the framework of the activities on biological samples, one further publication has been submitted and is planned to be published in 2009.

3.1.2. Presentations

Imaging of electrospun nanofibres with static and dynamic secondary ion mass spectrometry (S-SIMS and NANO-SIMS)

P. Van Royen, L. Van Vaeck, L. Ruys, A. M. dos Santos, P. Dubruel, E. Schacht, J.-N. Audinot and H.-N. Migeon

7th International Symposium on Frontiers in Biomedical Polymers, 24th – 27th June 2007 (Gent, Belgium)

Investigation of Tribological Boundary Layers of High-Speed Rolling Bearings Elements by AES, XPS and SIMS

U. Gunst, J. Guillot, N. Valle, W.-R. Zabel, H.-N. Migeon, G. Poll and H. Arlinghaus
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey 9th – 14th September 2007 (Belgium)

Effect on depth resolution of low impact energy, sample rotation and oxygen flooding during dynamic SIMS analyses of multilayer structures

N. Valle, J.-N. Audinot, P. Philipp, A. Merkulov, H.-N. Migeon
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey, 9th - 14th September 2007 (Belgium)

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c
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^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany
^c Agfa Graphics N.V., Mortsels, Belgium
(SIMS Europe 2008, Münster)

Investigation of Methods to Enhance the Secondary Ion Yields in TOF-SIMS of Organic Samples

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, P. Van Royen^d, L. Van Vaeck^d, H.F. Arlinghaus^a,
^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany
^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,
^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium
^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey, 9th - 14th September 2007 (Belgium)

Storing Matter: a new quantitative and sensitive surface analysis technique

T. Wirtz, L. Houssiau, J.-J. Pireaux, G. Slodzian, H.-N. Migeon
SIMS XVI Kanazawa (2007)

The Storing Matter technique: application to inorganic samples

P. Philipp, F. Lacour, T. Wirtz, L. Houssiau, J.-J. Pireaux, G. Slodzian, H.-N. Migeon
SIMS XVI Kanazawa (2007)

The Storing Matter technique: preliminary results on PS and PVC

P. Philipp, B. Douhard, F. Lacour, T. Wirtz, L. Houssiau, J.-J. Pireaux, H.-N. Migeon
SIMS XVI Kanazawa (2007)

Nano-characterisation by high resolution SIMS analysis

C. Grovenor, Invited talk at ECASIA, Brussels (2007).

High resolution surface analysis of metallic and biological specimens by NanoSIMS analysis

C. Grovenor, Invited talk at EMC Aachen (2008).

High resolution surface analysis of metallic and biological specimens by NanoSIMS

C. Grovenor, Invited talk at SIMS Europe 2008

3.1.3. Selection of Poster presentations

Use of S-SIMS for the surface analysis of nanofibres formed through electrospinning

P. Van Royen^a, L. Van Vaeck^a, L. Ruys^b, A.M. dos Santos^c, E. Schacht^c, J.-N. Audinot^d, H.-N. Migeon^d

^a University of Antwerp, Wilrijk, Belgium; ^b Centexbel-Gent, Zwijnaarde, Belgium;

^c University of Gent, Gent, Belgium; ^d Centre de Recherche Public, Belvaux, Luxembourg.

Status and future of nanofibers by electrospinning, CNT VII conference in Frankfurt, October 23rd and 24th, 2006

On the understanding of positive and negative ionization processes during ToF-SIMS depth profiling by co-sputtering Cesium and Xenon

J. Brison, J. Guillot, B. Douhard, H.-N. Migeon and L. Houssiau

SIMS XVI Kanazawa (2007)

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c

^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium

^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^c Agfa Graphics N.V., Mortsels, Belgium

(SIMS Europe 2008, Münster)

Investigation of Metal-Assisted SIMS and Cluster Ion Bombardement for Analysis of Polystyrene Surfaces

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, P. Soete^d, R. De Mondt^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

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^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

(SIMS Europe 2008, Münster)

3.1.4. Abstracts:

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c

^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium

^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^c Agfa Graphics N.V., Mortsels, Belgium

(SIMS Europe 2008, Münster)

Investigation of Metal-Assisted SIMS and Cluster Ion Bombardement for Analysis of Polystyrene Surfaces

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, P. Soete^d, R. De Mondt^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,

^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

(SIMS Europe 2008, Münster)

Characterisation of the co-ordination of nickel in frozen hydrated leaves of the hyperaccumulator plant *Alyssum lesbiacum* by ToF SIMS with principal component analysis

K.E. Smart^a, J. Möller^b, B. Tyler^c, J.A.C. Smith^c, H.F. Arlinghaus^b, C.R.M. Grovenor^a

^aUniversity of Oxford, ^bUniversity of Münster, ^cUniversity of Utah

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Applications of an In Vacuum-Cryo-Sectioning Instrument for ToF-SIMS Analyses of Non-Dehydrated Samples

J. Moeller^a, K. Smart^b, B.J. Tyler^c, D. Lipinsky^a, H.F. Arlinghaus^a

^aUniversity of Münster, ^bUniversity of Oxford, ^cUniversity of Utah

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Cationisation of polymers depending of the structure of the metallic deposition

L. Nittler^a, A. Delcorte^b, P. Bertrand^b, H.-N. Migeon^a

^aCentre de Recherche public - Gabriel Lippmann, Belvaux, Luxembourg; ^bUniversity of Louvain, Louvain-la-Neuve, Belgium

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Evaluation of the ion yield improvement for S-SIMS by the use of polyatomic primary ions for thermographic applications

R. de Mondt^a, L. Van Vaeck^a, A. Heile^b, H. Arlinghaus^b, N. Niewjaer^c, A. Delcorte^c, P. Bertrand^c, J. Lenaerts^d, F. Vangaeve^d

^aUniversity of Antwerp (CDE), Wilrijk, Belgium; ^bUniversity of Münster, IPM, Münster, Germany;

^cUniversity of Louvain, PCPM, Louvain-La-Neuve, Belgium; ^dAgfa-Gevaert, Mortsels, Belgium

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

3.2. Exploitable knowledge and its use

Table 2 shows the exploitable knowledge that resulted from the collaboration of the Nanobeams NoE partners:

Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Patents or other IPR protection	Owner & Other Partner(s) involved
“Tele-presence module”	Videoconferencing tool specifically designed to follow nano-analyses	Nano-analysis, Nanomedicine, Industry		CRP-GL
Sputtering Storing Matter instrument	Semi-quantitative nano-analysis tool	Nano-analysis, Fraud detection	patent pending	CRP-GL, LISE
Publications	19 joint publications	Physics, Chemistry, Biology, Materials Science (SIMS, TEM, AES, XPS, SPM)		All Nanobeams partners
PhD School	Lectures, practical sessions	Physics, Chemistry, Biology, Materials Science (SIMS, TEM, AES)		CRP-GL, IPM, PCPM, LISE, GFE, OXMAT, MiTAC, BioSIMS, Cameca, ION-TOF, University of Luxembourg

Table 2: The above table shows an overview of exploitable results and of how they can be exploited in future

3.3. Dissemination of knowledge

The tables here-underneath list all events organized within the frame of the Nanobeams NoE as well as the conferences attended by NoE partner in order to talk about the work done within the NoE (see tables 3, 4, 5 and 6).

Planned/actual date	Type	Type of audience	Countries addressed	Size of audience	Partner responsible/involved
19 th October 2004	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
19 th October 2004	Press release(press/radio/TV)	General Public	Luxembourg	80'000	CRP-GL
March 2005	Press release(press/radio/TV)	General Public	Luxembourg	80'000	CRP-GL
17 th March 2005	Launch of project web site	General Public/Research	Open to any country		CRP-GL
June/July 2005	Training of Users	Research	Open to any country	6	Cameca
September/October 2005	Press release(press/radio/TV)	Industry (economical sector)	Luxembourg	10'000	CRP-GL
October 2005	Training of Users	Research	Open to any country	6	ION-TOF
October 2005	Training of Users	Research	Open to any country	6	ION-TOF
23 rd October 2005	Open door event	General Public	Luxembourg	250	CRP-GL
22 nd & 23 rd and 29 th & 30 th October 2005	Poster	General Public	Luxembourg	10'000	CRP-GL
3 rd and 4 th November 2005	European Workshop	Research	Europe	29	PCPM
21 st - 25 th November 2005	European PhD School	Research	Europe	34	CRP-GL
25 th November 2005	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
29 th November 2005	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
5 th - 9 th December 2005	Training of Users	Research	The world	5	TE

Table 3: The above table summarizes the dissemination activities in the first 12 months and just before the start of the Nanobeams project.

Planned/actual date	Type	Type of audience	Countries addressed	Size audience	Partner responsible /involved	
February 7 th - 9 th , 2006	User session (XPS Academy)	Training (XPS)	Research	Europe	20	LISE
March 6 th - 10 th , 2006	User session	Training	Research	Europe	6	ION-TOF
March 13 th - 17 th , 2006	European School	PhD	Research	Luxembourg	20	CRP-GL
March 2006	Press release (press/radio/TV)	General public/Research	Europe	100'000		CRP-GL
June 12 th - 16 th , 2006	European School	PhD	Research	Europe	20	CRP-GL
June 18 th , 2006	Open Door event	General public	Luxembourg	250		CRP-GL
June 2006	Press release (press/radio/TV)	General public	Luxembourg	100'000		CRP-GL
September 11 th - 15 th , 2006	European School	PhD	Research	Europe	10	CRP-GL
September 24 th - 26 th , 2006	SIMS Europe 2006 (conference)		Research	Open to any country	230	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
October 19 th - 20 th , 2006	Conference		Research	Europe	190	CRP-GL
October 23 rd - 27 th , 2006	European Workshop		Research	Europe	22	PCPM
October 23 rd - 27 th , 2006	User session	Training	Research	Europe	6	ION-TOF
November 2006	21 st , Conference		Industry	Luxembourg	40	CRP-GL
November 27 th - December 1 st , 2006	European School	PhD	Research	Europe	24	CRP-GL
December 11 th - 15 th , 2006	User session	Training	Research	Europe	8	CAMECA

Table 4: The above table summarizes the dissemination activities within the in the second year of the Nanobeams project.

Actual date	Type	Type of audience	Countries addressed	Size audience	of Partner responsible /involved
January 29 th – 31 st , 2007	XPS Academy	Research	Europe	5	LISE
March 5 th – 9 th , 2007	User Training session	Research	Europe	6	ION-TOF
March 19 th – 23 rd , 2007	European PhD School	Research	Europe	11	CRP-GL
May 21 st – 25 th , 2007	European PhD School	Research	Europe	7	CRP-GL
June 18 th – 22 nd , 2007	European PhD School	Research	Europe	20	CRP-GL
September 9 th – 14 th , 2007	European Workshop/ ECASIA	Research	Europe	688	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
October 8 th – 10 th , 2007	TEM Academy	Research	Europe	3	GFE
October 8 th – 10 th , 2007	User Training session	Research	Europe	5	ION-TOF
SIMS XVI	Conference	Research	Open to any country	250	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
November 19 th – 23 rd , 2007	European PhD School	Research	Europe	15	CRP-GL
November 19 th – 23 rd , 2007	User Training session	Research	Europe	5	CAMECA
December 12 th – 14 th , 2007	European PhD School	Research	Europe	5	CRP-GL

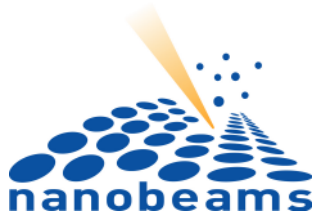
Table 5: The above table summarizes the dissemination activities in the third year of the Nanobeams project.

Actual date	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
January 29 th – 31 st , 2008	XPS Academy	Research	Europe	5	LISE
February 22 nd , 2008	User session Training	Research	Europe	6	Orsay Physics
March 3 rd – 8 th , 2008	European School PhD	Research	Europe	8	CRP-GL
March 10 th - 14 th , 2008	User session Training	Research	Europe	6	ION-TOF
June 9 th – 13 th , 2008	European School PhD	Research	Europe	12	CRP-GL
September 14 th – 16 th , 2008	SIMS Europe 2008	Research	Open to any country	200	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
September 22 nd – 26 th , 2008	European School PhD	Research	Europe	2	CRP-GL
September 29 th – October 3 rd , 2008	User session Training	Research	Europe	5	ION-TOF
October 20 th – 24 th , 2008	User session Training	Research	Europe	6	ION-TOF
November 17 th – 21 st , 2008	European School PhD	Research	Europe	16	CRP-GL
December 1 st – 5 th , 2008	User session Training	Research	Europe	5	CAMECA
December 10 th – 11 th , 2008	European Workshop	Research	Europe	26	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
December 8 th – 11 th , 2008	User session Training	Research	Europe	5	CAMECA

Table 6: The above table summarizes the dissemination activities in the fourth year of the Nanobeams project.

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Contract-NMP4-CT-2004-500440

NANOBEAMS

Nanoanalysis using finely focused ion and electron beams

Network of Excellence

Priority 3 - NMP

Publishable Final Activity Report

Period covered: from January 1st 2005 to December 31st, 2008

Date of preparation: December 31st, 2008

Start date of project: January 1st, 2005

Duration: 4 years

Prof. Henri-Noël Migeon
Département Science et Analyse des Matériaux (SAM)
CRP - Gabriel Lippmann

Revision [version 1.1]

Table of Contents

1.	Introduction.....	3
1.1.	Project Partners	3
1.2.	Contact	4
1.3.	Summary of project objectives.....	4
2.	Project Execution.....	5
2.1.	Work performed and end result.....	5
2.1.1.	Collaboration towards improved instrumentation	5
2.1.2.	Emission and ion formation processes in SIMS	11
2.1.3.	SIMS on organic and biological samples	17
2.1.4.	Contribution to standards	17
2.1.5.	Contribution to the dissemination of knowledge.....	19
2.1.6.	Project impact on industry and research sector	20
2.2.	Conclusion	21
3.	Dissemination and use	22
3.1.	Publications and presentations	22
3.1.1.	Full list of joint publications.....	22
3.1.2.	Presentations.....	24
3.1.3.	Selection of Poster presentations.....	26
3.1.4.	Abstracts:.....	26
3.2.	Exploitable knowledge and its use.....	28
3.3.	Dissemination of knowledge.....	29
4.	Further References	33

1. Introduction

The Nanobeams Network of Excellence (NoE) started on January 1st, 2005 and ran for a total of 48 months, funded by the European Commission under the “Nanotechnology and nanosciences, knowledge-based multifunctional materials and new production processes and devices” (NMP) component of the Sixth Framework Program (FP6). The NoE concentrated on analytical techniques using focussed ion and electron beams in order to develop analytical techniques and instruments matching future requirements for the analysis of nanomaterials. The three complementary techniques included in the NoE are listed below:

- Secondary Ion Mass Spectrometry (SIMS) and Laser-Secondary Neutrals Mass Spectrometry (Laser-SNMS);
- Auger Electron Spectrometry (AES);
- Transmission Electron Spectroscopy (TEM);

SIMS uses a focused beam of ions (primary ions) to sputter a material and produce a localized ion emission characteristic of the composition of the material itself (secondary ions). Typical primary ions are Cs⁺, Ga⁺ and O₂⁺. The secondary ions emitted by the specimen are analyzed by mass spectrometry (magnetic sector quadrupoles or time of flight analyzers). Modern spectrometers provide transmissions in the range of 50% at high mass resolution ($M/\Delta M = 5000$). The SIMS technique can be divided into two distinct types of instruments: dynamic SIMS (D-SIMS) which is a depth profiling and nano/micro volume analysis tool, and static SIMS (S-SIMS), essentially ToF-SIMS, which is specifically for the analysis of the surface monolayer and molecular adsorbates. The SIMS technique offers ppm-ppb sensitivity for the consumption of $<10^{-13}$ cm³ of material, and has the potential to determine the composition of even extremely small volumes – down to 1 nm³ containing approximately 50 atoms. Hence, SIMS is an obvious choice for probing the chemical composition of the sample on the 10 nm scale. When a primary ion impinges on a solid surface, it deposits its energy (several keV) into a subsurface volume in an area of less than 10 nm in diameter around the point of impact. The dissipation and recoil of the deposited energy leads to the desorption and ionization of elements, small clusters and even intact molecules. As a result, the chemical information obtained through mass analysis of the ions generated by a single primary ion is by definition “real” nanoscale analysis.

High-resolution Auger Electron Spectroscopy (AES) may be used to perform an analysis of the first 20 nm of a sample making use of the Auger process. The range of elements that may be analyzed by AES lies between lithium and uranium. AES has the advantage over SIMS that it is a quantitative technique. However, in order for it to discover an element, the latter must be present by at least a percentage of 1.

Transmission Electron Microscopy (TEM) is a powerful technique with extremely high resolutions at the atomic scale. The disadvantage of this technique is, however, that samples need to be very thin for analysis. Therefore this demands a high level of expertise in sample preparation, and the preparation of such samples is very time consuming. TEM is the method of choice for obtaining crystallographic information with very high spatial resolution.

1.1. Project Partners

The Nanobeams NoE was composed of manufacturers of scientific instruments, as well as the leading research laboratories in the field. Overall, it involved 80 researchers and 40 PhD students. The total budget for the NoE was approximately €30 million. The contractors are listed here-underneath:

- CRP-GL: Centre de Recherche Public - Gabriel Lippmann¹,
“Département Sciences et Analyse des Matériaux” (SAM)
and the “Département Informatique, Systèmes et Collaborations” (ISC), Luxembourg
(<http://www.lippman.lu/>);

¹ CRP-GL is also known as the CRP-Gabriel Lippmann

- IPM: Physikalisches Institut, Westfälischen Wilhelms-Universität Münster, Germany (<http://www.uni-muenster.de/Physik.PI/Arlinghaus/>);
- PCPM: Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Belgium (<http://www.pcpm.ucl.ac.be/>);
- LISE: Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix de Namur, Belgium (<http://www.fundp.ac.be/facultes/sciences/departements/physique/recherche/centres/lise/>);
- GFE: Gemeinschaftslabor für Elektronenmikroskopie, RWTH-Aachen, Germany (<http://www.gfe.rwth-aachen.de/>);
- OXMAT: SIMS Group, Department of Materials, Chancellor, Masters and Scholars of the University of Oxford, United Kingdom (<http://www.materials.ox.ac.uk/>);
- MITAC: Universiteit Antwerpen, Micro-Trace Analysis Centre, Belgium (http://www.ua.ac.be/main.aspx?c=*SCHEIKUN&n=12187&ct=007985&e=t16924);
- BioSIMS: Laboratoire et Assemblages Moléculaires: Modélisation et Imagerie SIMS, Université de Rouen, France (<http://www.univ-rouen.fr/>);
- CAMECA: Cameca S.A.S., France (<http://www.cameca.com/>);
- ION-TOF: Ion-TOF GmbH, R&D Lab, Germany (<http://www.ion-tof.com/>);
- TE: Thermo Electron Corporation, now Thermo Scientific(up to December 2006), Great Britain (<http://www.thermo.com/>);
- OP: Orsay Physics, France (<http://www.orsayphysics.com>).

1.2. Contact

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1.3. Summary of project objectives

The main activities of the different partners in the Nanobeams NoE were instrumental development, the coordination of fundamental research, the application of advanced analysis techniques to nanomaterials, the coordination of manufacturers, the organization of an annual European workshop and training sessions on the different instruments.

The project's objectives were the following:

- To improve SIMS for providing lateral resolutions down to 10 nm and a depth resolution of 1 nm;
- To develop new techniques for the measurement and analysis of nanostructured materials;
- To use these techniques for nanoscopic analysis and nano-metrology;
- To contribute to the development of Standards. This would also involve the definition of important parameters with regard to measurement systems;
- To disseminate knowledge via:
 - The implementation of a European PhD School on “Nanoanalysis using finely focused ion and electron beams”;
 - The organization of an annual European workshop;
 - The creation of two working groups for users in biology and materials science at a European level;
 - The organisation of various user training sessions on SIMS, TEM and XPS aimed at improving the skills of the machine operators.

2. Project Execution

2.1. *Work performed and end result*

Throughout the project period, the Nanobeams partners worked hard to achieve the aims set forth in the project. The partners collaborated by contributing novel ideas, which resulted in the submission of new research projects. In this respect, a number of feasibility studies were carried out and pilot ideas were developed.

2.1.1. Collaboration towards improved instrumentation

Throughout the project duration, the Network partners and especially WP3 partners have collaborated with the aim of developing more efficient instrumentation. This can be seen from the number of collaborative research project-proposals submitted in the frame of the Nanobeams NoE at a National or a European level. Section 2.1.1.1 of this report presents the efforts of the Nanobeams NoE to collaborate in various research projects in order to further improve their instruments.

Furthermore, the Nanobeams NoE partners have been involved in measuring the lateral and depth-resolutions of their state-of-the-art SIMS instruments on a range of different samples. The measurement procedures and results are shown in section 2.1.1.2 of this report.

2.1.1.1. Submitted project proposals

Introduction

Over the duration of the project, several project-proposals have been submitted for future funding, with a high success rate. 2 out of the 4 project-proposals were accepted, and so the Nanobeams NoE partners have had the opportunity for practical progress towards their aim of developing more efficient instrumentation. This has been underpinned with a number of feasibility studies.

In the frame of the „*Negative Ion Sources*“ project, stable prototype negative ion sources have been developed. These are in the phase of being tested. We have deliberately delayed submission of a number of journal papers on this work in order not to compromise a possible patent application on these sources.

In the frame of the “*3D-NanoChemiscope*” project, which started in September 2008 involving several Nanobeams partners, a new instrument combining SFM and TOF-SIMS will be developed. In this way, a resolution of less than 10 nm will be achieved by the end of the project in 2012. This is clear evidence that the NoE partners will continue active collaboration in this field of research after the end of the Nanobeams NoE.

The “*Negative Ion Sources*” project proposal, whose objective it is to develop high brightness negative ion sources, was submitted to the Luxembourgish “Fonds National de la Recherche” in the frame of the “Innovative materials and nanotechnology (NANO)” program in June 2005. This project-proposal included 3 NoE partners and 4 external partners and started in April 2006 for a duration of 30 months after acceptance by the FNR.

The German SIMS manufacturer ION-TOF and several network partners worked on the development of advanced ion sources in order to improve both the lateral and depth resolutions. Using Bi_3^+ multi-atomic guns the lateral resolution could be drastically improved from approximately 200 nm down to 40 nm (cf. section 2.1.1.2). These practical improvements in performance are already incorporated in commercial ToF-SIMS apparatus in the marketplace, and are thus adding to the ability of the EU to compete for market shares in this significant sales area.

Project-proposal objectives

“Negative Ion Sources” objectives

One major problem, which needed tackling at the beginning of the NOE, concerned the analysis of electropositive elements (which are detected as positive secondary ions in SIMS). To analyze these species with a good sensitivity, a primary ion beam of electronegative species is needed. Most SIMS instruments are as a consequence equipped with a duoplasmatron type ion source which can be run with an oxygen gas feeding in order to produce O_2^+ or O^- ion beams. These duoplasmatron ion sources unfortunately have an important handicap: their brightness is low and, as a consequence, the ion beam delivered by this source is quite broad and cannot be focussed down to a spot small enough to allow imaging applications with a good lateral resolution (cf. table 1).

This disadvantage becomes even more apparent on the CRP-Gabriel Lippmann’s NanoSIMS50 instrument. This instrument, which has known an enormous success since its installation in Luxembourg, is dedicated to ion imaging with a lateral resolution as good as 50 nm. However, this lateral resolution can only be reached when the Cs^+ primary ion source is in use (thus while detecting negative secondary ions), as the duoplasmatron source also available on the instrument cannot offer O^- spot sizes compatible with the required experimental resolution. As a consequence, the potential of the NanoSIMS50 (an instrument offered by an EU company with no effective competitor in the marketplace) cannot be fully exploited for positive secondary ions.

Up to the start of the project, only a few attempts had been made to introduce primary ions with electronegative species other than oxygen. Moreover, the consortium was been aware of any current projects trying to develop such negative ion sources. As a result, the partners introduced a project aimed at optimizing SIMS analysis with high sensitivity of electropositive elements by introducing new primary ion guns based on electronegative species (primarily on the NanoSIMS50, but also on the other instruments of the CRP-Gabriel Lippmann). The research work performed in the framework of this project consists both in a combined fundamental/analytical study of SIMS using negative primary ions and the development of sources producing such negative ions.

“3D NanoChemiscope” objectives

The objective of this “*Combined SIMS-SFM Instrument for the 3-dimensional chemical analysis of nanostructures*” project is to develop an innovative and novel combination of a new TOF-SIMS with substantially improved lateral resolution and sensitivity, combined with a new metrological high resolution SFM (Scanning Force Microscope). The two techniques provide complementary information on nanoscale surface chemistry and surface morphology. In combination with a layer by layer removal of material using low energy sputtering, quantitatively measured by SFM, this combined ultra-high vacuum (UHV) instrument will be unique for the 3-dimensional chemical characterization of nanostructured inorganic as well as organic materials with down to at least 10 nm lateral resolution and down to 1 nm in depth resolution. Combined with novel software for the calculation and display of 3-dimensional distributions of all chemical species, this leads to a totally new instrument – the 3D NanoChemiscope.

2.1.1.2. Measurement of SIMS lateral and depth resolutions

Introduction

This section will give an overview of the progress achieved by the NoE partners in the optimization of their instruments in order to reach better lateral and depth resolutions over the past four years. At first, the determination of the lateral and depth resolutions is discussed in sections 2.2.2 and 2.2.3. Then, the progress and results of the various NoE partners within this area is described (section 2.2.4).

Determination of lateral resolution

The diameter of the ion probe depends on the brightness of the ion source and on the optical properties of the column used to focus the ion beam on the sample. The brightness B of an ion source is defined as follows:

$$B = \frac{I}{S \cdot \Omega},$$

where I is the ion current, S the ion emitting surface and Ω the solid angle in which ions are emitted. High brightness ion sources thus allow the producing of very finely focussed probes while keeping a sufficient current for correct secondary ion intensities. Table 1 shows an overview of the characteristics of those ion sources, that are the most commonly used in SIMS. This table shows that the highest brightness can be reached with liquid metal ion sources (operating with field emission ionization).

	electron impact	duoplasmatron	surface ionization	liquid metal
species	Ar, Xe, O ₂ , SF ₆ , C ₆₀ ...	Ar, Xe, O ₂ , ...	Cs	Ga, In, Au _n , Bi _n
size of source	1 mm	200 μm	10 μm	3 nm (virtual)
ion energy	0.1 - 20 keV	0.1 - 10 keV	0.3 - 20 keV	2 - 30 keV
beam current	1 - 1000 μA	1 - 1000 mA	10 μA – 100 mA	1 - 1000 μA
brightness	1 A sr ⁻¹ cm ⁻²	10 ² A sr ⁻¹ cm ⁻²	10 ³ A sr ⁻¹ cm ⁻²	10 ⁷ A sr ⁻¹ cm ⁻²
energy dispersion	1 - 10 eV	5 - 20 eV	0,2 - 0,5 eV	5 – 50 eV

Table 1: Main characteristics of the ion sources, which are the most commonly used in SIMS

The determination of the lateral resolution of a SIMS instrument uses a conventional method based on imaging and performing a linescan of sharp edges of a test sample. The lateral resolution is defined as the separation of 16-84% contours in a plot of intensity of the elemental or molecular signal (see figure 1).

In the past, various SIMS users have used their own reference materials. More recently, a specifically developed Certified Reference Material (CRM) has been developed by the German Certification Authority Bundesanstalt für Materialforschung, BAM. This sample is constituted from polished cross-sections of a AlGaAs-InGaAs-GaAs layer stack. These layers form a complex stripe pattern at the surface whose gratings range from finely graded periods of 2 nm to 600 nm [20,21].

Determination of depth resolution

The depth resolution of a SIMS instrument can be determined by performing a depth-profile on a bulk sample including a so-called delta layer. There are several methods for determining the depth resolution: Usually, depth resolution cannot be better than surface roughness:

- According to [22], the “depth resolution corresponds to the distance (depth range) over which a 16% to 84% (or 84% to 16%) change in signal is measured” when profiling through an interface of two media. This definition was introduced by [23-25] and later adopted by IUPAC and the ASTM E-42 committee [26].
- According to [27], “depth resolution is measured in terms of the decay length, the distance over which the signal falls by a factor e , the natural log base. It is also sometimes described in nm/decade as this is easy to estimate from a graph since SIMS depth profiles are presented, almost universally, with a logarithmic concentration axis due to their high dynamic range.”

In general, depth resolution depends on several factors, one of the most important of which is surface roughness, which generally increases as depth profiling proceeds.

Progress and end result

Taking into account that the instruments were continuously improved in the frame of these collaborative projects as well as the feasibility studies performed by various Nanobeams NoE partners over the time span of the Nanobeams NoE, considerable progress has been achieved in the improvement of the lateral resolution in static and dynamic SIMS. Thus, OXMAT achieved a resolution of 29 nm when measuring a PMMA film following the optimization of their CAMECA NanoSIMS50 instrument’s parameters (see figure 1).

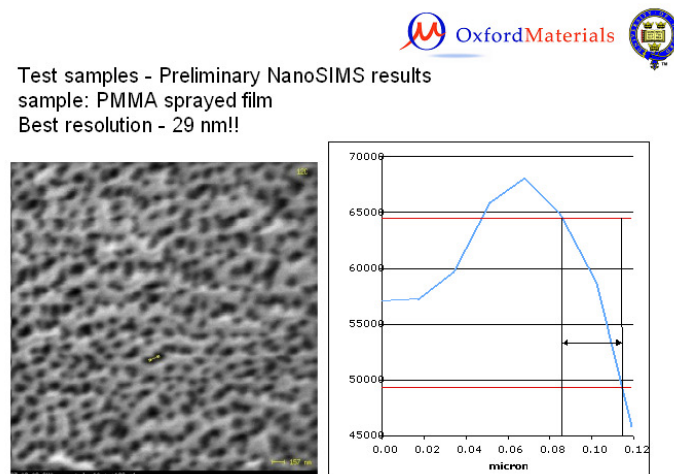


Figure 1: Measurement of lateral resolution using a PMMA sprayed film. The measurement of the distance corresponding to a 84-16% intensity variation shows a lateral resolution of 29 nm on OXMAT’s NanoSIMS50 instrument using a cesium ion gun.

In the frame of the “*NanoBioMaps*” project, which was integrated into the Nanobeams NoE and involves the German SIMS manufacturer ION-TOF and IPM (University of Münster), ION-TOF performed a number of measurements using their recently developed Bi_3^{++} cluster ion gun on their TOF-SIMS IV instrument [21]. As shown in table 1 above, Bi_3 ion sources are high brightness liquid ion metal sources. Such sources allow the production of very finely focussed probes as explained above. As can be deduced from figure 2, the German manufacturer determined the lateral resolution of their instrument using the recently developed CRM BAM-L200 as a sample. The result was that using a Bi_3^{++} cluster ion gun, the lateral resolution on their TOF-SIMS IV instrument was 40 nm. Before the development of such cluster ion guns, the lateral resolution for TOF-SIMS was in the range of 100 nm or above. This is a very significant improvement in a key performance metric over the duration of the NoE.

In order to achieve better depth resolutions, it is important to lower the impact energy, E , of the primary ion beam. As chromatic aberrations are inversely proportional to E , the lowering of the energy would drastically degrade the focus of the primary ion beam on conventional SIMS instruments. In order to overcome this problem, the SC-Ultra instrument has been specifically developed by the French SIMS manufacturer CAMECA. Unlike other SIMS instruments, this instrument uses a “Floating Low energy Ion Gun” (FLIG). As can be seen in the example of figure 2, the column is held at a high potential (e.g. 7500 V), even though the impact energy is kept low. This innovative concept allows for chromatic aberrations to be kept at a minimum and for the impact energy also to be kept low. As a consequence, the decay length within the target material is small, and high depth resolutions can be achieved.

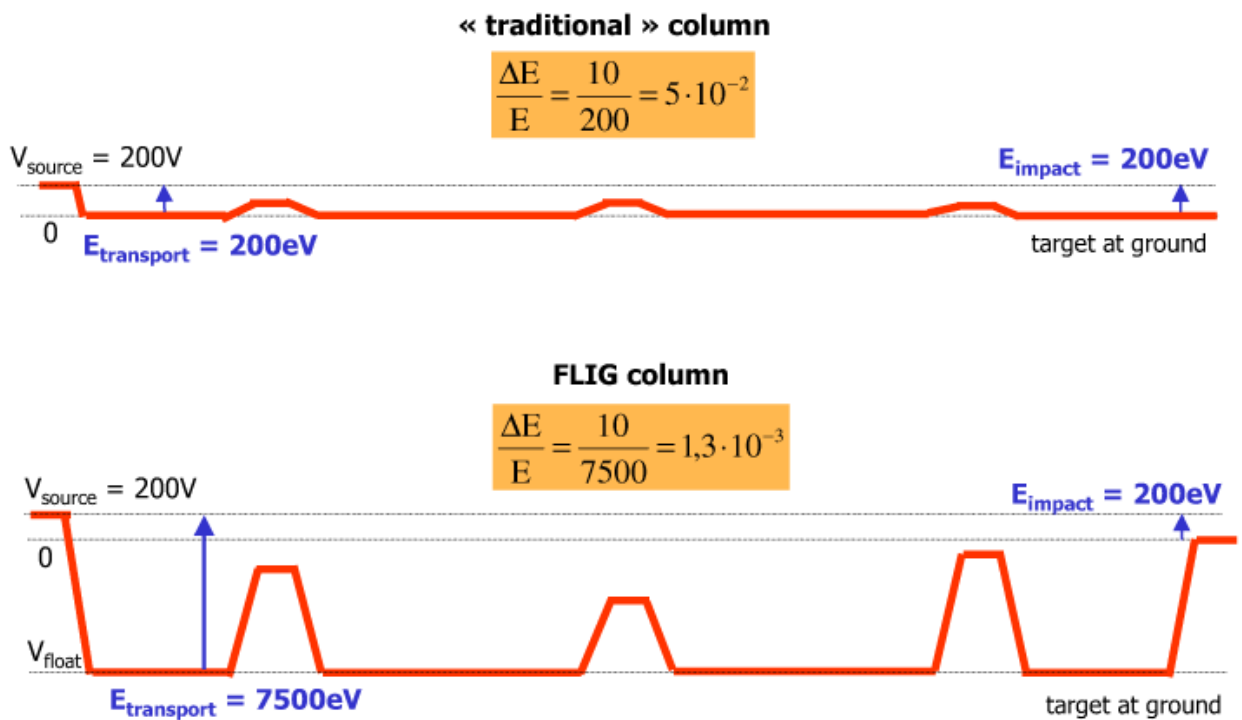


Figure 2 : The above figure depicts both the traditional and the recently developed FLIG column. Both of these columns include electromagnetic lenses, which are used for focussing the beam. In traditional columns, where the column itself is at ground and the ion source is held at a potential V_{source} , the impact energy is equal to the transport energy $E_{\text{transport}}$. In FLIG columns, the column is held at a negative potential V_{float} . This means that the transport energy of the ion beam is increased. As the beam passes a grounded electrode just before the impact on the sample, the impact energy is different from the transport energy. Using FLIG columns, aberrations can be kept at a minimum without increasing E_{impact} .

Using their recently developed SC-Ultra SIMS instrument, the NoE partner Cameca, the world leader in the manufacturing of dynamic SIMS instruments, performed a number of depth resolution studies on a Si sample including a boron delta layer. The depth resolution was determined according to the definition given in subsection entitled “Determination of depth resolution”. It was found that the distance over which a 16% to 84% (or 84% to 16%) change in signal is measured is less than 1 nm. Using the method suggested by [27], the

depth resolution corresponds to 0.75 nm/decade. The analysis was performed using an ultra-low energy sputtering O_2^+ ion beam of 150 eV. Whereas in 2005, the depth resolution on such samples was still around several nanometers, the latter has now been improved to less than 1 nm. Thus, it can be concluded that the Nanobeams consortium has also achieved a significant improvement in SIMS depth resolution during the project period.

2.1.1.3. Improvement of the sensitivity of SIMS

The effective application of fine incident beams to accurate nano-analysis is not only dependent on the focussing of the beam but also on the sensitivity of the instrument. The amount of material analyzed in a very tiny area (such as $10 \times 10 \text{ nm}^2$) is very limited and a high sensitivity is required to have reasonable counting statistics. Similarly, an image with good contrast can only be obtained if a very high signal is produced, which means a higher sputtering yield and a higher ionization yield. Therefore, improving lateral resolution is intimately linked to improving sensitivity. Hence, an important aim of the Nanobeams NoE was to turn innovative ideas and concepts related to improving the sensitivity and the resolution into instrumental prototypes. This required the collaboration of laboratories specialized in different fields. Thus, the Nanobeams NoE submitted several project-proposals at national and European levels in order to fulfil these objectives. The Nanobeams consortium worked in particular on one very successful project named “**Storing Matter**”. This project is described below.

The “Storing Matter” project

This project aimed to decouple the sputtering of the specimen from the subsequent analysis step in order to enable higher sensitivity than with usual SIMS techniques. By the end of the project in June 2006, a prototype instrument had been fully assembled at the CRP-Gabriel Lippmann. Experimental studies showed that the Sputtering Storing Matter Instrument (SSMI) was a highly sensitive technique, which allowed improved quantification and thus was expected to reduce the importance of the well-known matrix effect. Indeed this effect is one of the issues in accurate quantitative analysis with the SIMS technique. By reducing this issue, more accurate nano-measurements can be performed. Indeed, the sensitivity achieved in the project is even higher than the benchmark fixed at the initial stage. During the SIMS XVI conference in Japan in September 2007, several oral presentations regarding the new instrument were given [13-15]. Thus, the project was successfully completed. One picture of the prototype instrument is shown in figure 3. In 2008, the project partners decided to continue collaborating in order to apply the storing matter concept to polymers.



Figure 3: The Storing Matter prototype at the CRP-Gabriel Lippmann.

2.1.1.4. Submission of further projects

Over the project duration, the consortium also submitted other projects for funding of direct relevance to the NoE. One of these was the “**Nano²hybrids**” project, which was funded in the frame of the FP6 STREP program. “**Nano²hybrids**” (FP6-2004-NMP-TI-4-033311), and which started in October 2006 involving the CRP-Gabriel Lippmann, LISE and PCPM. This new project concerns the “Interface design of metal nanocluster-carbon nanotube hybrids via control of structural and chemical defects in a plasma discharge”. It was of strong relevance to the NoE as it concentrates on the further development of novel nanostructured materials for functional applications, and reliable analysis protocols for these materials will be very important.

Furthermore, the Nanobeams NoE launched several projects in the area of Biology. Tacking into account the improved resolution of SIMS as well as the improved sensitivity, SIMS has become more and more useful in Biology. In the ANR-funded research project “**1cell-nanoproteomics**”, the partners BioSIMS and OP aim at analyzing the single cell proteome by nano-electrophoric devices (NEDs) using the CAMECA NanoSIMS 50. The project started in March 2007 and will finish in 2011.

One further project-proposal aiming at using SIMS in biology was submitted under FP7’s Health theme in December 2008.

2.1.2. Emission and ion formation processes in SIMS

Introduction

As one of the Nanobeams NoE’s goals was to improve our knowledge regarding emission and ion formation processes in SIMS with special emphasis on the detection of large molecular fragments, the objective was to increase the sensitivity of the method thanks to better control of the physical parameters influencing the secondary ion yield and specifically by the use of laser beams to ionize sputtered neutrals (Laser-SNMS). This increase in sensitivity is especially needed when looking at nanostructures where the amount of material available for the analysis and imaging is rather limited (especially when static conditions are required for molecular surface characterization). Moreover, a better understanding of the basic processes involved will allow us to improve significantly the quantitative interpretation of SIMS data.

The specific tasks were to increase sensitivity, by considering either the emission processes (sputtering) or the ion formation mechanisms. As an example, to enhance the secondary yield of molecular fragments by the use of cluster and molecular primary ion beams instead of atomic beams, to improve the ionization of the emitted particles by different methods of cationization/ anionization or to efficiently ionize sputtered neutrals by laser photo-ionization processes. In order to gain insights about these basic mechanisms, the procedure consisted in comparing the experimental results with predictions of the theoretical models. The experimental information mainly consists in the secondary ion yield, energy and angular distribution dependence as well as on the experimental parameters such as the primary ion nature, energy and impact angle.

Thus, it was planned to perform molecular dynamics simulations using realistic interaction potentials with the goal of obtaining theoretical information concerning the sputtering processes. With regard to the charge formation process, different models were to be tested. As an example, the PCPM group proposed a model to explain the efficient cationization of organic molecules by complexation with substrate metal atoms to form ions. This model is based on an associative ionization mechanism consisting in the recombination of an excited molecule and a metal atom above the surface and the subsequent decay of the complex via the emission of an electron, locking the system in the ionized state. Electronic structure calculations were required to study the stability of the ionized complexes formed during the emission process.

The activity was thus divided into different pilot projects:

Pilot project 1: Ion formation of molecules from mono- and multilayers

Pilot project 2: Molecular ion yield enhancement induced by metal cluster deposition

Pilot project 3: Use of cesium for enhancement of ionization probabilities and quantification

Pilot project 4: Laser-SNMS project

Activities related to pilot project 1 :

In this activity, IPM and ION-TOF collaborated in improving our understanding of mechanisms of molecular ion yield enhancement induced by metal clusters bombardment on organic surfaces. The objective was to optimize parameters for detecting hybridized DNA fragments using different primary ions, including monatomic ions, as well as cluster metal ions. In this study, important new results have been obtained, for example it was found that cluster primary ions resulted in a significantly increased yield of DNA-correlated fragments (e.g. PO_3^-), enabling higher signal intensities and better secondary ion efficiencies [10,28].

For the monatomic primary ions Ne^+ , Ar^+ , Ga^+ , Kr^+ , and Xe^+ , a continuous increase with increasing projectile mass can be observed. Compared with Ar^+ , the use of polyatomic primary ions SF_3^+ and SF_5^+ for example, led to a significant increase in the PO_3^- secondary ion yield by about a factor of 250. Compared to all the “classical” primary ions studied, SF_3^+ and SF_5^+ do not only result in the highest PO_3^- secondary ion yields, due to their polyatomic nature, but also give the best values for the secondary ion efficiency (not shown) and therefore, in general, provide a high sensitive method for detection of hybridized DNA on biosensor chips.

In order to further investigate the influence of the ion energy on the secondary ion emission of PO_3^- , an evaluation of yields, disappearance cross sections and efficiencies as a function of different primary ion energies was carried out using Bi_3^+ as an exemplar primary ion projectile. In general, within the energy range from 10 to 50 keV only a minor energy dependence is observed. With increasing energy, the secondary ion yield increases by about a factor of 2.5 and the disappearance cross-section by about a factor of 3.5. As a result from this behaviour, the secondary ion efficiency decreases down to two-thirds of the value at 10 keV.

The variation of the secondary ion yields of PO_3^- as a function of Bi primary ion species was also investigated. In general, the highest relative increase of values is observed by changing from monatomic Bi^+ to polyatomic Bi_2^+ primary ions, which amounts to approximately an order of magnitude. With increasing cluster sizes, continuous enhancements can be observed, although the enhancement factors saturate for high cluster sizes.

In general, a similar development can be found for the disappearance cross-section and secondary ion efficiency of PO_3^- , displayed in the middle and right-hand graph. Nevertheless, the enhancement factors of the disappearance cross-section and, due to the combined influence of yield and disappearance cross-section, the secondary ion efficiency shows smaller enhancement factors [10].

Changing the substrate material from silicon to gold, an additional yield enhancement for PO_3^- was observed which was highest for monatomic primary ions (more than a decade) and smallest for polyatomic primary ions (factor 2-4).

It was found that a change from monatomic to polyatomic primary ions leads to an increase in secondary ion yield of about two orders of magnitude, whereas there are smaller differences in between Bi_3^+ , Bi_2^+ , Bi_3^+ and Bi_5^+ . The data also indicates that there is a kind of saturation of the secondary ion yield with increasing cluster size. An increase in the primary ion energy resulted only in small changes of secondary ion yield and efficiency, especially in the energy range from 20 keV to 50 keV. In conclusion, the data clearly shows that it should be possible to take advantage of a simplified low-energy cluster Liquid Metal Ion Gun (LMIG) supplying doubly charged Bi_3^{++} primary ions in future analysis and thus providing optimal bombardment conditions.

The results were presented on the SIMS XV and ECASIA'07 conferences and two joint publications were published [6,10].

Pilot projects 1 & 2: Ion formation of molecules from mono- and thicker layers and molecular ion yield enhancement induced by metal cluster deposition

Thin layer samples (about one monolayer in thickness) and thick layer samples (at least 10 nm thickness) were prepared for pilot project 1. Most of them were additionally used for pilot project 2, where the effect of metal deposition was investigated. Therefore, these results are shown together. Mainly gold was used for metallization.

Hundreds of samples were prepared by various partners:

- Polyethylene, polypropylene and Irganox 1010 ($M_w = 1177$ u) (PCPM, LISE)
- A thick layer of plasma polymerized polystyrene (LISE)
- Polystyrene with different molecular weight ($M_w = 500$ u, 1800 u and 10,000 u) as thin and thick layer samples (PCPM, LISE)
- Polymer samples containing different dyes (molecular weight of about 500 u) as thin and thick layer samples (MiTAC, LISE)
- Triacotane (molecular weight of about 422 u) prepared on silicon, gold and silver as thin layer samples (PCPM)

Most samples were analyzed by more than one partner (IPM, PCPM, MiTAC) using all the different primary ion species available within the project. Additionally, LISE did electron microscope measurements on selected samples.

Many of the results obtained in pilot project 2 show the same trends, regardless of which samples were analyzed and regardless of the choice of secondary fragment ions (cf. figure 4) or secondary ions of the whole molecules.

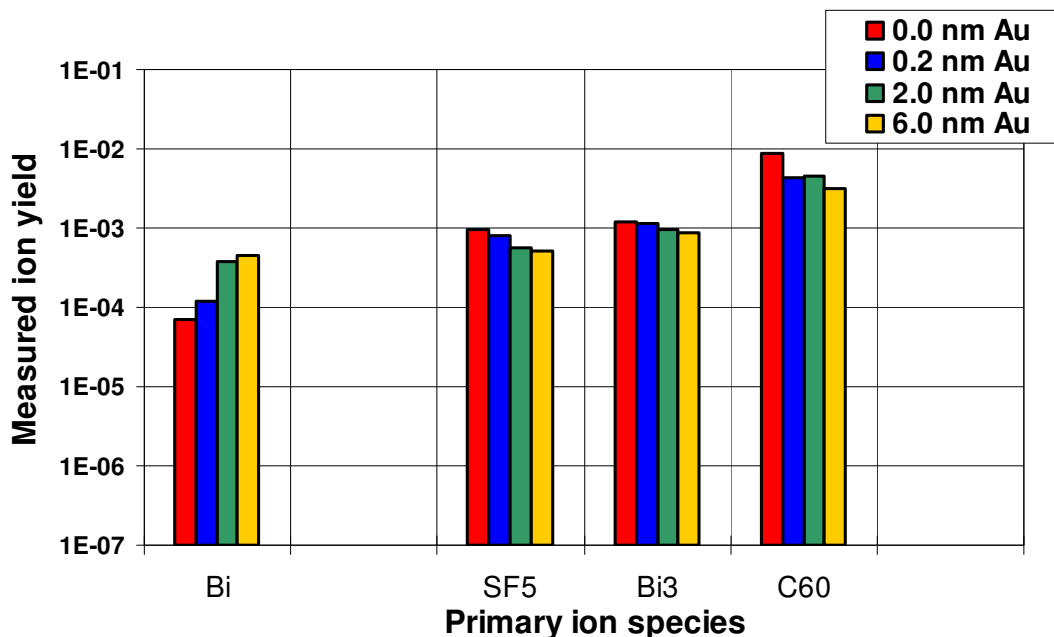


Figure 4: Secondary ion yield of a characteristic polystyrene fragment ion ($C_8H_5^+$) obtained from pristine and gold-covered samples using monatomic (Bi^+) and polyatomic primary ion bombardment (SF_5^+ , Bi_3^+ , C_{60}^+)

Due to the results obtained in this work-package, it concludes that some of the known methods to enhance the yield (thin layer/monolayer preparation, polyatomic instead of monatomic primary ion bombardment, metallization with gold) depend mainly on the same mechanism: They all help to deposit more energy near the sample surface. Therefore, when combining these methods, the yield increase is often much smaller than the sum of the single yield increases of each method. Sometimes even a yield decrease is observed. Many

results obtained in pilot projects 1 and 2 can be explained by arguments involving changes in energy deposition [7-9,11,17].

However, results from additional experiments, in which silver was used for metallization and gold and silver were used as substrate material, do not fit into the previous observations. Secondary ion yields of quasi-molecular and cationized ions obtained from these samples with C_{60}^+ and Ga^+ bombardment [11]. The yield obtained with Ga^+ from the sample with gold deposition is higher than the yield obtained from the sample with a gold substrate. This cannot be explained by the assumptions and arguments made above. Additionally, it cannot be explained why the yields of the cationized molecules are higher when using monatomic instead of polyatomic primary ions. Results obtained in pilot project 2 were presented at various conferences like ECASIA'07, SIMS XVI (Japan) and SIMS Europe 2008. Five joint publications were published on this subject [7-9,11,17]. The investigation of different metals' influence in metal-assisted SIMS will be carried on beyond the end of the Nanobeams NoE.

Pilot project 3 : Use of cesium for enhancement of ionization probabilities and quantification

Pilot project 3 dealt with ionization processes of secondary ions and clusters. These processes were studied by LISE and the CRP-Gabriel Lippmann. Thus, scientists from both institutions shared the available equipment in order to address, in a joint fundamental study, the improvement in SIMS quantification when depositing Cs at the surface.

When using the neutral cesium deposition system on a prototype SIMS instrument available at the CRP-Gabriel Lippmann, in conjunction with a simultaneous primary ion bombardment, a significant increase of the useful yields of negative secondary ions, and thus of the analysis sensitivity compared to traditional Cs^+ primary ion bombardment, is obtained. In this case, the overall useful yield qualitatively agrees with the predictions of the electron-tunnelling model. At maximal cesium surface concentrations, quantitative analyses become possible for elements with high electron affinities. For other elements, a significant increase of the analysis sensitivity is achieved.

Combining the knowledge gained on various samples using AES measurements and simulations, the two partners were able to convert the raw data, obtained from analyses using the Cs/Xe co-sputtering ToF-SIMS analysis mode, to positive and negative ionization probabilities of Cs and Si with respect to the decreasing work function. It was found that the negative Cs and Si signals increase exponentially with the Cs coverage, whereas the positive signals decrease. The data were interpreted by means of the electron-tunnelling model. During the Nanobeams project, this aforementioned technique was successfully applied to typical SIMS applications like depth profiling and the results were presented in a joint publication [16].

Pilot project 4 : Laser-SNMS

The quantification of the elemental composition of a sample surface by mass spectrometric analysis of secondary particles sputtered from solid surfaces under primary ion bombardment is limited by the fact that the flux of secondary particles of a certain element consists of both atomic particles and different kinds of molecules containing the respective element. Furthermore, some of these secondary particles are positively or negatively charged whereas the rest are neutral. These different kinds of secondary particles cannot be detected in a mass spectrometric analysis with identical probability. In contrast to the secondary ions, which can be analyzed directly (SIMS), neutral particles have to be ionized before mass separation, e.g. by the interaction with photons of a laser beam (Laser-SNMS). Depending on the photon energy, a desorbed atom can be post-ionized resonantly or non-resonantly. For sputtered molecules photo-ionization is possible as well, but – as a competitive process – also photo-fragmentation. Such photo-fragmentation processes can result in the generation of smaller fragments, which can be charged or neutral, including fragmentation into monatomic neutrals and ions (figure 5). As the composition of the flux of secondary particles depends on the chemical matrix of the respective element in the surface, changing flux compositions complicate quantitative interpretations of SIMS and Laser-SNMS data, because signal intensities obtained for the particular element

can depend strongly on the chemical matrix and do not always correlate with the elemental distribution on the surface.

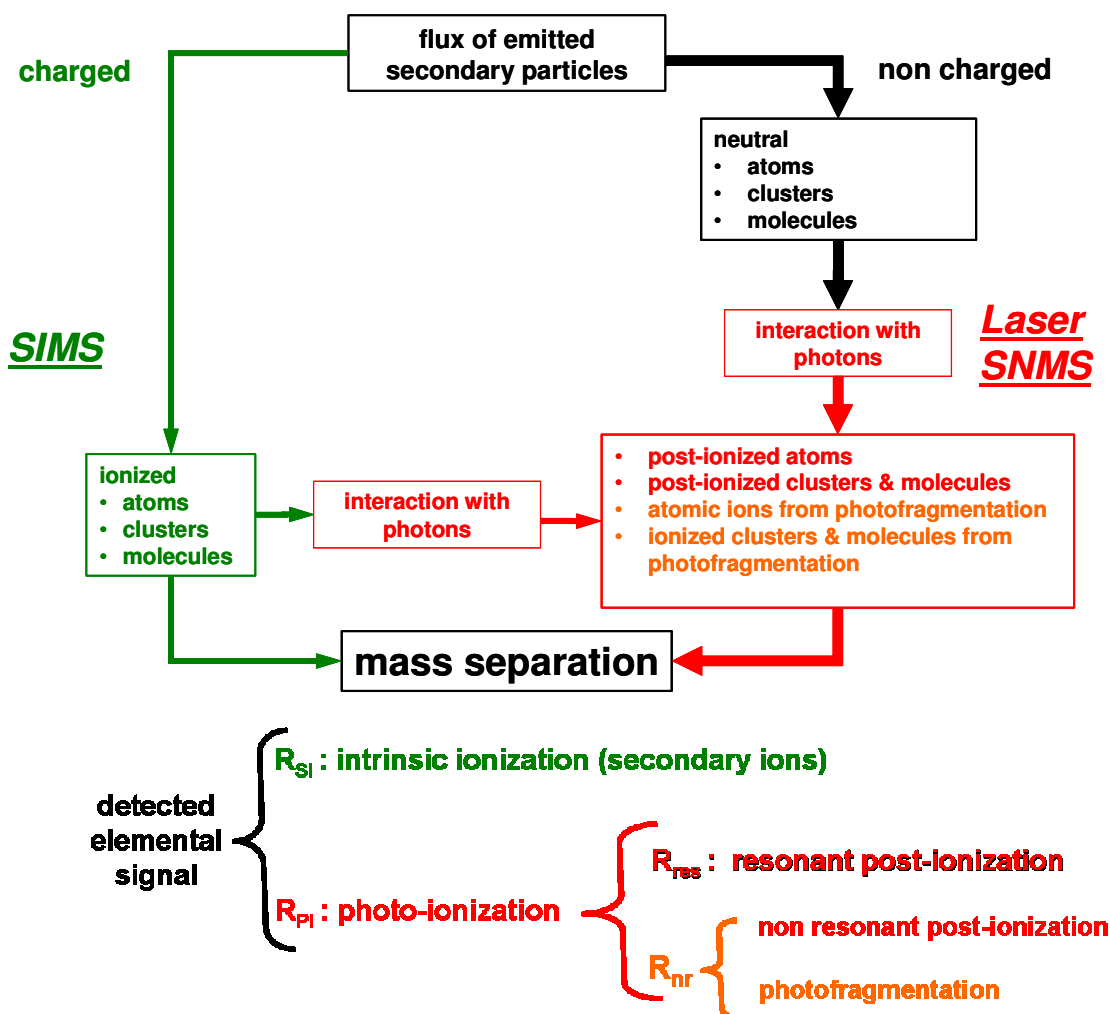


Figure 5 : Schematic diagram of the distribution of the sputtered particle flux (top) and the resulting composition of the detected elemental signal in resonant Laser-SNMS (bottom).

As a step closer towards quantitative elemental analysis using Laser-SNMS techniques, the aim was to develop a method to distinguish between different ion formation processes and to determine the influence of these processes on the total number of detected monatomic ions of a certain element. The knowledge about the composition of the detected ion yield can be used for characterizing the composition of the flux of secondary particles sputtered from different surfaces. To explain the origin of diverse fractions of differently generated ions contributing to the total yield of all monatomic ions of a certain element, a vector/matrix-formalism was developed, which describes the physical processes of sputtering, ion formation, mass separation and detection in Laser-SNMS.

In the framework of the method developed, based on this theoretic formalism, changes in the secondary flux contribution of the respective element were observed by comparing the detected monatomic ion yield obtained in specifically aligned (SIMS and) Laser-SNMS experiments. These were performed via systematic variations of certain laser parameters, ensuring that the sputter conditions and the chemical situation of the surface were kept strictly constant. The yields resulting from these experiments were used to calculate characteristic numbers to compare the flux composition from different surfaces. In particular, these characteristic numbers were utilized to indicate changes between the monatomic and the molecular part of the flux of secondary particles.

For these experimental investigations, two different laser systems were applied: a dye laser system and a 193 nm excimer laser. The dye laser system, with two separately tuneable beams, can be used to excite

resonant ionization processes of atomic neutrals, element and state selectively. In contrast, the excimer laser offers high non-resonant post-ionization and photo-fragmentation probabilities.

The potential of the method was demonstrated for the elements boron, iron and gadolinium by investigating the changes in the flux composition of secondary particles sputtered from metallic surfaces, as a function of the oxygen concentration at the surface. Exemplary analyses of various kinds of surfaces show that there is, in principle, no restriction on a general applicability of the presented method.

Laser-SNMS experiments using the dye laser system tuned for resonant post-ionization of atomic neutrals showed striking yield differences between clean and oxidized surfaces, which could not be explained by differences in surface stoichiometry or changes in sputter yield. Analyses of the composition of the detected ion yields, with the help of characteristic numbers, depicting the different influence of photo-fragmentation processes, indicate that the yield differences were mainly caused by a significant enhancement of the molecular fraction (oxides and clusters) and a tremendous reduction of the number of monatomic neutrals in the flux of secondary particles.

As the degree of photo-fragmentation depends strongly on the laser system applied, the percentage of ions generated by photo-fragmentation processes, of the yield of all monatomic ions (generated as result of the interaction of the sputtered particles with photons of the excimer laser beam) was estimated by a comparison between the yields obtained in Laser-SNMS experiments using the two different laser systems.

Furthermore, the combination of both laser systems in the same Laser-SNMS experiment was used to establish another ion formation process: the dye laser induced resonant post-ionization of atomic neutrals resulting from excimer laser induced photo-fragmentation of molecules. To examine such “pre-fragmentation” processes, the timing of the extraction voltage and the laser pulses was optimized for a separate extraction of the secondary ions and those ions generated as a result of excimer and dye laser irradiation, wherein the excimer laser pulse reaches the interaction volume before the arrival of the dye laser pulse. Applying this timing scheme, three different ion yields of the same element were recorded simultaneously in each analysis cycle. As the excimer laser induced ion signal and the dye laser induced ion signal were separated and simultaneously recorded, the influence of excimer laser irradiation on dye laser ion yield could be investigated and quantified.

Determination of the influence of pre-fragmentation on the dye laser signal allowed further quantitative estimations about changes in the flux composition and about the state of charge of the atomic products resulting from photo-fragmentation processes. Furthermore, pre-fragmentation might be an interesting way to enhance trace element signals, especially from surfaces characterized by a high molecular fraction in the flux of secondary particles.

Finally, combined Laser-SNMS depth profiles and images, obtained with both laser systems, were measured to demonstrate how the simultaneous detection of the three differently originated ion signals of the same element can be used to get additional information about the composition of the flux of sputtered particles. In this respect the presented method can be very helpful to prevent misleading interpretations of SIMS or Laser-SNMS data. Detailed information can be found in Guido Vering’s doctoral thesis (Münster (IPM), 2008).

Furthermore, experiments were carried out to compare the ionization efficiency of sputtered atoms using single photon ionization (SPI) and multiphoton ionization (MPI). It could be shown that with SPI (laser wavelength: 157 nm, photon energy: 7.9 eV) higher copper intensities can be obtained than with MPI (laser wavelength: 193 nm, photon energy: 6.4 eV).

For MPI the laser power density has to be increased by at least two orders of magnitude to get comparable count rates. These laser power densities can only be achieved by focusing the laser beam to a very small spot size. This reduces significantly the interaction volume between the laser beam and the sputtered particle cloud, thus reducing the amount of ionizable atoms.

SPI can also be used for efficiently post-ionizing sputtered molecules. For example, atmospheric aerosol particles collected on an aluminium foil were imaged with TOF-SIMS and Laser-SNMS [29]. Only in the case of Laser-SNMS in combination with a laser beam using photons with a wavelength of 157 nm, the

lateral distribution of polycyclic aromatic hydrocarbons (PAHs) could be determined. This can be explained by the fact that for some PAHs, SPI is possible because the photon energy of 157 nm radiation exceeds the first ionization potential (for example 7.43 eV in the case of pyrene). This will lead to higher yields in ionization processes while multiphoton ionization of molecules causes significant fragmentation. Detailed information can be found in Steffen Dambach's doctoral thesis (Münster (IPM), 2009).

A further decrease of fragmentation losses, although utilizing MPI processes, is expected by using fs-laser. In preliminary experiments, the effect of different laser radiation (ns-pulse laser, 157 nm and fs-pulse laser, 800 nm) on anthracene molecules released to gas phase on photo-ionization and photo-fragmentation was investigated. It was found that photo-ionization with fs-pulse laser generates less small fragments and the intact molecular ion signal shows the highest intensity compared to ns-pulse laser photo-ionization. This might be explained by the fact that with fs-pulses the number of photons needed for ionization in MPI can be absorbed within a shorter period compared to transition times known for fragmentation processes after photo-excitation. Therefore, less fragmentation processes can occur compared to MPI utilizing ns-pulse lasers, where fragmentation or ionization after preceding excitation are competing processes.

Also, a comparison between fs-laser-SMNS and TOF-SIMS spectra of tryptophan spin-coated on silicon showed that with fs-laser-SMNS much higher intensities of the two major tryptophan fragments could be obtained than with TOF-SIMS [28].

2.1.3. SIMS on organic and biological samples

As the Nanobeams NoE also wished to further promote SIMS for biological applications, the consortium also performed a number of round robin experiments on biological samples such as fixed cells and mixtures of isotopically labelled proteins. Furthermore, a number of PS-dPMMA samples were investigated using ToF-SIMS and NanoSIMS50 since polymer blends and biological samples show similar responses to SIMS analysis.

With respect to the biological samples, good progress in relation to aspects like the preparation and manipulation of biological specimens (cryofixation, use of different materials for supporting the sample), the systematic study of the behaviour of biological material bombarded with the primary ions (influence of sample heterogeneity, matrix effects, differential sputtering, insulating property of the sample, depth-profiling etc.), the study of formation of molecular ions (analytical potential of molecular emission) and the evaluation of methods of multi-isotope labelling (isotope recombination) was also made. From the results, it can be said that single amino acids can be detected. Further details about these activities can be found in two joint publications [3,18]. A further publication resulting from these activities has been submitted and is planned to be published in 2009.

With respect to the PS-PMMA measurements, one joint paper was written with four NoE partners contributing [5]

2.1.4. Contribution to standards

With the aim of improving the consistency of chemical measurements on the nanoscopic level with SIMS, the NoE partners LISE, IPM, MiTAC, PCPM and the CRP-Gabriel Lippmann made several measurements on a number of sample batches using static SIMS in order to develop adequate protocols to ensure a maximum of consistency between the results from different instruments in different laboratories. Bringing together the available competences within the network, the consortium members aimed at increasing the reliability of quantitative SIMS results and delineating the limitations of the experimental methodology. In this way, the results obtained in the frame of the Nanobeams NoE can play an essential role in the implementation of European standardization and conformity assessment procedures for a wide range of high-technology products.

S-SIMS has the unique capability to detect and quantify the molecular composition of the upper monolayer at the surface of solids with high sensitivity and an information depth of essentially one monolayer. S-SIMS is “powerful” because it probes directly and selectively the information that is relevant for the interaction of a material with its environment, because the outer surface layer is the interface at which all interactions occur and therefore its composition often determines a major fraction of the material’s behaviour in a given application. S-SIMS is “vulnerable” because the analysis of specific molecular information from only the upper monolayer with high lateral and depth resolution is unique in the field of molecular chemical analysis. No other method can deliver similar information. This also implies that the common procedures for sample preparation and handling (storage, transport) are no longer robust, i.e. they are often not calibrated sufficiently well to check for possible alterations of the chemical composition. For instance, the deposition of gaseous contaminants that stick to the solid’s outer surface becomes a problem when the method gives only information on the top monolayer. The objectives of this activity could most effectively be fulfilled by means of round-robin experiments. Four batches of test samples were circulated during the course of the project in order to assess the reproducibility in quantification and spatial resolution of the ToF-SIMS technique, to five different laboratories, using different ion sources with the aim of quantifying the concentration on a blue dye mixed with an IR dye in a matrix described in figure 6.

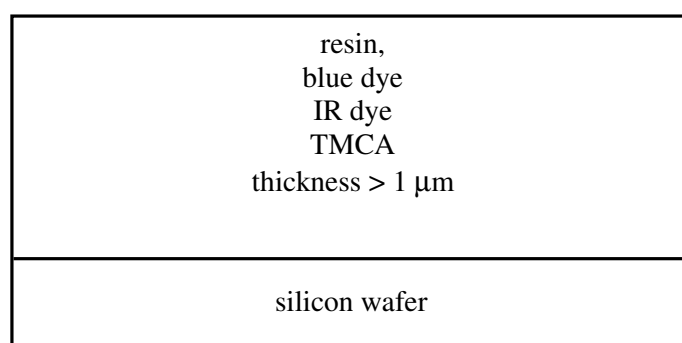


Figure 6 : The dye/polymer system.

The IR dye concentration was kept constant, as an internal standard, and the concentration of the blue dye was varied. Each participant was required to measure the intensities of molecular fragments related to the blue dye normalized by the intensities of the internal standard, versus the known concentration of the blue dye. This yielded calibration curves, which should be simply linear. A sample of unknown concentration was also distributed to all partners, who were asked to give an estimate of the blue dye concentration using the calibration curves.

Although the first round robin yielded mixed results, with some groups delivering an acceptable calibration curve and others were unable to do any quantification, owing to severe surface contamination with PDMS. The relative failure of this round robin forced the different partners to compare their different analysis protocols and to define a common analysis protocol in all laboratories. In a second batch of samples, all partners could produce good calibration curves, following the new procedure. An important outcome in this activity to standardize the analysis protocol, was that a reproducibility of about 10% could be reached. However, it appears that the best quantification accuracy is obtained when using the traditional “old” monatomic Ga^+ beams, which is quite surprising and not clearly understood. With the generalization of cluster beams, the poor quantification accuracy is an issue that should be addressed in further detail by the ToF-SIMS community.

Using this standardized analysis protocol, a last batch of samples was analyzed with the aim of determining the lateral resolution of the S-SIMS instrumentation available in the various labs. In this last batch, the nanofibres were aligned and laid flatly on the substrate. Sharp molecular images of the fibres were obtained with Bi_3^+ , with an excellent lateral resolution of 100 nm. The molecular signal was still high enough with Ga^+ to be able to visualize the fibres, but the low contrast was detrimental for the lateral resolution, limited to 200 nm at the best.

2.1.5. Contribution to the dissemination of knowledge

During the Nanobeams NoE, all project partners have been involved in dissemination of knowledge activities. The exact dates of these events are listed in section 3.3.

2.1.5.5. User schools and workshops

During the course of the Nanobeams NoE, the partners organized 4 workshops, of which one was organized in conjunction to the ECASIA conference. Furthermore, the world-leading SIMS manufacturers CAMECA and ION-TOF organized **15 user training sessions** on state-of-the-art instrumentation. Orsay Physics and Thermo Electron Cooperation organized one advanced training session each on their state-of-the-art Gallium sources and state-of-the-art high-resolution Auger Electron Spectroscopy respectively.

Moreover, due to the high demand from the nano-analysis community, the Nanobeams partners GFE, and BioSIMS organized one TEM and SPM academy respectively. Three further XPS academies were organized at LISE. These user schools, given by world-renowned experts in their field, were very successful and helped increase the knowledge amongst its user community (approx. 110 participants overall).

2.1.5.6. Exchange of personnel

During the Nanobeams project, the exchange of personnel was considered to be important for promoting the exchange of ideas between students and staff from the different institutions. These exchanges had the advantage that the collaboration in the various activities was much more effective.

Thus, for instance, several students from MiTAC visited IPM several times in order to analyze samples with organic compounds with different primary ion species and parameters. Furthermore, a researcher from PCPM visited IPM in order to measure triacontane samples within the frame of pilot project 2. Students from LISE visited the CRP-Gabriel Lippmann twice in order to analyze surface concentrations of caesium using AES. Researchers from OXMAT visited IPM in 2006 for high sensitivity experiments on frozen hydrated plant samples, and a different group of workers from OXMAT visited ION-TOF in 2008 to use the high resolution Bi source on the S-SIMS equipment for high sensitivity studies of steel and other metallic samples. 3 students theses were co-directed by 2 different NoE institutions, 2 at the CRP-GL and PCPM and 1 at the CRP-GL and LISE.

As a result of these exchanges, several joint papers could be published.

2.1.5.7. A European PhD School

As mentioned above, one of the aims of the Nanobeams NoE was the creation of a European PhD School in the area of “*Nanoanalysis using focused electron and ion beams*”. In order to reach this objective, the Nanobeams NoE created a scientific committee, the core-group, at the start of the project, which was responsible of the creation of the school as well as the overview the scientific content of the latter. The core-group was composed of the following members:

- Prof. Henri-Noël Migeon, CRP- Gabriel Lippmann
- Prof. Partick Bertrand, Université Catholique de Louvain
- Prof. Gradimir Misevic, Université de Rouen
- Prof. Joachim Mayer, RWTH-Aachen
- Prof. Susanne Siebentritt, Université du Luxembourg
- Prof. Alfred Benninghoven, Westfälische Wilhelms-Universität Münster

The European PhD School was organized such that the student finished a full cycle within 2 years. Each cycle consisted of four Teaching Weeks, the first being an overview week, and one Analysis Week. Upon fulfilling the full cycle, the student will receive a certificate as well as credit points from the University of Luxembourg. In this school, renowned professors and researchers from the Nanobeams NoE partner laboratories gave courses on the topics of SIMS, Laser-SNMS, AES and TEM. These are complemented by practical sessions on these instruments. With an average of 15 PhD students participating the various sessions, the PhD school was a real success. During the course of the project, four cycles of the European PhD School were started at CRP-Gabriel Lippmann in Belvaux (L). During this period, students that registered for the first and second cycles completed the fourth 'teaching week' and were the first to have completed the European PhD School (80 participants and 21 certificates of completion were obtained during that period).

In order to smooth the integration of this European PhD School into the University of Luxembourg's curriculum, Prof. S. Siebentritt from the University of Luxembourg was integrated into the core-group. Furthermore, the involved NoE partners have signed letters of support and thus engaged in supporting the European PhD School after the end of the Nanobeams NoE. At the beginning of the fourth project year, the core-group decided to integrate the first 'teaching week' of European PhD School organized in November 2008 into the university's curriculum. By the end of the project, a convention between the University of Luxembourg and the CRP-Gabriel Lippmann was signed engaging both partners to continue the European PhD School after the end of the Nanobeams NoE.

Thus, the European PhD School will continue to exist after the Nanobeams NoE and is an example of the strong intention of the NoE partners to continue to collaborate. The fact that the school has been integrated into the University of Luxembourg's curriculum is also an added value for the development of the Luxembourgish research sector.

All events related to the European PhD School on "Nano-analysis using finely focussed ion and electron beams" are listed in section 3.3 "Dissemination of knowledge".

2.1.6. Project impact on industry and research sector

Taking into account that the Nanobeams partners have been engaged in several projects including the world-leading SIMS manufacturers (i.e. CAMECA and ION-TOF), the Nanobeams NoE has had an enormous impact on its research sector, as well as industry. Thus, the outcome of the various research projects integrated within Nanobeams will enable the SIMS manufacturers to continue developing improved and efficient instrumentation and to keep the lead in the area of nano-analysis.

Thanks to the Nanobeams NoE, the development of a new technique combining SFM and ToF-SIMS is already underway. Being coordinated by the world leader for ToF-SIMS, this project will give the project partners the opportunity to submit further patents and to commercialize a new product.

During the course of the project, a prototype for performing quantitative analysis nano-analysis was developed (patent pending). The outcome of this project was presented at several conferences. Using the knowledge and experience gained within the Nanobeams NoE, the CRP-GABRIEL LIPPMANN is able to use this instrument for analysis.

The creation of the European PhD School on the topic of "Nano-analysis using finely focussed ion and electron beams" will have a large impact on the research sector of nano-analysis. Being the outcome of the collaboration between the Nanobeams partners as well as the University of Luxembourg, this PhD school is now integrated in the university's curriculum. Taking into account that the university was only created in 2003, the PhD school will also give a boost to the further development of the Luxembourgish research sector and as a consequence to the Luxembourgish economy.

The various user schools organized by the world-leader in SIMS and high-resolution Auger Spectroscopy as well as the advanced training courses on state-of-the-art TEM, XPS and SPM instrumentation gave the

opportunity to the user community to further improve their skills. Furthermore, the industry had the opportunity to present their latest state-of-the-art instrumentation to a large number of future customers in the research community.

2.2. Conclusion

Even though the objective for reaching a lateral resolution in SIMS was not fully achieved, the Nanobeams NoE has overall fulfilled its objectives. Technical progress has been made in several areas of key importance in the development of reliable techniques and methodologies for high resolution chemical analysis of a wide range of sample types, these have been widely reported in the scientific literature and to appropriate international audiences at major conferences, and some of these technical advances have led to improvements in commercial instrumentation. These outcomes all contribute to the international perception of the high quality of the science base in the EU, and to the competitiveness of EU industry in technical instrumentation.

3. Dissemination and use

This section provides a publishable summary of each exploitable result of the Nanobeams NoE.

3.1. Publications and presentations

3.1.1. Full list of joint publications

During the project period, the following joint publications have been submitted or published:

[1] Multitechnique characterization of thin films of immiscible polymer systems : PS-b-PMMA diblock copolymers and PS-PMMA symmetric blends

L. Kailas^a, B. Nysten^a, J.-N. Audinot^b, H.-N. Migeon^b, P. Bertrand^a

^aUniversité Catholique de Louvain, ^bCentre de Recherche Public – Gabriel Lippmann,
Surface and Interface Analysis 37 (2005) 435-443

[2] Surface segregational behaviour studied as an effect of thickness by SIMS and AFM in annealed PS-PMMA blend and block copolymer thin films

L. Kailas^a, J.-N. Audinot^b, H.-N. Migeon^b, P. Bertrand^a

^aUniversité Catholique de Louvain, ^bCentre de Recherche Public – Gabriel Lippmann,
Composite Interfaces, Vol.13, No.4-6 (2006) 423-439

[3] Method for macromolecular colocalization using atomic recombination in dynamic SIMS

G. Legent^{1,4}, A. Delaune^{1,2,4}, V. Norris^{1,4,5}, A. Delcorte^{3,4}, D. Gibouin^{1,4}, F. Lefebvre^{1,4}, G. Misevic^{1,4,5}, M. Thellier^{1,4,5} and C. Ripoll^{1,4,5*}, 2008.

¹ Laboratoire “Assemblages moléculaires: modélisation, et imagerie SIMS” (AMMIS), Faculté des Sciences de l’Université de Rouen, 76821 Mont Saint Aignan Cedex, France;

² UPRES EA 2123, Faculté de Médecine-Pharmacie de l’Université de Rouen, Boulevard Gambetta, 76000 Rouen, France;

³ PCPM, Université Catholique de Louvain, 1 Croix du Sud, B1348 Louvain-la-Neuve, Belgium;

⁴ “Nanobeams” European Network of Excellence;

⁵ Epigenomics Programme, Genopole®, 91000 Evry, France.

Journal of Phys. Chem. B 112 (2008), pp. 5534-5546, doi : 10.1021/jp7100489.

[4] Investigation of Laminated Fabric Cages Used in Rolling Bearings by ToF-SIMS

U. Gunst^a, W.- R. Zabel, N. Valle^b, H.- N. Migeon^b, G. Poll and H. F. Arlinghaus^a

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

Tribology International (2009), submitted and accepted

[5] Nanoscale characterization of PS-PMMA thin film blends

K-H. Lau^a, K.L. Moore^a, M. Schröder^a, J.-N Audinot^b, H.-G Cramer^c, D. Rading^c, B. Boschmans^e, R. De Mondt^e, L. Van Vaeck^e, D.G Bucknall^d, E. Niehuis^c, H.-N Migeon^b, C.R.M. Grovenor^a

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^bDépartement Science et Analyse des Matériaux (SAM), Centre de Recherche Public - Gabriel Lippmann, 41, rue du Brill, L-4422 Belvaux, Luxembourg

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^dSchool of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA30332-0295, USA

^eDept. of Chemistry, University of Antwerp (CDE), Universiteitsplein 1, 2610 Wilrijk, Belgium
Surface and Interface Analysis (2009), submitted

[6] Mass spectrometric characterization of DNA microarrays as a function of primary ion species

S. Hellweg^a, A. Jacob^b, J.D. Hoheisel^b, Thomas Grehl^c, and Heinrich F. Arlinghaus^a

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^b ION-TOF GmbH, Münster, Germany

Appl. Surf. Sci., 252 (2006), 6742-6745, doi:10.1016/j.apsusc.2006.02.281

[7] Metal-Assisted Secondary Ion Mass Spectrometry Using Atomic (Ga⁺, In⁺) and Fullerene Projectiles

A. Delcorte^{*†}, S. Yunus[†], N. Wehbe[†], N. Nieuwjaer[†], C. Poleunis[†], A. Felten[‡], L. Houssiau[‡], J.-J. Pireaux[‡], and P. Bertrand[†]

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[‡] LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Published in: *Anal. Chem.*, 79 (10), 3673 -3689, 2007, doi: 10.1021/ac062406l

[8] Molecular Ion Yield Enhancement Induced by Gold Deposition in Static Secondary Ion Mass Spectrometry

Wehbe, N. [†]; Delcorte, A. [†]; Heile, A. [‡]; Arlinghaus, H. [‡]; Bertrand, P. [†]

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[‡] IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

Applied Surface Science, 255 (2008), 824-827 (proceedings SIMS XVI conference), doi:10.1016/j.apsusc.2008.05.068

[9] Investigation of Methods to Enhance the Secondary Ion Yields in TOF-SIMS of Organic Samples

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, P. Van Royen^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

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^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

Surface and Interface Analysis, (proceedings ECASIA'07 conference), doi: 10.1002/sia.2810

[10] Influence of Different Primary Ion Species on the Secondary Ion Emission from PNA/DNA Biosensor Surfaces

Sebastian Hellweg^a, Andreas Heile^a, Thomas Grehl^b, and Heinrich F. Arlinghaus^a

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^b ION-TOF GmbH, Münster, Germany

Surf. Interface Anal., 40 (2008), 198-201 (proceedings ECASIA'07 conference), doi: 10.1002/sia.2684

[11] Effects of Metal Nanoparticles on the Secondary Ion Yields of a Model Alkane Molecule upon Atomic and Polyatomic Projectiles in Secondary Ion Mass Spectrometry

N. Wehbe^a, A. Heile^b, H. F. Arlinghaus^b, P. Bertrand^a and A. Delcorte^a

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^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

Anal. Chem., 80 (2008), 6235-6244 doi: 10.1021/ac800568y

[12] Ion yield improvement for S-SIMS by use of polyatomic primary ions

Roel De Mondt^{*a}, Luc Van Vaeck^a, Andreas Heile^b, Heinrich F. Arlinghaus^b, Nicolas Nieuwjaer^c, Arnaud Delcorte^c, Patrick Bertrand^c, Jens Lenaerts^d, Frank Vangaever^d

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Rapid Communications in Mass Spectrometry (2008), Vol. 22 Issue 10, 1481-1496, doi: 10.1002/rcm.3533

[13] Storing Matter: A new quantitative and sensitive surface analysis technique

T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, G. Slodzian^c, H.-N. Migeon^a

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Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.109

[14] The Storing Matter technique: application to inorganic samples

P. Philipp^a, F. Lacour^a, T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, G. Slodzian^c, H.-N. Migeon^a

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^b LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.075

[15] The Storing Matter technique: preliminary results on PS and PVC

P. Philipp^a, B. Douhard^b, F. Lacour^a, T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, H.-N. Migeon^a

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Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.070

[16] On the understanding of positive and negative ionization processes during ToF-SIMS depth profiling by co-sputtering Cesium and Xenon

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^d VITO, Boeretang 200, B-2400 Mol, Belgium since July 2007, previously in LISE

Nucl. Instr. Meth. Phys. Res. B, available online December, 2008, doi:10.1016/j.nimb.2008.11.026

[17] Metal-Assisted SIMS and Cluster Ion Bombardment for Ion Yield Enhancement

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, L. Van Vaeck^d, H. F. Arlinghaus^a

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^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

Appl. Surf. Sci., 255 (2008), 941-943 (proceedings SIMS XVI conference), doi:10.1016/j.apsusc.2008.05.007

[18] Biological sample preparation for chemical microscopy by dynamic mode Secondary Ion Mass Spectrometry (SIMS)

Gradimir N. Misevic^{1*}, Bernard Rasser², Vic Norris¹, Cédric Dérue¹, David Gibouin¹, Fabrice Lefebvre¹, Marie-Claire Verdus¹, Anthony Delaune¹, Guillaume Legent¹ and Camille Ripoll¹

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Published in February 2009 in:

Methods in Molecular Biology, Extracellular Matrix Protocols (second edition), Humana Press.

In the framework of the activities on biological samples, one further publication has been submitted and is planned to be published in 2009.

3.1.2. Presentations

Imaging of electrospun nanofibres with static and dynamic secondary ion mass spectrometry (S-SIMS and NANO-SIMS)

P. Van Royen, L. Van Vaeck, L. Ruys, A. M. dos Santos, P. Dubruel, E. Schacht, J.-N. Audinot and H.-N. Migeon

7th International Symposium on Frontiers in Biomedical Polymers, 24th – 27th June 2007 (Gent, Belgium)

Investigation of Tribological Boundary Layers of High-Speed Rolling Bearings Elements by AES, XPS and SIMS

U. Gunst, J. Guillot, N. Valle, W.-R. Zabel, H.-N. Migeon, G. Poll and H. Arlinghaus
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey 9th – 14th September 2007 (Belgium)

Effect on depth resolution of low impact energy, sample rotation and oxygen flooding during dynamic SIMS analyses of multilayer structures

N. Valle, J.-N. Audinot, P. Philipp, A. Merkulov, H.-N. Migeon
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey, 9th - 14th September 2007 (Belgium)

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c
^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium
^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany
^c Agfa Graphics N.V., Mortsel, Belgium
(SIMS Europe 2008, Münster)

Investigation of Methods to Enhance the Secondary Ion Yields in TOF-SIMS of Organic Samples

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, P. Van Royen^d, L. Van Vaeck^d, H.F. Arlinghaus^a,
^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany
^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,
^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium
^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey, 9th - 14th September 2007 (Belgium)

Storing Matter: a new quantitative and sensitive surface analysis technique

T. Wirtz, L. Houssiau, J.-J. Pireaux, G. Slodzian, H.-N. Migeon
SIMS XVI Kanazawa (2007)

The Storing Matter technique: application to inorganic samples

P. Philipp, F. Lacour, T. Wirtz, L. Houssiau, J.-J. Pireaux, G. Slodzian, H.-N. Migeon
SIMS XVI Kanazawa (2007)

The Storing Matter technique: preliminary results on PS and PVC

P. Philipp, B. Douhard, F. Lacour, T. Wirtz, L. Houssiau, J.-J. Pireaux, H.-N. Migeon
SIMS XVI Kanazawa (2007)

Nano-characterisation by high resolution SIMS analysis

C. Grovenor, Invited talk at ECASIA, Brussels (2007).

High resolution surface analysis of metallic and biological specimens by NanoSIMS analysis

C. Grovenor, Invited talk at EMC Aachen (2008).

High resolution surface analysis of metallic and biological specimens by NanoSIMS

C. Grovenor, Invited talk at SIMS Europe 2008

3.1.3. Selection of Poster presentations

Use of S-SIMS for the surface analysis of nanofibres formed through electrospinning

P. Van Royen^a, L. Van Vaeck^a, L. Ruys^b, A.M. dos Santos^c, E. Schacht^c, J.-N. Audinot^d, H.-N. Migeon^d

^a University of Antwerp, Wilrijk, Belgium; ^b Centexbel-Gent, Zwijnaarde, Belgium;

^c University of Gent, Gent, Belgium; ^d Centre de Recherche Public, Belvaux, Luxembourg.

Status and future of nanofibers by electrospinning, CNT VII conference in Frankfurt, October 23rd and 24th, 2006

On the understanding of positive and negative ionization processes during ToF-SIMS depth profiling by co-sputtering Cesium and Xenon

J. Brison, J. Guillot, B. Douhard, H.-N. Migeon and L. Houssiau

SIMS XVI Kanazawa (2007)

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c

^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium

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^c Agfa Graphics N.V., Mortsel, Belgium

(SIMS Europe 2008, Münster)

Investigation of Metal-Assisted SIMS and Cluster Ion Bombardement for Analysis of Polystyrene Surfaces

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, P. Soete^d, R. De Mondt^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

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^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

(SIMS Europe 2008, Münster)

3.1.4. Abstracts:

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c

^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium

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^c Agfa Graphics N.V., Mortsel, Belgium

(SIMS Europe 2008, Münster)

Investigation of Metal-Assisted SIMS and Cluster Ion Bombardement for Analysis of Polystyrene Surfaces

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, P. Soete^d, R. De Mondt^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,

^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

(SIMS Europe 2008, Münster)

Characterisation of the co-ordination of nickel in frozen hydrated leaves of the hyperaccumulator plant *Alyssum lesbiacum* by ToF SIMS with principal component analysis

K.E. Smart^a, J. Möller^b, B. Tyler^c, J.A.C. Smith^c, H.F. Arlinghaus^b, C.R.M. Grovenor^a

^aUniversity of Oxford, ^bUniversity of Münster, ^cUniversity of Utah

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Applications of an In Vacuum-Cryo-Sectioning Instrument for ToF-SIMS Analyses of Non-Dehydrated Samples

J. Moeller^a, K. Smart^b, B.J. Tyler^c, D. Lipinsky^a, H.F. Arlinghaus^a

^aUniversity of Münster, ^bUniversity of Oxford, ^cUniversity of Utah

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Cationisation of polymers depending of the structure of the metallic deposition

L. Nittler^a, A. Delcorte^b, P. Bertrand^b, H.-N. Migeon^a

^aCentre de Recherche public - Gabriel Lippmann, Belvaux, Luxembourg; ^bUniversity of Louvain, Louvain-la-Neuve, Belgium

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Evaluation of the ion yield improvement for S-SIMS by the use of polyatomic primary ions for thermographic applications

R. de Mondt^a, L. Van Vaeck^a, A. Heile^b, H. Arlinghaus^b, N. Niewjaer^c, A. Delcorte^c, P. Bertrand^c, J. Lenaerts^d, F. Vangaeve^d

^aUniversity of Antwerp (CDE), Wilrijk, Belgium; ^bUniversity of Münster, IPM, Münster, Germany;

^cUniversity of Louvain, PCPM, Louvain-La-Neuve, Belgium; ^dAgfa-Gevaert, Mortsels, Belgium

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

3.2. Exploitable knowledge and its use

Table 2 shows the exploitable knowledge that resulted from the collaboration of the Nanobeams NoE partners:

Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Patents or other IPR protection	Owner & Other Partner(s) involved
“Tele-presence module”	Videoconferencing tool specifically designed to follow nano-analyses	Nano-analysis, Nanomedicine, Industry		CRP-GL
Sputtering Storing Matter instrument	Semi-quantitative nano-analysis tool	Nano-analysis, Fraud detection	patent pending	CRP-GL, LISE
Publications	19 joint publications	Physics, Chemistry, Biology, Materials Science (SIMS, TEM, AES, XPS, SPM)		All Nanobeams partners
PhD School	Lectures, practical sessions	Physics, Chemistry, Biology, Materials Science (SIMS, TEM, AES)		CRP-GL, IPM, PCPM, LISE, GFE, OXMAT, MiTAC, BioSIMS, Cameca, ION-TOF, University of Luxembourg

Table 2: The above table shows an overview of exploitable results and of how they can be exploited in future

3.3. Dissemination of knowledge

The tables here-underneath list all events organized within the frame of the Nanobeams NoE as well as the conferences attended by NoE partner in order to talk about the work done within the NoE (see tables 3, 4, 5 and 6).

Planned/actual date	Type	Type of audience	Countries addressed	Size of audience	Partner responsible/involved
19 th October 2004	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
19 th October 2004	Press release(press/radio/TV)	General Public	Luxembourg	80'000	CRP-GL
March 2005	Press release(press/radio/TV)	General Public	Luxembourg	80'000	CRP-GL
17 th March 2005	Launch of project web site	General Public/Research	Open to any country		CRP-GL
June/July 2005	Training of Users	Research	Open to any country	6	Cameca
September/October 2005	Press release(press/radio/TV)	Industry (economical sector)	Luxembourg	10'000	CRP-GL
October 2005	Training of Users	Research	Open to any country	6	ION-TOF
October 2005	Training of Users	Research	Open to any country	6	ION-TOF
23 rd October 2005	Open door event	General Public	Luxembourg	250	CRP-GL
22 nd & 23 rd and 29 th & 30 th October 2005	Poster	General Public	Luxembourg	10'000	CRP-GL
3 rd and 4 th November 2005	European Workshop	Research	Europe	29	PCPM
21 st - 25 th November 2005	European PhD School	Research	Europe	34	CRP-GL
25 th November 2005	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
29 th November 2005	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
5 th - 9 th December 2005	Training of Users	Research	The world	5	TE

Table 3: The above table summarizes the dissemination activities in the first 12 months and just before the start of the Nanobeams project.

Planned/actual date	Type	Type of audience	Countries addressed	Size audience	Partner responsible /involved
February 7 th - 9 th , 2006	User session Training (XPS Academy)	Research	Europe	20	LISE
March 6 th - 10 th , 2006	User session Training	Research	Europe	6	ION-TOF
March 13 th - 17 th , 2006	European School PhD	Research	Luxembourg	20	CRP-GL
March 2006	Press release (press/radio/TV)	General public/Research	Europe	100'000	CRP-GL
June 12 th - 16 th , 2006	European School PhD	Research	Europe	20	CRP-GL
June 18 th , 2006	Open Door event	General public	Luxembourg	250	CRP-GL
June 2006	Press release (press/radio/TV)	General public	Luxembourg	100'000	CRP-GL
September 11 th - 15 th , 2006	European School PhD	Research	Europe	10	CRP-GL
September 24 th - 26 th , 2006	SIMS Europe 2006 (conference)	Research	Open to any country	230	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
October 19 th - 20 th , 2006	Conference	Research	Europe	190	CRP-GL
October 23 rd - 27 th , 2006	European Workshop	Research	Europe	22	PCPM
October 23 rd - 27 th , 2006	User session Training	Research	Europe	6	ION-TOF
November 21 st , 2006	Conference	Industry	Luxembourg	40	CRP-GL
November 27 th - December 1 st , 2006	European School PhD	Research	Europe	24	CRP-GL
December 11 th - 15 th , 2006	User session Training	Research	Europe	8	CAMECA

Table 4: The above table summarizes the dissemination activities within the in the second year of the Nanobeams project.

Actual date	Type	Type of audience	Countries addressed	Size audience	Partner responsible /involved
January 29 th – 31 st , 2007	XPS Academy	Research	Europe	5	LISE
March 5 th – 9 th , 2007	User Training session	Research	Europe	6	ION-TOF
March 19 th – 23 rd , 2007	European PhD School	Research	Europe	11	CRP-GL
May 21 st – 25 th , 2007	European PhD School	Research	Europe	7	CRP-GL
June 18 th – 22 nd , 2007	European PhD School	Research	Europe	20	CRP-GL
September 9 th – 14 th , 2007	European Workshop/ ECASIA	Research	Europe	688	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
October 8 th – 10 th , 2007	TEM Academy	Research	Europe	3	GFE
October 8 th – 10 th , 2007	User Training session	Research	Europe	5	ION-TOF
SIMS XVI	Conference	Research	Open to any country	250	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
November 19 th – 23 rd , 2007	European PhD School	Research	Europe	15	CRP-GL
November 19 th – 23 rd , 2007	User Training session	Research	Europe	5	CAMECA
December 12 th – 14 th , 2007	European PhD School	Research	Europe	5	CRP-GL

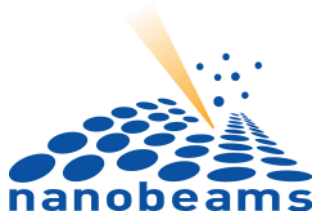
Table 5: The above table summarizes the dissemination activities in the third year of the Nanobeams project.

Actual date	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
January 29 th – 31 st , 2008	XPS Academy	Research	Europe	5	LISE
February 22 nd , 2008	User session Training	Research	Europe	6	Orsay Physics
March 3 rd – 8 th , 2008	European School PhD	Research	Europe	8	CRP-GL
March 10 th - 14 th , 2008	User session Training	Research	Europe	6	ION-TOF
June 9 th – 13 th , 2008	European School PhD	Research	Europe	12	CRP-GL
September 14 th – 16 th , 2008	SIMS Europe 2008	Research	Open to any country	200	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
September 22 nd – 26 th , 2008	European School PhD	Research	Europe	2	CRP-GL
September 29 th – October 3 rd , 2008	User session Training	Research	Europe	5	ION-TOF
October 20 th – 24 th , 2008	User session Training	Research	Europe	6	ION-TOF
November 17 th – 21 st , 2008	European School PhD	Research	Europe	16	CRP-GL
December 1 st – 5 th , 2008	User session Training	Research	Europe	5	CAMECA
December 10 th – 11 th , 2008	European Workshop	Research	Europe	26	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
December 8 th – 11 th , 2008	User session Training	Research	Europe	5	CAMECA

Table 6: The above table summarizes the dissemination activities in the fourth year of the Nanobeams project.

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Contract-NMP4-CT-2004-500440

NANOBEAMS

Nanoanalysis using finely focused ion and electron beams

Network of Excellence

Priority 3 - NMP

Publishable Final Activity Report

Period covered: from January 1st 2005 to December 31st, 2008

Date of preparation: December 31st, 2008

Start date of project: January 1st, 2005

Duration: 4 years

Prof. Henri-Noël Migeon
Département Science et Analyse des Matériaux (SAM)
CRP - Gabriel Lippmann

Revision [version 1.1]

Table of Contents

1.	Introduction.....	3
1.1.	Project Partners	3
1.2.	Contact	4
1.3.	Summary of project objectives.....	4
2.	Project Execution.....	5
2.1.	Work performed and end result.....	5
2.1.1.	Collaboration towards improved instrumentation	5
2.1.2.	Emission and ion formation processes in SIMS	11
2.1.3.	SIMS on organic and biological samples	17
2.1.4.	Contribution to standards	17
2.1.5.	Contribution to the dissemination of knowledge.....	19
2.1.6.	Project impact on industry and research sector	20
2.2.	Conclusion	21
3.	Dissemination and use	22
3.1.	Publications and presentations	22
3.1.1.	Full list of joint publications.....	22
3.1.2.	Presentations.....	24
3.1.3.	Selection of Poster presentations.....	26
3.1.4.	Abstracts:.....	26
3.2.	Exploitable knowledge and its use.....	28
3.3.	Dissemination of knowledge.....	29
4.	Further References	33

1. Introduction

The Nanobeams Network of Excellence (NoE) started on January 1st, 2005 and ran for a total of 48 months, funded by the European Commission under the “Nanotechnology and nanosciences, knowledge-based multifunctional materials and new production processes and devices” (NMP) component of the Sixth Framework Program (FP6). The NoE concentrated on analytical techniques using focussed ion and electron beams in order to develop analytical techniques and instruments matching future requirements for the analysis of nanomaterials. The three complementary techniques included in the NoE are listed below:

- Secondary Ion Mass Spectrometry (SIMS) and Laser-Secondary Neutrals Mass Spectrometry (Laser-SNMS);
- Auger Electron Spectrometry (AES);
- Transmission Electron Spectroscopy (TEM);

SIMS uses a focused beam of ions (primary ions) to sputter a material and produce a localized ion emission characteristic of the composition of the material itself (secondary ions). Typical primary ions are Cs⁺, Ga⁺ and O₂⁺. The secondary ions emitted by the specimen are analyzed by mass spectrometry (magnetic sector quadrupoles or time of flight analyzers). Modern spectrometers provide transmissions in the range of 50% at high mass resolution ($M/\Delta M = 5000$). The SIMS technique can be divided into two distinct types of instruments: dynamic SIMS (D-SIMS) which is a depth profiling and nano/micro volume analysis tool, and static SIMS (S-SIMS), essentially ToF-SIMS, which is specifically for the analysis of the surface monolayer and molecular adsorbates. The SIMS technique offers ppm-ppb sensitivity for the consumption of $<10^{-13}$ cm³ of material, and has the potential to determine the composition of even extremely small volumes – down to 1 nm³ containing approximately 50 atoms. Hence, SIMS is an obvious choice for probing the chemical composition of the sample on the 10 nm scale. When a primary ion impinges on a solid surface, it deposits its energy (several keV) into a subsurface volume in an area of less than 10 nm in diameter around the point of impact. The dissipation and recoil of the deposited energy leads to the desorption and ionization of elements, small clusters and even intact molecules. As a result, the chemical information obtained through mass analysis of the ions generated by a single primary ion is by definition “real” nanoscale analysis.

High-resolution Auger Electron Spectroscopy (AES) may be used to perform an analysis of the first 20 nm of a sample making use of the Auger process. The range of elements that may be analyzed by AES lies between lithium and uranium. AES has the advantage over SIMS that it is a quantitative technique. However, in order for it to discover an element, the latter must be present by at least a percentage of 1.

Transmission Electron Microscopy (TEM) is a powerful technique with extremely high resolutions at the atomic scale. The disadvantage of this technique is, however, that samples need to be very thin for analysis. Therefore this demands a high level of expertise in sample preparation, and the preparation of such samples is very time consuming. TEM is the method of choice for obtaining crystallographic information with very high spatial resolution.

1.1. Project Partners

The Nanobeams NoE was composed of manufacturers of scientific instruments, as well as the leading research laboratories in the field. Overall, it involved 80 researchers and 40 PhD students. The total budget for the NoE was approximately €30 million. The contractors are listed here-underneath:

- CRP-GL: Centre de Recherche Public - Gabriel Lippmann¹,
“Département Sciences et Analyse des Matériaux” (SAM)
and the “Département Informatique, Systèmes et Collaborations” (ISC), Luxembourg
(<http://www.lippman.lu/>);

¹ CRP-GL is also known as the CRP-Gabriel Lippmann

- IPM: Physikalisches Institut, Westfälischen Wilhelms-Universität Münster, Germany (<http://www.uni-muenster.de/Physik.PI/Arlinghaus/>);
- PCPM: Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Belgium (<http://www.pcpm.ucl.ac.be/>);
- LISE: Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix de Namur, Belgium (<http://www.fundp.ac.be/facultes/sciences/departements/physique/recherche/centres/lise/>);
- GFE: Gemeinschaftslabor für Elektronenmikroskopie, RWTH-Aachen, Germany (<http://www.gfe.rwth-aachen.de/>);
- OXMAT: SIMS Group, Department of Materials, Chancellor, Masters and Scholars of the University of Oxford, United Kingdom (<http://www.materials.ox.ac.uk/>);
- MITAC: Universiteit Antwerpen, Micro-Trace Analysis Centre, Belgium (http://www.ua.ac.be/main.aspx?c=*SCHEIKUN&n=12187&ct=007985&e=t16924);
- BioSIMS: Laboratoire et Assemblages Moléculaires: Modélisation et Imagerie SIMS, Université de Rouen, France (<http://www.univ-rouen.fr/>);
- CAMECA: Cameca S.A.S., France (<http://www.cameca.com/>);
- ION-TOF: Ion-TOF GmbH, R&D Lab, Germany (<http://www.ion-tof.com/>);
- TE: Thermo Electron Corporation, now Thermo Scientific(up to December 2006), Great Britain (<http://www.thermo.com/>);
- OP: Orsay Physics, France (<http://www.orsayphysics.com>).

1.2. Contact

Coordinator: Prof. Henri-Noël Migeon,
Centre de Recherche Public – Gabriel Lippmann (CRP-GL),
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Email: migeon@lippmann.lu, www.nanobeams.org

1.3. Summary of project objectives

The main activities of the different partners in the Nanobeams NoE were instrumental development, the coordination of fundamental research, the application of advanced analysis techniques to nanomaterials, the coordination of manufacturers, the organization of an annual European workshop and training sessions on the different instruments.

The project's objectives were the following:

- To improve SIMS for providing lateral resolutions down to 10 nm and a depth resolution of 1 nm;
- To develop new techniques for the measurement and analysis of nanostructured materials;
- To use these techniques for nanoscopic analysis and nano-metrology;
- To contribute to the development of Standards. This would also involve the definition of important parameters with regard to measurement systems;
- To disseminate knowledge via:
 - The implementation of a European PhD School on “Nanoanalysis using finely focused ion and electron beams”;
 - The organization of an annual European workshop;
 - The creation of two working groups for users in biology and materials science at a European level;
 - The organisation of various user training sessions on SIMS, TEM and XPS aimed at improving the skills of the machine operators.

2. Project Execution

2.1. *Work performed and end result*

Throughout the project period, the Nanobeams partners worked hard to achieve the aims set forth in the project. The partners collaborated by contributing novel ideas, which resulted in the submission of new research projects. In this respect, a number of feasibility studies were carried out and pilot ideas were developed.

2.1.1. Collaboration towards improved instrumentation

Throughout the project duration, the Network partners and especially WP3 partners have collaborated with the aim of developing more efficient instrumentation. This can be seen from the number of collaborative research project-proposals submitted in the frame of the Nanobeams NoE at a National or a European level. Section 2.1.1.1 of this report presents the efforts of the Nanobeams NoE to collaborate in various research projects in order to further improve their instruments.

Furthermore, the Nanobeams NoE partners have been involved in measuring the lateral and depth-resolutions of their state-of-the-art SIMS instruments on a range of different samples. The measurement procedures and results are shown in section 2.1.1.2 of this report.

2.1.1.1. Submitted project proposals

Introduction

Over the duration of the project, several project-proposals have been submitted for future funding, with a high success rate. 2 out of the 4 project-proposals were accepted, and so the Nanobeams NoE partners have had the opportunity for practical progress towards their aim of developing more efficient instrumentation. This has been underpinned with a number of feasibility studies.

In the frame of the „*Negative Ion Sources*“ project, stable prototype negative ion sources have been developed. These are in the phase of being tested. We have deliberately delayed submission of a number of journal papers on this work in order not to compromise a possible patent application on these sources.

In the frame of the “*3D-NanoChemiscope*” project, which started in September 2008 involving several Nanobeams partners, a new instrument combining SFM and TOF-SIMS will be developed. In this way, a resolution of less than 10 nm will be achieved by the end of the project in 2012. This is clear evidence that the NoE partners will continue active collaboration in this field of research after the end of the Nanobeams NoE.

The “*Negative Ion Sources*” project proposal, whose objective it is to develop high brightness negative ion sources, was submitted to the Luxembourgish “Fonds National de la Recherche” in the frame of the “Innovative materials and nanotechnology (NANO)” program in June 2005. This project-proposal included 3 NoE partners and 4 external partners and started in April 2006 for a duration of 30 months after acceptance by the FNR.

The German SIMS manufacturer ION-TOF and several network partners worked on the development of advanced ion sources in order to improve both the lateral and depth resolutions. Using Bi_3^+ multi-atomic guns the lateral resolution could be drastically improved from approximately 200 nm down to 40 nm (cf. section 2.1.1.2). These practical improvements in performance are already incorporated in commercial ToF-SIMS apparatus in the marketplace, and are thus adding to the ability of the EU to compete for market shares in this significant sales area.

Project-proposal objectives

“Negative Ion Sources” objectives

One major problem, which needed tackling at the beginning of the NOE, concerned the analysis of electropositive elements (which are detected as positive secondary ions in SIMS). To analyze these species with a good sensitivity, a primary ion beam of electronegative species is needed. Most SIMS instruments are as a consequence equipped with a duoplasmatron type ion source which can be run with an oxygen gas feeding in order to produce O_2^+ or O^- ion beams. These duoplasmatron ion sources unfortunately have an important handicap: their brightness is low and, as a consequence, the ion beam delivered by this source is quite broad and cannot be focussed down to a spot small enough to allow imaging applications with a good lateral resolution (cf. table 1).

This disadvantage becomes even more apparent on the CRP-Gabriel Lippmann’s NanoSIMS50 instrument. This instrument, which has known an enormous success since its installation in Luxembourg, is dedicated to ion imaging with a lateral resolution as good as 50 nm. However, this lateral resolution can only be reached when the Cs^+ primary ion source is in use (thus while detecting negative secondary ions), as the duoplasmatron source also available on the instrument cannot offer O^- spot sizes compatible with the required experimental resolution. As a consequence, the potential of the NanoSIMS50 (an instrument offered by an EU company with no effective competitor in the marketplace) cannot be fully exploited for positive secondary ions.

Up to the start of the project, only a few attempts had been made to introduce primary ions with electronegative species other than oxygen. Moreover, the consortium was been aware of any current projects trying to develop such negative ion sources. As a result, the partners introduced a project aimed at optimizing SIMS analysis with high sensitivity of electropositive elements by introducing new primary ion guns based on electronegative species (primarily on the NanoSIMS50, but also on the other instruments of the CRP-Gabriel Lippmann). The research work performed in the framework of this project consists both in a combined fundamental/analytical study of SIMS using negative primary ions and the development of sources producing such negative ions.

“3D NanoChemiscope” objectives

The objective of this “*Combined SIMS-SFM Instrument for the 3-dimensional chemical analysis of nanostructures*” project is to develop an innovative and novel combination of a new TOF-SIMS with substantially improved lateral resolution and sensitivity, combined with a new metrological high resolution SFM (Scanning Force Microscope). The two techniques provide complementary information on nanoscale surface chemistry and surface morphology. In combination with a layer by layer removal of material using low energy sputtering, quantitatively measured by SFM, this combined ultra-high vacuum (UHV) instrument will be unique for the 3-dimensional chemical characterization of nanostructured inorganic as well as organic materials with down to at least 10 nm lateral resolution and down to 1 nm in depth resolution. Combined with novel software for the calculation and display of 3-dimensional distributions of all chemical species, this leads to a totally new instrument – the 3D NanoChemiscope.

2.1.1.2. Measurement of SIMS lateral and depth resolutions

Introduction

This section will give an overview of the progress achieved by the NoE partners in the optimization of their instruments in order to reach better lateral and depth resolutions over the past four years. At first, the determination of the lateral and depth resolutions is discussed in sections 2.2.2 and 2.2.3. Then, the progress and results of the various NoE partners within this area is described (section 2.2.4).

Determination of lateral resolution

The diameter of the ion probe depends on the brightness of the ion source and on the optical properties of the column used to focus the ion beam on the sample. The brightness B of an ion source is defined as follows:

$$B = \frac{I}{S \cdot \Omega},$$

where I is the ion current, S the ion emitting surface and Ω the solid angle in which ions are emitted. High brightness ion sources thus allow the producing of very finely focussed probes while keeping a sufficient current for correct secondary ion intensities. Table 1 shows an overview of the characteristics of those ion sources, that are the most commonly used in SIMS. This table shows that the highest brightness can be reached with liquid metal ion sources (operating with field emission ionization).

	electron impact	duoplasmatron	surface ionization	liquid metal
species	Ar, Xe, O ₂ , SF ₆ , C ₆₀ ...	Ar, Xe, O ₂ , ...	Cs	Ga, In, Au _n , Bi _n
size of source	1 mm	200 μm	10 μm	3 nm (virtual)
ion energy	0.1 - 20 keV	0.1 - 10 keV	0.3 - 20 keV	2 - 30 keV
beam current	1 - 1000 μA	1 - 1000 mA	10 μA – 100 mA	1 - 1000 μA
brightness	1 A sr ⁻¹ cm ⁻²	10 ² A sr ⁻¹ cm ⁻²	10 ³ A sr ⁻¹ cm ⁻²	10 ⁷ A sr ⁻¹ cm ⁻²
energy dispersion	1 - 10 eV	5 - 20 eV	0,2 - 0,5 eV	5 – 50 eV

Table 1: Main characteristics of the ion sources, which are the most commonly used in SIMS

The determination of the lateral resolution of a SIMS instrument uses a conventional method based on imaging and performing a linescan of sharp edges of a test sample. The lateral resolution is defined as the separation of 16-84% contours in a plot of intensity of the elemental or molecular signal (see figure 1).

In the past, various SIMS users have used their own reference materials. More recently, a specifically developed Certified Reference Material (CRM) has been developed by the German Certification Authority Bundesanstalt für Materialforschung, BAM. This sample is constituted from polished cross-sections of a AlGaAs-InGaAs-GaAs layer stack. These layers form a complex stripe pattern at the surface whose gratings range from finely graded periods of 2 nm to 600 nm [20,21].

Determination of depth resolution

The depth resolution of a SIMS instrument can be determined by performing a depth-profile on a bulk sample including a so-called delta layer. There are several methods for determining the depth resolution: Usually, depth resolution cannot be better than surface roughness:

- According to [22], the “depth resolution corresponds to the distance (depth range) over which a 16% to 84% (or 84% to 16%) change in signal is measured” when profiling through an interface of two media. This definition was introduced by [23-25] and later adopted by IUPAC and the ASTM E-42 committee [26].
- According to [27], “depth resolution is measured in terms of the decay length, the distance over which the signal falls by a factor e , the natural log base. It is also sometimes described in nm/decade as this is easy to estimate from a graph since SIMS depth profiles are presented, almost universally, with a logarithmic concentration axis due to their high dynamic range.”

In general, depth resolution depends on several factors, one of the most important of which is surface roughness, which generally increases as depth profiling proceeds.

Progress and end result

Taking into account that the instruments were continuously improved in the frame of these collaborative projects as well as the feasibility studies performed by various Nanobeams NoE partners over the time span of the Nanobeams NoE, considerable progress has been achieved in the improvement of the lateral resolution in static and dynamic SIMS. Thus, OXMAT achieved a resolution of 29 nm when measuring a PMMA film following the optimization of their CAMECA NanoSIMS50 instrument’s parameters (see figure 1).

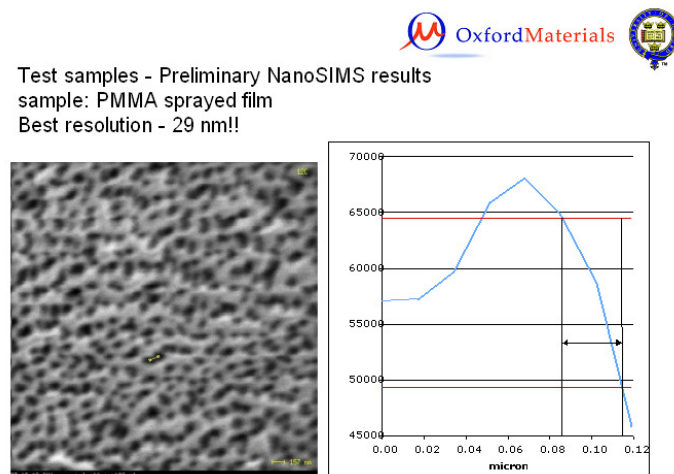


Figure 1: Measurement of lateral resolution using a PMMA sprayed film. The measurement of the distance corresponding to a 84-16% intensity variation shows a lateral resolution of 29 nm on OXMAT’s NanoSIMS50 instrument using a cesium ion gun.

In the frame of the “*NanoBioMaps*” project, which was integrated into the Nanobeams NoE and involves the German SIMS manufacturer ION-TOF and IPM (University of Münster), ION-TOF performed a number of measurements using their recently developed Bi_3^{++} cluster ion gun on their TOF-SIMS IV instrument [21]. As shown in table 1 above, Bi_3 ion sources are high brightness liquid ion metal sources. Such sources allow the production of very finely focussed probes as explained above. As can be deduced from figure 2, the German manufacturer determined the lateral resolution of their instrument using the recently developed CRM BAM-L200 as a sample. The result was that using a Bi_3^{++} cluster ion gun, the lateral resolution on their TOF-SIMS IV instrument was 40 nm. Before the development of such cluster ion guns, the lateral resolution for TOF-SIMS was in the range of 100 nm or above. This is a very significant improvement in a key performance metric over the duration of the NoE.

In order to achieve better depth resolutions, it is important to lower the impact energy, E , of the primary ion beam. As chromatic aberrations are inversely proportional to E , the lowering of the energy would drastically degrade the focus of the primary ion beam on conventional SIMS instruments. In order to overcome this problem, the SC-Ultra instrument has been specifically developed by the French SIMS manufacturer CAMECA. Unlike other SIMS instruments, this instrument uses a “Floating Low energy Ion Gun” (FLIG). As can be seen in the example of figure 2, the column is held at a high potential (e.g. 7500 V), even though the impact energy is kept low. This innovative concept allows for chromatic aberrations to be kept at a minimum and for the impact energy also to be kept low. As a consequence, the decay length within the target material is small, and high depth resolutions can be achieved.

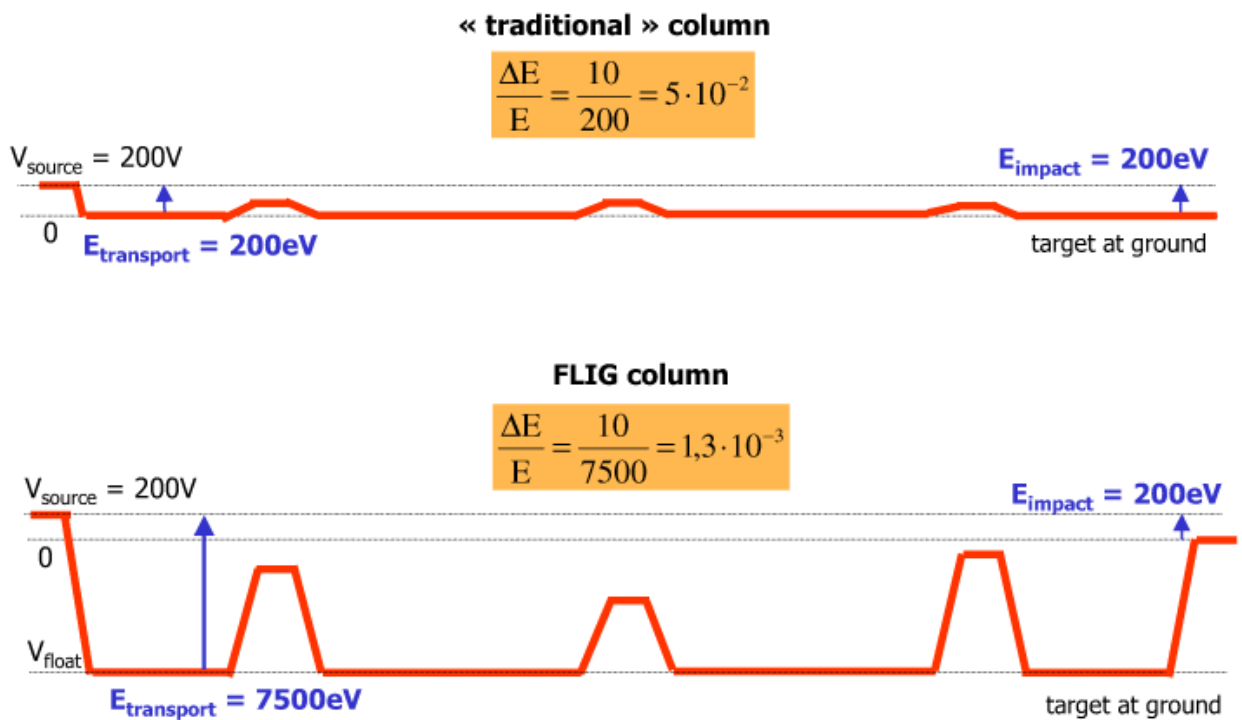


Figure 2 : The above figure depicts both the traditional and the recently developed FLIG column. Both of these columns include electromagnetic lenses, which are used for focussing the beam. In traditional columns, where the column itself is at ground and the ion source is held at a potential V_{source} , the impact energy is equal to the transport energy $E_{\text{transport}}$. In FLIG columns, the column is held at a negative potential V_{float} . This means that the transport energy of the ion beam is increased. As the beam passes a grounded electrode just before the impact on the sample, the impact energy is different from the transport energy. Using FLIG columns, aberrations can be kept at a minimum without increasing E_{impact} .

Using their recently developed SC-Ultra SIMS instrument, the NoE partner Cameca, the world leader in the manufacturing of dynamic SIMS instruments, performed a number of depth resolution studies on a Si sample including a boron delta layer. The depth resolution was determined according to the definition given in subsection entitled “Determination of depth resolution”. It was found that the distance over which a 16% to 84% (or 84% to 16%) change in signal is measured is less than 1 nm. Using the method suggested by [27], the

depth resolution corresponds to 0.75 nm/decade. The analysis was performed using an ultra-low energy sputtering O_2^+ ion beam of 150 eV. Whereas in 2005, the depth resolution on such samples was still around several nanometers, the latter has now been improved to less than 1 nm. Thus, it can be concluded that the Nanobeams consortium has also achieved a significant improvement in SIMS depth resolution during the project period.

2.1.1.3. Improvement of the sensitivity of SIMS

The effective application of fine incident beams to accurate nano-analysis is not only dependent on the focussing of the beam but also on the sensitivity of the instrument. The amount of material analyzed in a very tiny area (such as $10 \times 10 \text{ nm}^2$) is very limited and a high sensitivity is required to have reasonable counting statistics. Similarly, an image with good contrast can only be obtained if a very high signal is produced, which means a higher sputtering yield and a higher ionization yield. Therefore, improving lateral resolution is intimately linked to improving sensitivity. Hence, an important aim of the Nanobeams NoE was to turn innovative ideas and concepts related to improving the sensitivity and the resolution into instrumental prototypes. This required the collaboration of laboratories specialized in different fields. Thus, the Nanobeams NoE submitted several project-proposals at national and European levels in order to fulfil these objectives. The Nanobeams consortium worked in particular on one very successful project named “**Storing Matter**”. This project is described below.

The “Storing Matter” project

This project aimed to decouple the sputtering of the specimen from the subsequent analysis step in order to enable higher sensitivity than with usual SIMS techniques. By the end of the project in June 2006, a prototype instrument had been fully assembled at the CRP-Gabriel Lippmann. Experimental studies showed that the Sputtering Storing Matter Instrument (SSMI) was a highly sensitive technique, which allowed improved quantification and thus was expected to reduce the importance of the well-known matrix effect. Indeed this effect is one of the issues in accurate quantitative analysis with the SIMS technique. By reducing this issue, more accurate nano-measurements can be performed. Indeed, the sensitivity achieved in the project is even higher than the benchmark fixed at the initial stage. During the SIMS XVI conference in Japan in September 2007, several oral presentations regarding the new instrument were given [13-15]. Thus, the project was successfully completed. One picture of the prototype instrument is shown in figure 3. In 2008, the project partners decided to continue collaborating in order to apply the storing matter concept to polymers.



Figure 3: The Storing Matter prototype at the CRP-Gabriel Lippmann.

2.1.1.4. Submission of further projects

Over the project duration, the consortium also submitted other projects for funding of direct relevance to the NoE. One of these was the “**Nano²hybrids**” project, which was funded in the frame of the FP6 STREP program. “**Nano²hybrids**” (FP6-2004-NMP-TI-4-033311), and which started in October 2006 involving the CRP-Gabriel Lippmann, LISE and PCPM. This new project concerns the “Interface design of metal nanocluster-carbon nanotube hybrids via control of structural and chemical defects in a plasma discharge”. It was of strong relevance to the NoE as it concentrates on the further development of novel nanostructured materials for functional applications, and reliable analysis protocols for these materials will be very important.

Furthermore, the Nanobeams NoE launched several projects in the area of Biology. Tacking into account the improved resolution of SIMS as well as the improved sensitivity, SIMS has become more and more useful in Biology. In the ANR-funded research project “**1cell-nanoproteomics**”, the partners BioSIMS and OP aim at analyzing the single cell proteome by nano-electrophoric devices (NEDs) using the CAMECA NanoSIMS 50. The project started in March 2007 and will finish in 2011.

One further project-proposal aiming at using SIMS in biology was submitted under FP7’s Health theme in December 2008.

2.1.2. Emission and ion formation processes in SIMS

Introduction

As one of the Nanobeams NoE’s goals was to improve our knowledge regarding emission and ion formation processes in SIMS with special emphasis on the detection of large molecular fragments, the objective was to increase the sensitivity of the method thanks to better control of the physical parameters influencing the secondary ion yield and specifically by the use of laser beams to ionize sputtered neutrals (Laser-SNMS). This increase in sensitivity is especially needed when looking at nanostructures where the amount of material available for the analysis and imaging is rather limited (especially when static conditions are required for molecular surface characterization). Moreover, a better understanding of the basic processes involved will allow us to improve significantly the quantitative interpretation of SIMS data.

The specific tasks were to increase sensitivity, by considering either the emission processes (sputtering) or the ion formation mechanisms. As an example, to enhance the secondary yield of molecular fragments by the use of cluster and molecular primary ion beams instead of atomic beams, to improve the ionization of the emitted particles by different methods of cationization/ anionization or to efficiently ionize sputtered neutrals by laser photo-ionization processes. In order to gain insights about these basic mechanisms, the procedure consisted in comparing the experimental results with predictions of the theoretical models. The experimental information mainly consists in the secondary ion yield, energy and angular distribution dependence as well as on the experimental parameters such as the primary ion nature, energy and impact angle.

Thus, it was planned to perform molecular dynamics simulations using realistic interaction potentials with the goal of obtaining theoretical information concerning the sputtering processes. With regard to the charge formation process, different models were to be tested. As an example, the PCPM group proposed a model to explain the efficient cationization of organic molecules by complexation with substrate metal atoms to form ions. This model is based on an associative ionization mechanism consisting in the recombination of an excited molecule and a metal atom above the surface and the subsequent decay of the complex via the emission of an electron, locking the system in the ionized state. Electronic structure calculations were required to study the stability of the ionized complexes formed during the emission process.

The activity was thus divided into different pilot projects:

Pilot project 1: Ion formation of molecules from mono- and multilayers

Pilot project 2: Molecular ion yield enhancement induced by metal cluster deposition

Pilot project 3: Use of cesium for enhancement of ionization probabilities and quantification

Pilot project 4: Laser-SNMS project

Activities related to pilot project 1 :

In this activity, IPM and ION-TOF collaborated in improving our understanding of mechanisms of molecular ion yield enhancement induced by metal clusters bombardment on organic surfaces. The objective was to optimize parameters for detecting hybridized DNA fragments using different primary ions, including monatomic ions, as well as cluster metal ions. In this study, important new results have been obtained, for example it was found that cluster primary ions resulted in a significantly increased yield of DNA-correlated fragments (e.g. PO_3^-), enabling higher signal intensities and better secondary ion efficiencies [10,28].

For the monatomic primary ions Ne^+ , Ar^+ , Ga^+ , Kr^+ , and Xe^+ , a continuous increase with increasing projectile mass can be observed. Compared with Ar^+ , the use of polyatomic primary ions SF_3^+ and SF_5^+ for example, led to a significant increase in the PO_3^- secondary ion yield by about a factor of 250. Compared to all the “classical” primary ions studied, SF_3^+ and SF_5^+ do not only result in the highest PO_3^- secondary ion yields, due to their polyatomic nature, but also give the best values for the secondary ion efficiency (not shown) and therefore, in general, provide a high sensitive method for detection of hybridized DNA on biosensor chips.

In order to further investigate the influence of the ion energy on the secondary ion emission of PO_3^- , an evaluation of yields, disappearance cross sections and efficiencies as a function of different primary ion energies was carried out using Bi_3^+ as an exemplar primary ion projectile. In general, within the energy range from 10 to 50 keV only a minor energy dependence is observed. With increasing energy, the secondary ion yield increases by about a factor of 2.5 and the disappearance cross-section by about a factor of 3.5. As a result from this behaviour, the secondary ion efficiency decreases down to two-thirds of the value at 10 keV.

The variation of the secondary ion yields of PO_3^- as a function of Bi primary ion species was also investigated. In general, the highest relative increase of values is observed by changing from monatomic Bi^+ to polyatomic Bi_2^+ primary ions, which amounts to approximately an order of magnitude. With increasing cluster sizes, continuous enhancements can be observed, although the enhancement factors saturate for high cluster sizes.

In general, a similar development can be found for the disappearance cross-section and secondary ion efficiency of PO_3^- , displayed in the middle and right-hand graph. Nevertheless, the enhancement factors of the disappearance cross-section and, due to the combined influence of yield and disappearance cross-section, the secondary ion efficiency shows smaller enhancement factors [10].

Changing the substrate material from silicon to gold, an additional yield enhancement for PO_3^- was observed which was highest for monatomic primary ions (more than a decade) and smallest for polyatomic primary ions (factor 2-4).

It was found that a change from monatomic to polyatomic primary ions leads to an increase in secondary ion yield of about two orders of magnitude, whereas there are smaller differences in between Bi_3^+ , Bi_2^+ , Bi_3^+ and Bi_5^+ . The data also indicates that there is a kind of saturation of the secondary ion yield with increasing cluster size. An increase in the primary ion energy resulted only in small changes of secondary ion yield and efficiency, especially in the energy range from 20 keV to 50 keV. In conclusion, the data clearly shows that it should be possible to take advantage of a simplified low-energy cluster Liquid Metal Ion Gun (LMIG) supplying doubly charged Bi_3^{++} primary ions in future analysis and thus providing optimal bombardment conditions.

The results were presented on the SIMS XV and ECASIA'07 conferences and two joint publications were published [6,10].

Pilot projects 1 & 2: Ion formation of molecules from mono- and thicker layers and molecular ion yield enhancement induced by metal cluster deposition

Thin layer samples (about one monolayer in thickness) and thick layer samples (at least 10 nm thickness) were prepared for pilot project 1. Most of them were additionally used for pilot project 2, where the effect of metal deposition was investigated. Therefore, these results are shown together. Mainly gold was used for metallization.

Hundreds of samples were prepared by various partners:

- Polyethylene, polypropylene and Irganox 1010 ($M_w = 1177$ u) (PCPM, LISE)
- A thick layer of plasma polymerized polystyrene (LISE)
- Polystyrene with different molecular weight ($M_w = 500$ u, 1800 u and 10,000 u) as thin and thick layer samples (PCPM, LISE)
- Polymer samples containing different dyes (molecular weight of about 500 u) as thin and thick layer samples (MiTAC, LISE)
- Triacotane (molecular weight of about 422 u) prepared on silicon, gold and silver as thin layer samples (PCPM)

Most samples were analyzed by more than one partner (IPM, PCPM, MiTAC) using all the different primary ion species available within the project. Additionally, LISE did electron microscope measurements on selected samples.

Many of the results obtained in pilot project 2 show the same trends, regardless of which samples were analyzed and regardless of the choice of secondary fragment ions (cf. figure 4) or secondary ions of the whole molecules.

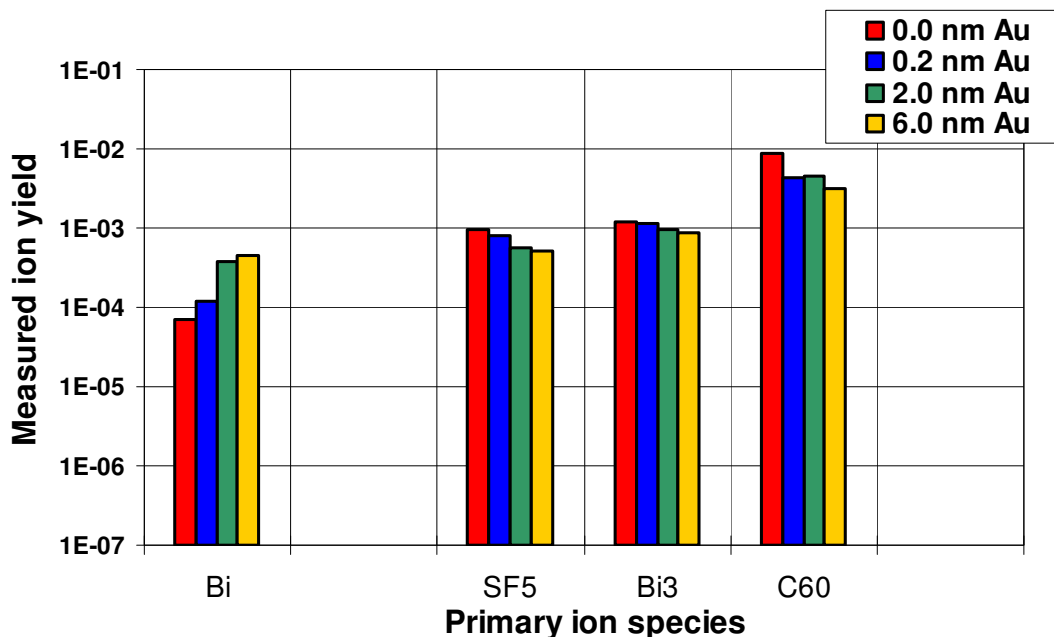


Figure 4: Secondary ion yield of a characteristic polystyrene fragment ion ($C_8H_9^+$) obtained from pristine and gold-covered samples using monatomic (Bi^+) and polyatomic primary ion bombardment (SF_5^+ , Bi_3^+ , C_{60}^+)

Due to the results obtained in this work-package, it concludes that some of the known methods to enhance the yield (thin layer/monolayer preparation, polyatomic instead of monatomic primary ion bombardment, metallization with gold) depend mainly on the same mechanism: They all help to deposit more energy near the sample surface. Therefore, when combining these methods, the yield increase is often much smaller than the sum of the single yield increases of each method. Sometimes even a yield decrease is observed. Many

results obtained in pilot projects 1 and 2 can be explained by arguments involving changes in energy deposition [7-9,11,17].

However, results from additional experiments, in which silver was used for metallization and gold and silver were used as substrate material, do not fit into the previous observations. Secondary ion yields of quasi-molecular and cationized ions obtained from these samples with C_{60}^+ and Ga^+ bombardment [11]. The yield obtained with Ga^+ from the sample with gold deposition is higher than the yield obtained from the sample with a gold substrate. This cannot be explained by the assumptions and arguments made above. Additionally, it cannot be explained why the yields of the cationized molecules are higher when using monatomic instead of polyatomic primary ions. Results obtained in pilot project 2 were presented at various conferences like ECASIA'07, SIMS XVI (Japan) and SIMS Europe 2008. Five joint publications were published on this subject [7-9,11,17]. The investigation of different metals' influence in metal-assisted SIMS will be carried on beyond the end of the Nanobeams NoE.

Pilot project 3 : Use of cesium for enhancement of ionization probabilities and quantification

Pilot project 3 dealt with ionization processes of secondary ions and clusters. These processes were studied by LISE and the CRP-Gabriel Lippmann. Thus, scientists from both institutions shared the available equipment in order to address, in a joint fundamental study, the improvement in SIMS quantification when depositing Cs at the surface.

When using the neutral cesium deposition system on a prototype SIMS instrument available at the CRP-Gabriel Lippmann, in conjunction with a simultaneous primary ion bombardment, a significant increase of the useful yields of negative secondary ions, and thus of the analysis sensitivity compared to traditional Cs^+ primary ion bombardment, is obtained. In this case, the overall useful yield qualitatively agrees with the predictions of the electron-tunnelling model. At maximal cesium surface concentrations, quantitative analyses become possible for elements with high electron affinities. For other elements, a significant increase of the analysis sensitivity is achieved.

Combining the knowledge gained on various samples using AES measurements and simulations, the two partners were able to convert the raw data, obtained from analyses using the Cs/Xe co-sputtering ToF-SIMS analysis mode, to positive and negative ionization probabilities of Cs and Si with respect to the decreasing work function. It was found that the negative Cs and Si signals increase exponentially with the Cs coverage, whereas the positive signals decrease. The data were interpreted by means of the electron-tunnelling model. During the Nanobeams project, this aforementioned technique was successfully applied to typical SIMS applications like depth profiling and the results were presented in a joint publication [16].

Pilot project 4 : Laser-SNMS

The quantification of the elemental composition of a sample surface by mass spectrometric analysis of secondary particles sputtered from solid surfaces under primary ion bombardment is limited by the fact that the flux of secondary particles of a certain element consists of both atomic particles and different kinds of molecules containing the respective element. Furthermore, some of these secondary particles are positively or negatively charged whereas the rest are neutral. These different kinds of secondary particles cannot be detected in a mass spectrometric analysis with identical probability. In contrast to the secondary ions, which can be analyzed directly (SIMS), neutral particles have to be ionized before mass separation, e.g. by the interaction with photons of a laser beam (Laser-SNMS). Depending on the photon energy, a desorbed atom can be post-ionized resonantly or non-resonantly. For sputtered molecules photo-ionization is possible as well, but – as a competitive process – also photo-fragmentation. Such photo-fragmentation processes can result in the generation of smaller fragments, which can be charged or neutral, including fragmentation into monatomic neutrals and ions (figure 5). As the composition of the flux of secondary particles depends on the chemical matrix of the respective element in the surface, changing flux compositions complicate quantitative interpretations of SIMS and Laser-SNMS data, because signal intensities obtained for the particular element

can depend strongly on the chemical matrix and do not always correlate with the elemental distribution on the surface.

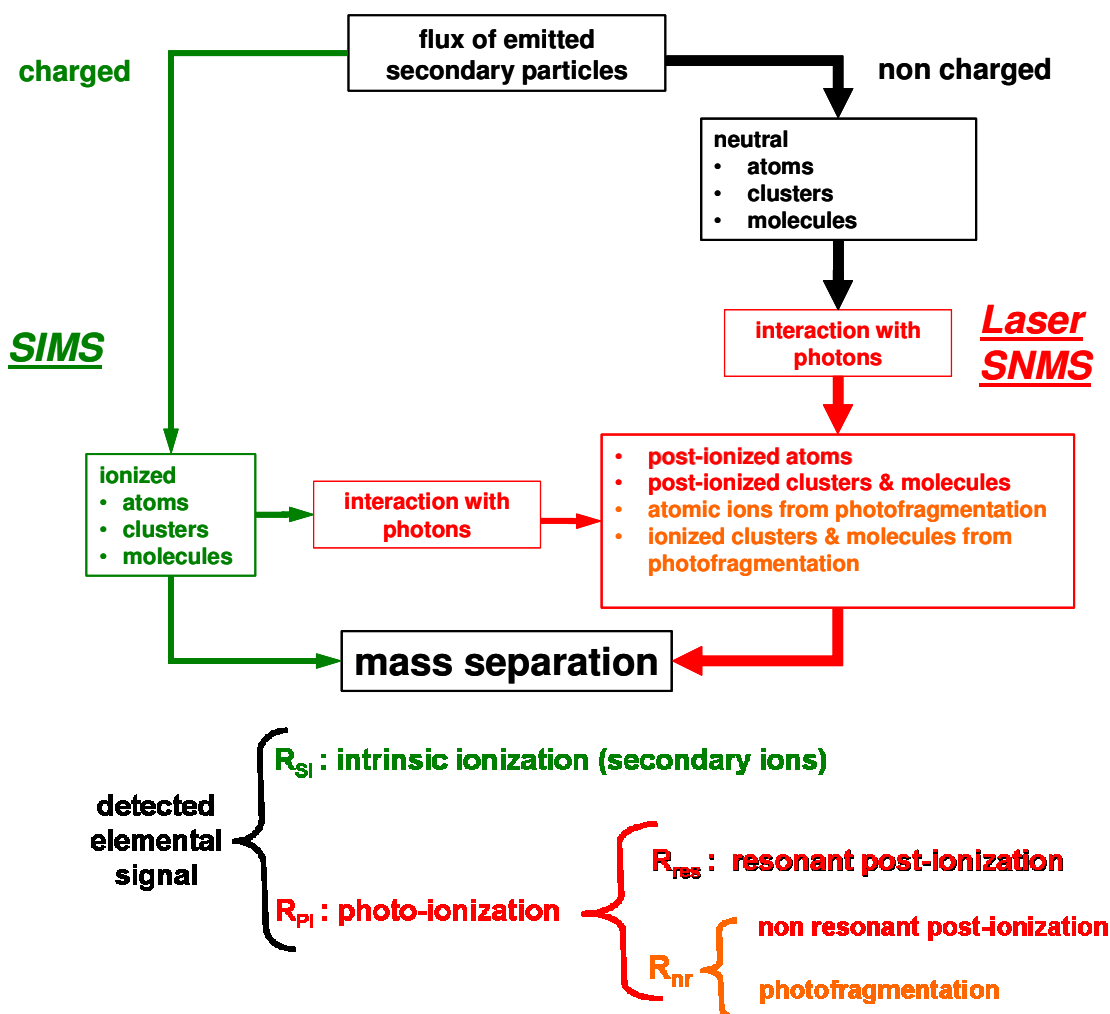


Figure 5 : Schematic diagram of the distribution of the sputtered particle flux (top) and the resulting composition of the detected elemental signal in resonant Laser-SNMS (bottom).

As a step closer towards quantitative elemental analysis using Laser-SNMS techniques, the aim was to develop a method to distinguish between different ion formation processes and to determine the influence of these processes on the total number of detected monatomic ions of a certain element. The knowledge about the composition of the detected ion yield can be used for characterizing the composition of the flux of secondary particles sputtered from different surfaces. To explain the origin of diverse fractions of differently generated ions contributing to the total yield of all monatomic ions of a certain element, a vector/matrix-formalism was developed, which describes the physical processes of sputtering, ion formation, mass separation and detection in Laser-SNMS.

In the framework of the method developed, based on this theoretic formalism, changes in the secondary flux contribution of the respective element were observed by comparing the detected monatomic ion yield obtained in specifically aligned (SIMS and) Laser-SNMS experiments. These were performed via systematic variations of certain laser parameters, ensuring that the sputter conditions and the chemical situation of the surface were kept strictly constant. The yields resulting from these experiments were used to calculate characteristic numbers to compare the flux composition from different surfaces. In particular, these characteristic numbers were utilized to indicate changes between the monatomic and the molecular part of the flux of secondary particles.

For these experimental investigations, two different laser systems were applied: a dye laser system and a 193 nm excimer laser. The dye laser system, with two separately tuneable beams, can be used to excite

resonant ionization processes of atomic neutrals, element and state selectively. In contrast, the excimer laser offers high non-resonant post-ionization and photo-fragmentation probabilities.

The potential of the method was demonstrated for the elements boron, iron and gadolinium by investigating the changes in the flux composition of secondary particles sputtered from metallic surfaces, as a function of the oxygen concentration at the surface. Exemplary analyses of various kinds of surfaces show that there is, in principle, no restriction on a general applicability of the presented method.

Laser-SNMS experiments using the dye laser system tuned for resonant post-ionization of atomic neutrals showed striking yield differences between clean and oxidized surfaces, which could not be explained by differences in surface stoichiometry or changes in sputter yield. Analyses of the composition of the detected ion yields, with the help of characteristic numbers, depicting the different influence of photo-fragmentation processes, indicate that the yield differences were mainly caused by a significant enhancement of the molecular fraction (oxides and clusters) and a tremendous reduction of the number of monatomic neutrals in the flux of secondary particles.

As the degree of photo-fragmentation depends strongly on the laser system applied, the percentage of ions generated by photo-fragmentation processes, of the yield of all monatomic ions (generated as result of the interaction of the sputtered particles with photons of the excimer laser beam) was estimated by a comparison between the yields obtained in Laser-SNMS experiments using the two different laser systems.

Furthermore, the combination of both laser systems in the same Laser-SNMS experiment was used to establish another ion formation process: the dye laser induced resonant post-ionization of atomic neutrals resulting from excimer laser induced photo-fragmentation of molecules. To examine such “pre-fragmentation” processes, the timing of the extraction voltage and the laser pulses was optimized for a separate extraction of the secondary ions and those ions generated as a result of excimer and dye laser irradiation, wherein the excimer laser pulse reaches the interaction volume before the arrival of the dye laser pulse. Applying this timing scheme, three different ion yields of the same element were recorded simultaneously in each analysis cycle. As the excimer laser induced ion signal and the dye laser induced ion signal were separated and simultaneously recorded, the influence of excimer laser irradiation on dye laser ion yield could be investigated and quantified.

Determination of the influence of pre-fragmentation on the dye laser signal allowed further quantitative estimations about changes in the flux composition and about the state of charge of the atomic products resulting from photo-fragmentation processes. Furthermore, pre-fragmentation might be an interesting way to enhance trace element signals, especially from surfaces characterized by a high molecular fraction in the flux of secondary particles.

Finally, combined Laser-SNMS depth profiles and images, obtained with both laser systems, were measured to demonstrate how the simultaneous detection of the three differently originated ion signals of the same element can be used to get additional information about the composition of the flux of sputtered particles. In this respect the presented method can be very helpful to prevent misleading interpretations of SIMS or Laser-SNMS data. Detailed information can be found in Guido Vering’s doctoral thesis (Münster (IPM), 2008).

Furthermore, experiments were carried out to compare the ionization efficiency of sputtered atoms using single photon ionization (SPI) and multiphoton ionization (MPI). It could be shown that with SPI (laser wavelength: 157 nm, photon energy: 7.9 eV) higher copper intensities can be obtained than with MPI (laser wavelength: 193 nm, photon energy: 6.4 eV).

For MPI the laser power density has to be increased by at least two orders of magnitude to get comparable count rates. These laser power densities can only be achieved by focusing the laser beam to a very small spot size. This reduces significantly the interaction volume between the laser beam and the sputtered particle cloud, thus reducing the amount of ionizable atoms.

SPI can also be used for efficiently post-ionizing sputtered molecules. For example, atmospheric aerosol particles collected on an aluminium foil were imaged with TOF-SIMS and Laser-SNMS [29]. Only in the case of Laser-SNMS in combination with a laser beam using photons with a wavelength of 157 nm, the

lateral distribution of polycyclic aromatic hydrocarbons (PAHs) could be determined. This can be explained by the fact that for some PAHs, SPI is possible because the photon energy of 157 nm radiation exceeds the first ionization potential (for example 7.43 eV in the case of pyrene). This will lead to higher yields in ionization processes while multiphoton ionization of molecules causes significant fragmentation. Detailed information can be found in Steffen Dambach's doctoral thesis (Münster (IPM), 2009).

A further decrease of fragmentation losses, although utilizing MPI processes, is expected by using fs-laser. In preliminary experiments, the effect of different laser radiation (ns-pulse laser, 157 nm and fs-pulse laser, 800 nm) on anthracene molecules released to gas phase on photo-ionization and photo-fragmentation was investigated. It was found that photo-ionization with fs-pulse laser generates less small fragments and the intact molecular ion signal shows the highest intensity compared to ns-pulse laser photo-ionization. This might be explained by the fact that with fs-pulses the number of photons needed for ionization in MPI can be absorbed within a shorter period compared to transition times known for fragmentation processes after photo-excitation. Therefore, less fragmentation processes can occur compared to MPI utilizing ns-pulse lasers, where fragmentation or ionization after preceding excitation are competing processes.

Also, a comparison between fs-laser-SMNS and TOF-SIMS spectra of tryptophan spin-coated on silicon showed that with fs-laser-SMNS much higher intensities of the two major tryptophan fragments could be obtained than with TOF-SIMS [28].

2.1.3. SIMS on organic and biological samples

As the Nanobeams NoE also wished to further promote SIMS for biological applications, the consortium also performed a number of round robin experiments on biological samples such as fixed cells and mixtures of isotopically labelled proteins. Furthermore, a number of PS-dPMMA samples were investigated using ToF-SIMS and NanoSIMS50 since polymer blends and biological samples show similar responses to SIMS analysis.

With respect to the biological samples, good progress in relation to aspects like the preparation and manipulation of biological specimens (cryofixation, use of different materials for supporting the sample), the systematic study of the behaviour of biological material bombarded with the primary ions (influence of sample heterogeneity, matrix effects, differential sputtering, insulating property of the sample, depth-profiling etc.), the study of formation of molecular ions (analytical potential of molecular emission) and the evaluation of methods of multi-isotope labelling (isotope recombination) was also made. From the results, it can be said that single amino acids can be detected. Further details about these activities can be found in two joint publications [3,18]. A further publication resulting from these activities has been submitted and is planned to be published in 2009.

With respect to the PS-PMMA measurements, one joint paper was written with four NoE partners contributing [5]

2.1.4. Contribution to standards

With the aim of improving the consistency of chemical measurements on the nanoscopic level with SIMS, the NoE partners LISE, IPM, MiTAC, PCPM and the CRP-Gabriel Lippmann made several measurements on a number of sample batches using static SIMS in order to develop adequate protocols to ensure a maximum of consistency between the results from different instruments in different laboratories. Bringing together the available competences within the network, the consortium members aimed at increasing the reliability of quantitative SIMS results and delineating the limitations of the experimental methodology. In this way, the results obtained in the frame of the Nanobeams NoE can play an essential role in the implementation of European standardization and conformity assessment procedures for a wide range of high-technology products.

S-SIMS has the unique capability to detect and quantify the molecular composition of the upper monolayer at the surface of solids with high sensitivity and an information depth of essentially one monolayer. S-SIMS is “powerful” because it probes directly and selectively the information that is relevant for the interaction of a material with its environment, because the outer surface layer is the interface at which all interactions occur and therefore its composition often determines a major fraction of the material’s behaviour in a given application. S-SIMS is “vulnerable” because the analysis of specific molecular information from only the upper monolayer with high lateral and depth resolution is unique in the field of molecular chemical analysis. No other method can deliver similar information. This also implies that the common procedures for sample preparation and handling (storage, transport) are no longer robust, i.e. they are often not calibrated sufficiently well to check for possible alterations of the chemical composition. For instance, the deposition of gaseous contaminants that stick to the solid’s outer surface becomes a problem when the method gives only information on the top monolayer. The objectives of this activity could most effectively be fulfilled by means of round-robin experiments. Four batches of test samples were circulated during the course of the project in order to assess the reproducibility in quantification and spatial resolution of the ToF-SIMS technique, to five different laboratories, using different ion sources with the aim of quantifying the concentration on a blue dye mixed with an IR dye in a matrix described in figure 6.

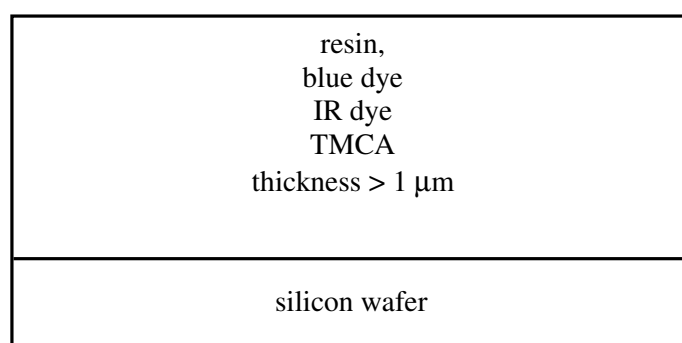


Figure 6 : The dye/polymer system.

The IR dye concentration was kept constant, as an internal standard, and the concentration of the blue dye was varied. Each participant was required to measure the intensities of molecular fragments related to the blue dye normalized by the intensities of the internal standard, versus the known concentration of the blue dye. This yielded calibration curves, which should be simply linear. A sample of unknown concentration was also distributed to all partners, who were asked to give an estimate of the blue dye concentration using the calibration curves.

Although the first round robin yielded mixed results, with some groups delivering an acceptable calibration curve and others were unable to do any quantification, owing to severe surface contamination with PDMS. The relative failure of this round robin forced the different partners to compare their different analysis protocols and to define a common analysis protocol in all laboratories. In a second batch of samples, all partners could produce good calibration curves, following the new procedure. An important outcome in this activity to standardize the analysis protocol, was that a reproducibility of about 10% could be reached. However, it appears that the best quantification accuracy is obtained when using the traditional “old” monatomic Ga^+ beams, which is quite surprising and not clearly understood. With the generalization of cluster beams, the poor quantification accuracy is an issue that should be addressed in further detail by the ToF-SIMS community.

Using this standardized analysis protocol, a last batch of samples was analyzed with the aim of determining the lateral resolution of the S-SIMS instrumentation available in the various labs. In this last batch, the nanofibres were aligned and laid flatly on the substrate. Sharp molecular images of the fibres were obtained with Bi_3^+ , with an excellent lateral resolution of 100 nm. The molecular signal was still high enough with Ga^+ to be able to visualize the fibres, but the low contrast was detrimental for the lateral resolution, limited to 200 nm at the best.

2.1.5. Contribution to the dissemination of knowledge

During the Nanobeams NoE, all project partners have been involved in dissemination of knowledge activities. The exact dates of these events are listed in section 3.3.

2.1.5.5. User schools and workshops

During the course of the Nanobeams NoE, the partners organized 4 workshops, of which one was organized in conjunction to the ECASIA conference. Furthermore, the world-leading SIMS manufacturers CAMECA and ION-TOF organized **15 user training sessions** on state-of-the-art instrumentation. Orsay Physics and Thermo Electron Cooperation organized one advanced training session each on their state-of-the-art Gallium sources and state-of-the-art high-resolution Auger Electron Spectroscopy respectively.

Moreover, due to the high demand from the nano-analysis community, the Nanobeams partners GFE, and BioSIMS organized one TEM and SPM academy respectively. Three further XPS academies were organized at LISE. These user schools, given by world-renowned experts in their field, were very successful and helped increase the knowledge amongst its user community (approx. 110 participants overall).

2.1.5.6. Exchange of personnel

During the Nanobeams project, the exchange of personnel was considered to be important for promoting the exchange of ideas between students and staff from the different institutions. These exchanges had the advantage that the collaboration in the various activities was much more effective.

Thus, for instance, several students from MiTAC visited IPM several times in order to analyze samples with organic compounds with different primary ion species and parameters. Furthermore, a researcher from PCPM visited IPM in order to measure triacontane samples within the frame of pilot project 2. Students from LISE visited the CRP-Gabriel Lippmann twice in order to analyze surface concentrations of caesium using AES. Researchers from OXMAT visited IPM in 2006 for high sensitivity experiments on frozen hydrated plant samples, and a different group of workers from OXMAT visited ION-TOF in 2008 to use the high resolution Bi source on the S-SIMS equipment for high sensitivity studies of steel and other metallic samples. 3 students theses were co-directed by 2 different NoE institutions, 2 at the CRP-GL and PCPM and 1 at the CRP-GL and LISE.

As a result of these exchanges, several joint papers could be published.

2.1.5.7. A European PhD School

As mentioned above, one of the aims of the Nanobeams NoE was the creation of a European PhD School in the area of “*Nanoanalysis using focused electron and ion beams*”. In order to reach this objective, the Nanobeams NoE created a scientific committee, the core-group, at the start of the project, which was responsible of the creation of the school as well as the overview the scientific content of the latter. The core-group was composed of the following members:

- Prof. Henri-Noël Migeon, CRP- Gabriel Lippmann
- Prof. Partick Bertrand, Université Catholique de Louvain
- Prof. Gradimir Misevic, Université de Rouen
- Prof. Joachim Mayer, RWTH-Aachen
- Prof. Susanne Siebentritt, Université du Luxembourg
- Prof. Alfred Benninghoven, Westfälische Wilhelms-Universität Münster

The European PhD School was organized such that the student finished a full cycle within 2 years. Each cycle consisted of four Teaching Weeks, the first being an overview week, and one Analysis Week. Upon fulfilling the full cycle, the student will receive a certificate as well as credit points from the University of Luxembourg. In this school, renowned professors and researchers from the Nanobeams NoE partner laboratories gave courses on the topics of SIMS, Laser-SNMS, AES and TEM. These are complemented by practical sessions on these instruments. With an average of 15 PhD students participating the various sessions, the PhD school was a real success. During the course of the project, four cycles of the European PhD School were started at CRP-Gabriel Lippmann in Belvaux (L). During this period, students that registered for the first and second cycles completed the fourth 'teaching week' and were the first to have completed the European PhD School (80 participants and 21 certificates of completion were obtained during that period).

In order to smooth the integration of this European PhD School into the University of Luxembourg's curriculum, Prof. S. Siebentritt from the University of Luxembourg was integrated into the core-group. Furthermore, the involved NoE partners have signed letters of support and thus engaged in supporting the European PhD School after the end of the Nanobeams NoE. At the beginning of the fourth project year, the core-group decided to integrate the first 'teaching week' of European PhD School organized in November 2008 into the university's curriculum. By the end of the project, a convention between the University of Luxembourg and the CRP-Gabriel Lippmann was signed engaging both partners to continue the European PhD School after the end of the Nanobeams NoE.

Thus, the European PhD School will continue to exist after the Nanobeams NoE and is an example of the strong intention of the NoE partners to continue to collaborate. The fact that the school has been integrated into the University of Luxembourg's curriculum is also an added value for the development of the Luxembourgish research sector.

All events related to the European PhD School on "Nano-analysis using finely focussed ion and electron beams" are listed in section 3.3 "Dissemination of knowledge".

2.1.6. Project impact on industry and research sector

Taking into account that the Nanobeams partners have been engaged in several projects including the world-leading SIMS manufacturers (i.e. CAMECA and ION-TOF), the Nanobeams NoE has had an enormous impact on its research sector, as well as industry. Thus, the outcome of the various research projects integrated within Nanobeams will enable the SIMS manufacturers to continue developing improved and efficient instrumentation and to keep the lead in the area of nano-analysis.

Thanks to the Nanobeams NoE, the development of a new technique combining SFM and ToF-SIMS is already underway. Being coordinated by the world leader for ToF-SIMS, this project will give the project partners the opportunity to submit further patents and to commercialize a new product.

During the course of the project, a prototype for performing quantitative analysis nano-analysis was developed (patent pending). The outcome of this project was presented at several conferences. Using the knowledge and experience gained within the Nanobeams NoE, the CRP-GABRIEL LIPPMANN is able to use this instrument for analysis.

The creation of the European PhD School on the topic of "Nano-analysis using finely focussed ion and electron beams" will have a large impact on the research sector of nano-analysis. Being the outcome of the collaboration between the Nanobeams partners as well as the University of Luxembourg, this PhD school is now integrated in the university's curriculum. Taking into account that the university was only created in 2003, the PhD school will also give a boost to the further development of the Luxembourgish research sector and as a consequence to the Luxembourgish economy.

The various user schools organized by the world-leader in SIMS and high-resolution Auger Spectroscopy as well as the advanced training courses on state-of-the-art TEM, XPS and SPM instrumentation gave the

opportunity to the user community to further improve their skills. Furthermore, the industry had the opportunity to present their latest state-of-the-art instrumentation to a large number of future customers in the research community.

2.2. Conclusion

Even though the objective for reaching a lateral resolution in SIMS was not fully achieved, the Nanobeams NoE has overall fulfilled its objectives. Technical progress has been made in several areas of key importance in the development of reliable techniques and methodologies for high resolution chemical analysis of a wide range of sample types, these have been widely reported in the scientific literature and to appropriate international audiences at major conferences, and some of these technical advances have led to improvements in commercial instrumentation. These outcomes all contribute to the international perception of the high quality of the science base in the EU, and to the competitiveness of EU industry in technical instrumentation.

3. Dissemination and use

This section provides a publishable summary of each exploitable result of the Nanobeams NoE.

3.1. Publications and presentations

3.1.1. Full list of joint publications

During the project period, the following joint publications have been submitted or published:

[1] Multitechnique characterization of thin films of immiscible polymer systems : PS-b-PMMA diblock copolymers and PS-PMMA symmetric blends

L. Kailas^a, B. Nysten^a, J.-N. Audinot^b, H.-N. Migeon^b, P. Bertrand^a

^aUniversité Catholique de Louvain, ^bCentre de Recherche Public – Gabriel Lippmann,
Surface and Interface Analysis 37 (2005) 435-443

[2] Surface segregational behaviour studied as an effect of thickness by SIMS and AFM in annealed PS-PMMA blend and block copolymer thin films

L. Kailas^a, J.-N. Audinot^b, H.-N. Migeon^b, P. Bertrand^a

^aUniversité Catholique de Louvain, ^bCentre de Recherche Public – Gabriel Lippmann,
Composite Interfaces, Vol.13, No.4-6 (2006) 423-439

[3] Method for macromolecular colocalization using atomic recombination in dynamic SIMS

G. Legent^{1,4}, A. Delaune^{1,2,4}, V. Norris^{1,4,5}, A. Delcorte^{3,4}, D. Gibouin^{1,4}, F. Lefebvre^{1,4}, G. Misevic^{1,4,5}, M. Thellier^{1,4,5} and C. Ripoll^{1,4,5*}, 2008.

¹ Laboratoire “Assemblages moléculaires: modélisation, et imagerie SIMS” (AMMIS), Faculté des Sciences de l’Université de Rouen, 76821 Mont Saint Aignan Cedex, France;

² UPRES EA 2123, Faculté de Médecine-Pharmacie de l’Université de Rouen, Boulevard Gambetta, 76000 Rouen, France;

³ PCPM, Université Catholique de Louvain, 1 Croix du Sud, B1348 Louvain-la-Neuve, Belgium;

⁴ “Nanobeams” European Network of Excellence;

⁵ Epigenomics Programme, Genopole®, 91000 Evry, France.

Journal of Phys. Chem. B 112 (2008), pp. 5534-5546, doi : 10.1021/jp7100489.

[4] Investigation of Laminated Fabric Cages Used in Rolling Bearings by ToF-SIMS

U. Gunst^a, W.- R. Zabel, N. Valle^b, H.- N. Migeon^b, G. Poll and H. F. Arlinghaus^a

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

Tribology International (2009), submitted and accepted

[5] Nanoscale characterization of PS-PMMA thin film blends

K.-H. Lau^a, K.L. Moore^a, M. Schröder^a, J.-N Audinot^b, H.-G Cramer^c, D. Rading^c, B. Boschmans^e, R. De Mondt^e, L. Van Vaeck^e, D.G Bucknall^d, E. Niehuis^c, H.-N Migeon^b, C.R.M. Grovenor^a

^aDepartment of Materials, Oxford University, Parks Road, Oxford, OX1 3PH, UK

^bDépartement Science et Analyse des Matériaux (SAM), Centre de Recherche Public - Gabriel Lippmann, 41, rue du Brill, L-4422 Belvaux, Luxembourg

^cION-TOF GmbH, Heisenberg Str. 15, D-48149 Münster, Germany,

^dSchool of Polymer, Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA30332-0295, USA

^eDept. of Chemistry, University of Antwerp (CDE), Universiteitsplein 1, 2610 Wilrijk, Belgium
Surface and Interface Analysis (2009), submitted

[6] Mass spectrometric characterization of DNA microarrays as a function of primary ion species

S. Hellweg^a, A. Jacob^b, J.D. Hoheisel^b, Thomas Grehl^c, and Heinrich F. Arlinghaus^a

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^c Deutsches Krebsforschungszentrum Heidelberg, Heidelberg, Germany

^b ION-TOF GmbH, Münster, Germany

Appl. Surf. Sci., 252 (2006), 6742-6745, doi:10.1016/j.apsusc.2006.02.281

[7] Metal-Assisted Secondary Ion Mass Spectrometry Using Atomic (Ga⁺, In⁺) and Fullerene Projectiles

A. Delcorte^{*†}, S. Yunus[†], N. Wehbe[†], N. Nieuwjaer[†], C. Poleunis[†], A. Felten[‡], L. Houssiau[‡], J.-J. Pireaux[‡], and P. Bertrand[†]

[†] PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium, and

[‡] LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Published in: *Anal. Chem.*, 79 (10), 3673 -3689, 2007, doi: 10.1021/ac062406l

[8] Molecular Ion Yield Enhancement Induced by Gold Deposition in Static Secondary Ion Mass Spectrometry

Wehbe, N. [†]; Delcorte, A. [†]; Heile, A. [‡]; Arlinghaus, H. [‡]; Bertrand, P. [†]

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[‡] IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

Applied Surface Science, 255 (2008), 824-827 (proceedings SIMS XVI conference), doi:10.1016/j.apsusc.2008.05.068

[9] Investigation of Methods to Enhance the Secondary Ion Yields in TOF-SIMS of Organic Samples

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, P. Van Royen^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

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^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

Surface and Interface Analysis, (proceedings ECASIA'07 conference), doi: 10.1002/sia.2810

[10] Influence of Different Primary Ion Species on the Secondary Ion Emission from PNA/DNA Biosensor Surfaces

Sebastian Hellweg^a, Andreas Heile^a, Thomas Grehl^b, and Heinrich F. Arlinghaus^a

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b ION-TOF GmbH, Münster, Germany

Surf. Interface Anal., 40 (2008), 198-201 (proceedings ECASIA'07 conference), doi: 10.1002/sia.2684

[11] Effects of Metal Nanoparticles on the Secondary Ion Yields of a Model Alkane Molecule upon Atomic and Polyatomic Projectiles in Secondary Ion Mass Spectrometry

N. Wehbe^a, A. Heile^b, H. F. Arlinghaus^b, P. Bertrand^a and A. Delcorte^a

^a PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

Anal. Chem., 80 (2008), 6235-6244 doi: 10.1021/ac800568y

[12] Ion yield improvement for S-SIMS by use of polyatomic primary ions

Roel De Mondt^{*a}, Luc Van Vaeck^a, Andreas Heile^b, Heinrich F. Arlinghaus^b, Nicolas Nieuwjaer^c, Arnaud Delcorte^c, Patrick Bertrand^c, Jens Lenaerts^d, Frank Vangaever^d

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^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^c PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,

^d Agfa-Gevaert N.V., Septestraat 27, B-2640 Mortsels, Belgium

Rapid Communications in Mass Spectrometry (2008), Vol. 22 Issue 10, 1481-1496, doi: 10.1002/rcm.3533

[13] Storing Matter: A new quantitative and sensitive surface analysis technique

T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, G. Slodzian^c, H.-N. Migeon^a

^a Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

^b LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.109

[14] The Storing Matter technique: application to inorganic samples

P. Philipp^a, F. Lacour^a, T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, G. Slodzian^c, H.-N. Migeon^a

^a Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

^b LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.075

[15] The Storing Matter technique: preliminary results on PS and PVC

P. Philipp^a, B. Douhard^b, F. Lacour^a, T. Wirtz^a, L. Houssiau^b, J.-J. Pireaux^b, H.-N. Migeon^a

^a Centre de Recherche Public-Gabriel Lippmann, Belvaux, Luxembourg

^b LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

Applied Surface Science (2008), doi:10.1016/j.apsusc.2008.05.070

[16] On the understanding of positive and negative ionization processes during ToF-SIMS depth profiling by co-sputtering Cesium and Xenon

J. Brison^c, J. Guillot^b, B. Douhard^a, R. Vitchev^d, H.-N. Migeon^b, L. Houssiau^a

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^b Centre de Recherche Public Gabriel Lippmann, SAM Laboratory, 41, rue du Brill, L 4422 Belvaux

^c University of Washington (Seattle) since October 2007, previously in LISE

^d VITO, Boeretang 200, B-2400 Mol, Belgium since July 2007, previously in LISE

Nucl. Instr. Meth. Phys. Res. B, available online December, 2008, doi:10.1016/j.nimb.2008.11.026

[17] Metal-Assisted SIMS and Cluster Ion Bombardment for Ion Yield Enhancement

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, L. Van Vaeck^d, H. F. Arlinghaus^a

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^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

Appl. Surf. Sci., 255 (2008), 941-943 (proceedings SIMS XVI conference), doi:10.1016/j.apsusc.2008.05.007

[18] Biological sample preparation for chemical microscopy by dynamic mode Secondary Ion Mass Spectrometry (SIMS)

Gradimir N. Misevic^{1*}, Bernard Rasser², Vic Norris¹, Cédric Dérue¹, David Gibouin¹, Fabrice Lefebvre¹, Marie-Claire Verdus¹, Anthony Delaune¹, Guillaume Legent¹ and Camille Ripoll¹

¹ AMMIS, University of Rouen, France,

² Orsay Physics, Fuveau, France

Published in February 2009 in:

Methods in Molecular Biology, Extracellular Matrix Protocols (second edition), Humana Press.

In the framework of the activities on biological samples, one further publication has been submitted and is planned to be published in 2009.

3.1.2. Presentations

Imaging of electrospun nanofibres with static and dynamic secondary ion mass spectrometry (S-SIMS and NANO-SIMS)

P. Van Royen, L. Van Vaeck, L. Ruys, A. M. dos Santos, P. Dubruel, E. Schacht, J.-N. Audinot and H.-N. Migeon

7th International Symposium on Frontiers in Biomedical Polymers, 24th – 27th June 2007 (Gent, Belgium)

Investigation of Tribological Boundary Layers of High-Speed Rolling Bearings Elements by AES, XPS and SIMS

U. Gunst, J. Guillot, N. Valle, W.-R. Zabel, H.-N. Migeon, G. Poll and H. Arlinghaus
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey 9th – 14th September 2007 (Belgium)

Effect on depth resolution of low impact energy, sample rotation and oxygen flooding during dynamic SIMS analyses of multilayer structures

N. Valle, J.-N. Audinot, P. Philipp, A. Merkulov, H.-N. Migeon
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey, 9th - 14th September 2007 (Belgium)

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c
^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium
^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany
^c Agfa Graphics N.V., Mortsels, Belgium
(SIMS Europe 2008, Münster)

Investigation of Methods to Enhance the Secondary Ion Yields in TOF-SIMS of Organic Samples

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, R. De Mondt^d, P. Van Royen^d, L. Van Vaeck^d, H.F. Arlinghaus^a,
^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany
^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,
^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium
^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium
ECASIA '07, 12th European Conference on Applications of Surface and Interface Analysis
Bruxelles-Flagey, 9th - 14th September 2007 (Belgium)

Storing Matter: a new quantitative and sensitive surface analysis technique

T. Wirtz, L. Houssiau, J.-J. Pireaux, G. Slodzian, H.-N. Migeon
SIMS XVI Kanazawa (2007)

The Storing Matter technique: application to inorganic samples

P. Philipp, F. Lacour, T. Wirtz, L. Houssiau, J.-J. Pireaux, G. Slodzian, H.-N. Migeon
SIMS XVI Kanazawa (2007)

The Storing Matter technique: preliminary results on PS and PVC

P. Philipp, B. Douhard, F. Lacour, T. Wirtz, L. Houssiau, J.-J. Pireaux, H.-N. Migeon
SIMS XVI Kanazawa (2007)

Nano-characterisation by high resolution SIMS analysis

C. Grovenor, Invited talk at ECASIA, Brussels (2007).

High resolution surface analysis of metallic and biological specimens by NanoSIMS analysis

C. Grovenor, Invited talk at EMC Aachen (2008).

High resolution surface analysis of metallic and biological specimens by NanoSIMS

C. Grovenor, Invited talk at SIMS Europe 2008

3.1.3. Selection of Poster presentations

Use of S-SIMS for the surface analysis of nanofibres formed through electrospinning

P. Van Royen^a, L. Van Vaeck^a, L. Ruys^b, A.M. dos Santos^c, E. Schacht^c, J.-N. Audinot^d, H.-N. Migeon^d

^a University of Antwerp, Wilrijk, Belgium; ^b Centexbel-Gent, Zwijnaarde, Belgium;

^c University of Gent, Gent, Belgium; ^d Centre de Recherche Public, Belvaux, Luxembourg.

Status and future of nanofibers by electrospinning, CNT VII conference in Frankfurt, October 23rd and 24th, 2006

On the understanding of positive and negative ionization processes during ToF-SIMS depth profiling by co-sputtering Cesium and Xenon

J. Brison, J. Guillot, B. Douhard, H.-N. Migeon and L. Houssiau

SIMS XVI Kanazawa (2007)

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a, L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c

^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium

^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^c Agfa Graphics N.V., Mortsel, Belgium

(SIMS Europe 2008, Münster)

Investigation of Metal-Assisted SIMS and Cluster Ion Bombardement for Analysis of Polystyrene Surfaces

A. Heile^a, D. Lipinsky^a, N. Wehbe^b, A. Delcorte^b, P. Bertrand^b, A. Felten^c, L. Houssiau^c, J.-J. Pireaux^c, P. Soete^d, R. De Mondt^d, L. Van Vaeck^d, H.F. Arlinghaus^a,

^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,

^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

(SIMS Europe 2008, Münster)

3.1.4. Abstracts:

TOF-S-SIMS molecular depth profiling using mechanical wear test methodology

R. De Mondt^a, L. Van Vaeck^a, A. Heile^b, H.F. Arlinghaus^b, F. Vangaever^c, J. Lenaerts^c

^a MiTAC, Universiteit Antwerpen, Antwerp, Belgium

^b IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^c Agfa Graphics N.V., Mortsel, Belgium

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Investigation of Metal-Assisted SIMS and Cluster Ion Bombardement for Analysis of Polystyrene Surfaces

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^a IPM, Westfälische Wilhelms-Universität Münster, Münster, Germany

^b PCPM, Université Catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium,

^c LISE, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

^d MiTAC, Universiteit Antwerpen, Antwerp, Belgium

(SIMS Europe 2008, Münster)

Characterisation of the co-ordination of nickel in frozen hydrated leaves of the hyperaccumulator plant *Alyssum lesbiacum* by ToF SIMS with principal component analysis

K.E. Smart^a, J. Möller^b, B. Tyler^c, J.A.C. Smith^c, H.F. Arlinghaus^b, C.R.M. Grovenor^a

^aUniversity of Oxford, ^bUniversity of Münster, ^cUniversity of Utah

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Applications of an In Vacuum-Cryo-Sectioning Instrument for ToF-SIMS Analyses of Non-Dehydrated Samples

J. Moeller^a, K. Smart^b, B.J. Tyler^c, D. Lipinsky^a, H.F. Arlinghaus^a

^aUniversity of Münster, ^bUniversity of Oxford, ^cUniversity of Utah

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Cationisation of polymers depending of the structure of the metallic deposition

L. Nittler^a, A. Delcorte^b, P. Bertrand^b, H.-N. Migeon^a

^aCentre de Recherche public - Gabriel Lippmann, Belvaux, Luxembourg; ^bUniversity of Louvain, Louvain-la-Neuve, Belgium

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

Evaluation of the ion yield improvement for S-SIMS by the use of polyatomic primary ions for thermographic applications

R. de Mondt^a, L. Van Vaeck^a, A. Heile^b, H. Arlinghaus^b, N. Niewjaer^c, A. Delcorte^c, P. Bertrand^c, J. Lenaerts^d, F. Vangaeve^d

^aUniversity of Antwerp (CDE), Wilrijk, Belgium; ^bUniversity of Münster, IPM, Münster, Germany;

^cUniversity of Louvain, PCPM, Louvain-La-Neuve, Belgium; ^dAgfa-Gevaert, Mortsels, Belgium

Published in: 5th European Workshop on Secondary Ion Mass Spectrometry (SIMS Europe 2006): Final Program and Book of Abstracts

3.2. Exploitable knowledge and its use

Table 2 shows the exploitable knowledge that resulted from the collaboration of the Nanobeams NoE partners:

Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Patents or other IPR protection	Owner & Other Partner(s) involved
“Tele-presence module”	Videoconferencing tool specifically designed to follow nano-analyses	Nano-analysis, Nanomedicine, Industry		CRP-GL
Sputtering Storing Matter instrument	Semi-quantitative nano-analysis tool	Nano-analysis, Fraud detection	patent pending	CRP-GL, LISE
Publications	19 joint publications	Physics, Chemistry, Biology, Materials Science (SIMS, TEM, AES, XPS, SPM)		All Nanobeams partners
PhD School	Lectures, practical sessions	Physics, Chemistry, Biology, Materials Science (SIMS, TEM, AES)		CRP-GL, IPM, PCPM, LISE, GFE, OXMAT, MiTAC, BioSIMS, Cameca, ION-TOF, University of Luxembourg

Table 2: The above table shows an overview of exploitable results and of how they can be exploited in future

3.3. Dissemination of knowledge

The tables here-underneath list all events organized within the frame of the Nanobeams NoE as well as the conferences attended by NoE partner in order to talk about the work done within the NoE (see tables 3, 4, 5 and 6).

Planned/actual date	Type	Type of audience	Countries addressed	Size of audience	Partner responsible/involved
19 th October 2004	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
19 th October 2004	Press release(press/radio/TV)	General Public	Luxembourg	80'000	CRP-GL
March 2005	Press release(press/radio/TV)	General Public	Luxembourg	80'000	CRP-GL
17 th March 2005	Launch of project web site	General Public/Research	Open to any country		CRP-GL
June/July 2005	Training of Users	Research	Open to any country	6	Cameca
September/October 2005	Press release(press/radio/TV)	Industry (economical sector)	Luxembourg	10'000	CRP-GL
October 2005	Training of Users	Research	Open to any country	6	ION-TOF
October 2005	Training of Users	Research	Open to any country	6	ION-TOF
23 rd October 2005	Open door event	General Public	Luxembourg	250	CRP-GL
22 nd & 23 rd and 29 th & 30 th October 2005	Poster	General Public	Luxembourg	10'000	CRP-GL
3 rd and 4 th November 2005	European Workshop	Research	Europe	29	PCPM
21 st - 25 th November 2005	European PhD School	Research	Europe	34	CRP-GL
25 th November 2005	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
29 th November 2005	Press release(press/radio/TV)	General Public	Luxembourg	100'000	CRP-GL
5 th - 9 th December 2005	Training of Users	Research	The world	5	TE

Table 3: The above table summarizes the dissemination activities in the first 12 months and just before the start of the Nanobeams project.

Planned/actual date	Type	Type of audience	Countries addressed	Size audience	Partner responsible /involved
February 7 th - 9 th , 2006	User session Training (XPS Academy)	Research	Europe	20	LISE
March 6 th - 10 th , 2006	User session Training	Research	Europe	6	ION-TOF
March 13 th - 17 th , 2006	European School PhD	Research	Luxembourg	20	CRP-GL
March 2006	Press release (press/radio/TV)	General public/Research	Europe	100'000	CRP-GL
June 12 th - 16 th , 2006	European School PhD	Research	Europe	20	CRP-GL
June 18 th , 2006	Open Door event	General public	Luxembourg	250	CRP-GL
June 2006	Press release (press/radio/TV)	General public	Luxembourg	100'000	CRP-GL
September 11 th - 15 th , 2006	European School PhD	Research	Europe	10	CRP-GL
September 24 th - 26 th , 2006	SIMS Europe 2006 (conference)	Research	Open to any country	230	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
October 19 th - 20 th , 2006	Conference	Research	Europe	190	CRP-GL
October 23 rd - 27 th , 2006	European Workshop	Research	Europe	22	PCPM
October 23 rd - 27 th , 2006	User session Training	Research	Europe	6	ION-TOF
November 21 st , 2006	Conference	Industry	Luxembourg	40	CRP-GL
November 27 th - December 1 st , 2006	European School PhD	Research	Europe	24	CRP-GL
December 11 th - 15 th , 2006	User session Training	Research	Europe	8	CAMECA

Table 4: The above table summarizes the dissemination activities within the in the second year of the Nanobeams project.

Actual date	Type	Type of audience	Countries addressed	Size audience	of Partner responsible /involved
January 29 th – 31 st , 2007	XPS Academy	Research	Europe	5	LISE
March 5 th – 9 th , 2007	User Training session	Research	Europe	6	ION-TOF
March 19 th – 23 rd , 2007	European PhD School	Research	Europe	11	CRP-GL
May 21 st – 25 th , 2007	European PhD School	Research	Europe	7	CRP-GL
June 18 th – 22 nd , 2007	European PhD School	Research	Europe	20	CRP-GL
September 9 th – 14 th , 2007	European Workshop/ ECASIA	Research	Europe	688	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
October 8 th – 10 th , 2007	TEM Academy	Research	Europe	3	GFE
October 8 th – 10 th , 2007	User Training session	Research	Europe	5	ION-TOF
SIMS XVI	Conference	Research	Open to any country	250	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
November 19 th – 23 rd , 2007	European PhD School	Research	Europe	15	CRP-GL
November 19 th – 23 rd , 2007	User Training session	Research	Europe	5	CAMECA
December 12 th – 14 th , 2007	European PhD School	Research	Europe	5	CRP-GL

Table 5: The above table summarizes the dissemination activities in the third year of the Nanobeams project.

Actual date	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
January 29 th – 31 st , 2008	XPS Academy	Research	Europe	5	LISE
February 22 nd , 2008	User session Training	Research	Europe	6	Orsay Physics
March 3 rd – 8 th , 2008	European School PhD	Research	Europe	8	CRP-GL
March 10 th - 14 th , 2008	User session Training	Research	Europe	6	ION-TOF
June 9 th – 13 th , 2008	European School PhD	Research	Europe	12	CRP-GL
September 14 th – 16 th , 2008	SIMS Europe 2008	Research	Open to any country	200	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
September 22 nd – 26 th , 2008	European School PhD	Research	Europe	2	CRP-GL
September 29 th – October 3 rd , 2008	User session Training	Research	Europe	5	ION-TOF
October 20 th – 24 th , 2008	User session Training	Research	Europe	6	ION-TOF
November 17 th – 21 st , 2008	European School PhD	Research	Europe	16	CRP-GL
December 1 st – 5 th , 2008	User session Training	Research	Europe	5	CAMECA
December 10 th – 11 th , 2008	European Workshop	Research	Europe	26	CRP-GL, IPM, PCPM, LISE, OXMAT, MiTAC, BioSIMS, CAMECA, ION-TOF
December 8 th – 11 th , 2008	User session Training	Research	Europe	5	CAMECA

Table 6: The above table summarizes the dissemination activities in the fourth year of the Nanobeams project.

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