Co-Nanomet

Co-ordination of Nanometrology in Europe

Consultation on a

European Strategy for Nanometrology

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Introduction

Nanotechnology is a pervasive technology that allows manufacturers to design the functionality of a product by using the novel dimensional, chemical, material, mechanical and electromagnetic properties found at the nanoscale. As products based on aspects of nanotechnology increasingly enter the commercial marketplace, for example, in sun protection creams or sports equipment, quality control of the manufacturing process is required particularly where product characteristics at the nanoscale are of concern, for example, potential health risks or other performance requirements. A key enabling technology for quality control at this scale is nanometrology [1,2]: *the measurement and characterisation of structures or materials with at least one dimension less than or equal to 100 nm*[1]. Since nanotechnology is an enabling technology worldwide research institutes, universities as well as national metrology institutes (NMIs) are working on this field. Many governments worldwide have existing nanotechnology policies and are taking the preliminary steps towards nanometrology strategies, for example in support of pre-normative R&D and standardisation work. As part of the EC-funded project, Co-nanomet, a foresight review document [3] has been produced that surveys the current nanometrology requirements and future strategies in support of the development of European nanotechnology as formulated by a number of European Nanometrology Action Groups. The technical findings of the foresight review are summarised in this consultative paper, and the scientific and political communities are invited to feedback comments.

This consultative paper addresses the field of nanometrology through seven discipline areas. Dimensional and chemical nanometrology, being all-pervasive, are treated first. Applications for the measurement of thin film parameters and nanostructured materials and surfaces, which are seen as key materials areas having specific metrology challenges, are covered next. As two of the most widely relevant families of functional properties, measurement of mechanical and electrical properties at the nanoscale are then reviewed. The final section describes biological nanometrology, which is perhaps the most interdisciplinary applications area, and presents unique challenges. Within each area, a review is provided of current status, the capabilities and limitations of current techniques and instruments, and future directions being driven by emerging industrial measurement requirements.

NMIs, both within Europe (nineteen in total) and worldwide (eleven in total), were contacted for the foresight review to identify their existing nanometrology activities, strategies and future priorities. Other non-NMI research into nanometrology was also addressed. Input to the foresight review was provided through the discussion papers published by the European Nanometrology Action Groups instigated under the Co-nanomet programme [4]. This consultative document focuses on technical aspects and challenges of nanometrology. Issues of regulation and skills development will be discussed in a further strategy document (see below).

Feedback from the foresight review and this consultative paper (following industrial circulation) will form input to a European strategy for nanometrology. The draft strategy will be published on the Co-nanomet website in February 2010 and will be updated to a final document within one year. Such a strategy will allow Europe to benefit from its multi-national expertise and to rationalise activities where multiple countries are carrying out similar research. It is expected that the strategy proposed will be considered by the European Commission when planning future Framework programmes. Co-nanomet activities are also expected to stimulate proposals for research topics and projects where nanometrology enters

[1] Note that it is common for nanometrology to cover, not just dimensions, but measurement uncertainties and tolerances. In this case, we could consider the measurement of a 1 m diameter telescope mirror with only a few nanometres of surface form deviation as being part of nanometrology. However, the scope of the Co-nanomet project only covers structures or materials with dimensions less than or equal to 100 nm.

into the various calls of the major (400 M€) European Metrology Research Programme, which EURAMET is implementing on behalf of the European Commission during the coming seven years[2].

In the following, each expertise area will be summarised, followed by a short review of existing nanometrology policies across the world.

Dimensional Nanometrology

The term nanotechnology was used for the first time by Taniguchi [5] for the classification of measurement techniques necessary in the field of dimensional metrology to ensure and to control future production processes. The key measurement methods used for dimensional nanometrology are shown using a so-called amplitude-wavelength graph, which plots vertical against lateral dynamic ranges (see Figure 1).

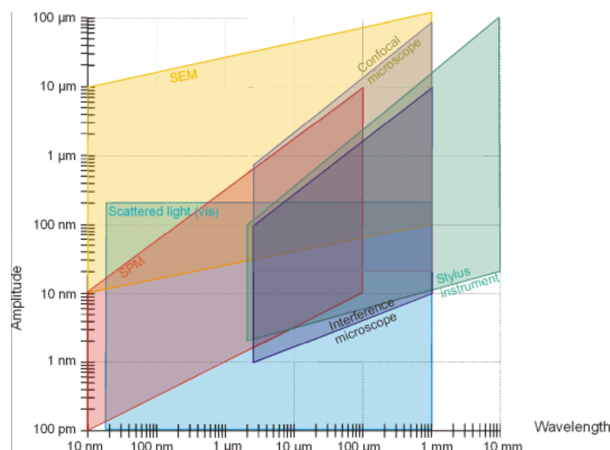


Figure 1 Measurement techniques and their typical dynamic ranges in the lateral (wavelength) and vertical (amplitude) directions

[2] Co-nanomet has an agreement with EURAMET, the European Association of National Metrology Institutes (www.euramet.org) to exchange information about nanometrology and future strategy.

A recent review of the area has been published [6] and covers most of the instruments used in this area. Within the scanning probe techniques, scanning force microscopes (SFM), for example the atomic force microscope (AFM), are essential tools for nanotechnology [7]. There are many commercially available SFMs and most NMIs have, or are developing, metrological SFMs, i.e. instruments with laser interferometry or other high-stability SFMs with traceable displacement measurement of their scale axes. The Co-nanomet foresight review highlighted several areas of SFM research that need addressing:

- The lateral scanning range of SFMs needs to be increased. Currently SFMs have lateral scanning ranges, at best, of hundreds of micrometres, but this needs to be increased to several tens of millimetres to allow the measurement of large area structured surfaces, wafers and optics [8]. This will involve increases in the scanning speed and the use of both intelligent probing and control systems, and sampling strategies that may include combining SFMs with other instrumentation for overview and 'coarse' scanning [9]. Intelligent multi-sensor concepts with improved data fusion algorithms and automated detection of possible regions of interests will help to fill the large dynamic range and improve efficiency.

- The resolution of SFMs, both metrological and non-metrological, needs to be improved to allow the measurement of ever-smaller structures with higher accuracy. This requires, among others things, a better theoretical understanding of surface-probe interactions and refined probe characterization.

- SFMs are inherently areal measurement techniques (2.5D) but increasingly true three-dimensional (3D) measurements are required. This is especially true in the semiconductor industry where high aspect ratio (HAR) structures and critical dimensions (CDs) need to be measured [10], and for the development of MEMS and NEMS. New probing strategies need to be developed with the ability to carry out 3D probing and scanning (similar to methods used with co-ordinate measuring machines (CMMs)) that can access sidewalls, undercuts, bores, etc.

- The understanding of the interaction between an SFM probe and a surface is essential for the metrology and should be better understood so that appropriate corrections or allowances can be made for true quantification of dimensional measurements [11].

- All the above SFM research areas need to be supported by an appropriate traceability infrastructure. This includes the further development of metrological SFMs, transfer artefacts[3] and optical interferometers to provide the route to traceability.

There is an increasing use of structured surfaces to affect the functionality of a part [12]. This requires fast and accurate areal measurement and characterisation techniques. SFM is commonly used to measure structure with lateral scales less than 500 nm, but for larger scale, stylus and optical instruments are used with sub-nanometre vertical resolution. Areal specification standards will be published within the next year and the traceability infrastructure is now being developed [13].

Scatterometry (or diffractometry) is a method that is used extensively in the semiconductor industry to measure grating periods and structured surfaces. Issues that still need to be addressed include: the effect of imperfections, how to measure increasingly smaller areas and computing time. Spectroscopic ellipsometry (SE) is a special case of scatterometry that is important for the measurement of nanometric thin films, including multi-layers (see later). Further research is required to standardise scatterometry techniques and compare them to other optical and contact methods.

Scanning electron microscopy (SEM) is a very versatile and well-established tool that has a large dynamic range and is capable of high magnification. Recently, novel 3D transfer artefacts applicable to stereoscopic SEM (as well as SFM and many optical methods) have been developed with corresponding analysis software [14]. Transmission electron microscopy (TEM) is also a well-established techniques but research is still required to increase its versatility, whilst keeping the cost of the instrument down, and into methods for sample preparation. Although electron microscopy methods are highly advanced and have contributed extensively to various areas of life science research, the interaction of internationally recognized laboratories with complementary expertise is limited. Other particle beam methods, such as focussed ion beam (FIB) and helium ion microscopy are starting to be used widely, but traceability routes are only in their infancy.

Optical interferometry is often the method used to gain direct calibration of displacements in other instrument, for example metrological SPMs. The EMRP-funded NANOTRACE project [15] involves several NMIs and aims to develop a range of sub-nanometre resolution interferometers that have their non-linearity determined using an x-ray interferometry facility [16]. NANOTRACE is going some way towards meeting the requirements of the next generation of optical interferometers, but the challenge will be to disseminate these requirements to users outside of NMIs and to make displacement measurements with picometre resolution and accuracy less challenging.

Chemical Nanometrology

An overview of the techniques used for chemical analysis at the nanoscale is presented in Figure 2 [17], together with their associated spatial resolutions. It is important to point out that none of these techniques alone can provide a complete chemical analysis. However, combined information can be given, such as structural properties, composition of chemical species or chemical states contained in the measured sample.

Of the techniques shown in Figure 2, some are primary methods that directly measure an amount of chemical or elemental species, whilst others determine an amount, either after a specific calibration step or expressed as the thickness of the film considered. The traceability of measurements through the mole or the metre is then necessary to provide some metrological analysis.

The world-wide review of NMI activity, carried out under the Co-nanomet project, distinguished three priority areas being addressed to meet industrial needs:

[3] Transfer artefacts, material measures, physical standards or calibration artefacts are all kinds of reference materials, some of which may be certified reference materials. The characteristics of reference materials and certified reference materials are described in ISO Guides 31 to 35.

- Instrumentation dedicated to the measurement of the chemical composition of thin films or materials and for the concentration of species.
- Techniques related to the characterisation of the structural properties.
- Techniques measuring the granulometry of nanoparticles in different media (liquids, gases).

A further focus is on preserving molecular information whilst depth profiling at high spatial resolution enabling the determination of the full three-dimensional chemical nano-structure.

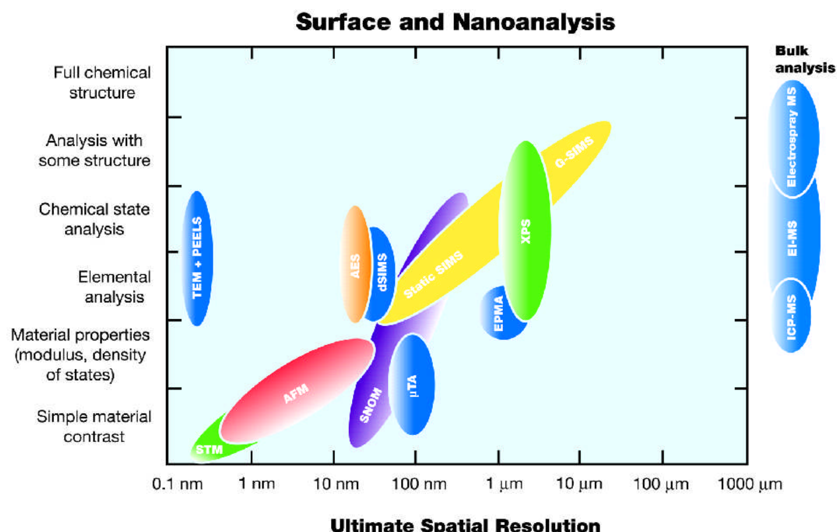


Figure 2 Methods of surface chemical analysis (courtesy of NPL) [17]

X-ray photoelectron spectroscopy (XPS) is one of the most quantitative techniques to determine both atomic concentration and the chemical environment of the species at the surface of a sample. Under special conditions, XPS is well suited for the characterization of nanopowders. A survey on the state-of-the art and future challenges has been recently published [18]. The content of this paper has been developed in to a new work item under ISO TC 201, 'X-ray photoelectron spectroscopy -- Guidelines for analysis'. XPS has also recently been used to provide traceable measurements of the thickness of ultra thin (<1.5 nm) layers of silicon dioxide on silicon, key for the electronics industry [19]. This work confirms uncertainties as low as 0.068 nm. XPS has a high potential for non-destructive depth profiling (<10 nm from the surface) in angle resolved mode [20] or by using synchrotron radiation for variable excitation energy XPS. Proofs of principle have been published for nanostructured samples as self assembled monolayers and particles [21]. The metrological underpinning of those approaches is a future challenge.

Scanning Auger electron spectroscopy is also used to probe the surface chemical composition of nanostructures down to the 10 nm length scale. This technique is used to determine the stoichiometry in semiconductor quantum dots and other nanostructures. It is also applied to the identification of chemical contaminants in electronic devices and diverse layered structures at the sub-micrometre length scale.

Secondary ion mass spectroscopy (SIMS) is a highly sensitive technique that may be used to determine the composition of a material, typically, at or near the surface. Deduced from specific calibrations, a quantity of atoms as a function of their mass charge ratios is measured as a function of depth. Detection limits for trace elements are typically between 10^{12} and 10^{16} atoms per cm^3. In static mode, the technique is able to provide information about the topmost single atomic layer of the surface. For organic surfaces, recent developments with time of flight SIMS (ToF-SIMS) and cluster ion beam sources have extended molecular structure analysis to near-surface layers. The electronic materials industries (semiconductors, optoelectronic devices, etc.) are the largest users of SIMS. The geological community also uses SIMS for laterally resolved isotopic and elemental measurements. Applications of CAMECA's nanoSIMS, instrument having a probe diameter at around 50 nm to biological samples has been reviewed recently revealing a lateral resolution at the deeper sub-micrometre scale [22]. However, there are two main limitations of SIMS. Firstly, SIMS is a destructive technique. The second limitation is related to the ionization efficiency of the method which means that results have to be analysed in a very different way from one elemental species to another.

Energy dispersive x-ray (EDX) analysis and electron energy loss spectroscopy (EELS) are used in (scanning) TEM to study the chemical composition of nanostructures. In the EDX technique, the displacement of target material electrons by primary electrons triggers the release of x-ray photons, the energies of which are characteristic of the atom from which they were released. In the EELS technique characteristic energy loss features are measured for the transmitting primary electrons by using a kinetic energy analyzer. Information on elements and their chemical state are obtained from EELS analysis. Spatial resolutions down to approximately 2 nm can be achieved when applied to cross-sections thinned to electron transparency (i.e. about 100 nm or less) as prepared for scanning TEM (STEM) analysis. Nanoparticles on high BET[4] area supports, that are often used as catalysts, are another important application of analytical TEM, for example, platinum nanoparticles on a catalytically active membrane-electrode-assembly [23]. Electron-beam-spreading effects result in poorer resolution in plan-view SEM from bulk surfaces, although layers down to about 10 nm thickness can be detected.

Fourier Transform infra-red spectroscopy (FTIR) can be applied for the quantitative chemical analysis of solids, liquids and gasses by identifying the chemical bonds. The wavelength of light absorbed by the sample in the infra-red region, is the direct signature of the chemical bonds contained in the sample. Inherently the lateral resolution of FTIR is limited to the micrometre range. By using specialized modes of FTIR, thin film analysis is enabled down to thicknesses of some 10 nm. For most common materials, the spectrum of an unknown sample can be identified by comparison to a library of known compounds. To identify less common materials, FTIR needs to be combined with nuclear magnetic resonance (NMR), mass spectrometry, emission spectroscopy, x-ray diffraction and/or other techniques.

Dynamic light scattering (DLS) is the only widely used instrumentation to provide a measurement of size and concentration of nanoparticles in liquid media. In DLS, only a very small region of solution is focused for the measurement, inducing fluctuations in the intensity of the scattered light. Moreover, the hydrodynamic radius deduced from the measurements can differ significantly from the true physical size. However, this technique is particularly efficient at sensing the presence of very small amounts of aggregated protein (less than 0.01 % by weight) and studying samples containing a very large range of masses. Recently DLS has been used to correlate sizes of colloidal silver nanoparticles with their antibacterial activity [24].

The distribution of concentration as a function of their size may be assessed for aerosol nanoparticles by scanning mobility particle sizer (SMPS) or electrical low pressure impactor techniques. SMPS combines an aerosol particle mass analyser (APM) that selects particles as a function of their size and a classifier counter that allows a determination of a quantity of particles for each size. Sizes associated are deduced from a calculation with simulation of the physical phenomena, and are actually expressed as an equivalent diameter. This outlines the limit of such a measurement, being highly dependent on the model implemented in the equipment. Moreover, only a few studies present some uncertainties [25] and sampling is the crucial point to overcome in order to measure a significant (quantity and quality) of gas extract.

The Surface Analysis Working Group at the CCQM/BIPM has identified the challenging areas for surface chemical and structural analysis as:

- microelectronics;
- life sciences, bio-nano-objects;
- manufactured nano-objects.

With regard to microelectronics, this area has been a key driver of metrology and standardisation developments in surface analysis for the last forty years. The current introduction of 32 nm technology has continued to bring great challenges, for example in the quantitative depth profiling of gate oxides at or below 1 nm thickness. The International Technology Roadmap for Semiconductors, 2007 Metrology Edition provides further detailed definitions of future challenges existing in this area.

In the life science area the challenge is the traceable quantification of functional groups in monolayers and multilayers nano-scaled in one or two dimensions. The latter case points to

[4] BET theory is a rule for the physical adsoption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material

the requirement to develop appropriate imaging methods. However, other relevant industrial technologies also require those measurement capabilities. Examples are MEMS, OLEDs, organic and dye sensitised solar cells, fuel cells and micro batteries. In many cases, molecular information has to be preserved whilst depth profiling and appropriate depth profiling methods have to be developed either based on sputtering (SIMS and XPS with cluster ion sputter sources) or non-destructive techniques based on XPS.

Analysis of bio-nano objects and manufactured nano-objects (including films made thereof) is required at a level of a full determination of the 3D nano-structure. There is also an increasing need to determine the composition of very small quantities of matter or chemical species. This is specifically the case in the biological area, for the analysis of DNA for example. Currently, in such cases, the concentration of matter has first to be multiplied, prior to analysis. Improving the sensitivity of measurements leading to chemical composition would avoid such a step. Consequently new approaches have to be developed and existing ones based on XPS, XAS, SPM and SIMS have to be improved in terms of better spectral and spatial resolution, better contrast and better sensitivity for elements and molecular species. Ideally new methods should have capabilities to work in situ, at ambient air and/or in liquid surroundings.

In order to establish traceability in chemical nanometrology efforts are needed in the development of certified reference materials useful for chemical analysis at the nanoscale. As part of recent ISO TC229 activities a list of worldwide commercially available nanoscale reference materials is available as well as links to manufacturers and vendors [26]. The number useful for chemical analysis at the nanoscale is relatively small and there is a strong need for further developments.

Finally, links between dimensional or chemical properties of nanoparticles with toxicity in human bodies needs to be studied. Correlation between distribution sizes, chemical compounds and tracheal diseases are of great interest.

Thin Film Nanometrology

The applications and economic impact of thin films for nanotechnological products are large, and extend over a wide range of industry sectors. As buried layers, thin films are core to the performance of state-of-art microelectronics and magnetic data storage devices. As surface functional layers they are employed for wear-, impact- and scratch-resistance, friction-control, lubrication, anti-reflection coatings, bio-activity or passivation, wettability, and easy-to-clean or self-cleaning surfaces. Their importance is not limited to the major end-user industries: the industrial impact of companies specialising in manufacture of thin film deposition equipment and provision of services, as well as in associated metrology and characterisation, is significant in its own right and well-developed in Europe.

The generic measurement tasks to be performed in nanometrology of thin films are: thickness, chemical composition, structure, conformity, uniformity and integrity, surfaces and interfaces (chemistry, structure, roughness, inter-diffusion, etc.), impurities and dopants, and mechanical properties. Several of these (for example chemical and mechanical nanometrology) have been covered previously within this document. Techniques available for accurate film thickness measurement in the sub-100 nm range fall into two broad categories: length-based methods, potentially traceable back to the SI unit of length, and areal-mass based methods, potentially traceable to mass or mole (per unit area) (see Figure 3). Many factors come into consideration when selecting the appropriate technique (or techniques). X-ray reflectivity is unique amongst the dimensional metrology methods in providing an essentially absolute measure of thickness and direct traceability to the SI unit of length. Chemical metrology methods, with areal mass as the measurand, may be chosen for reasons of relevance to the application, or for ease or accuracy of measurement. Film thickness measurements are reviewed in more detail elsewhere [27-29].

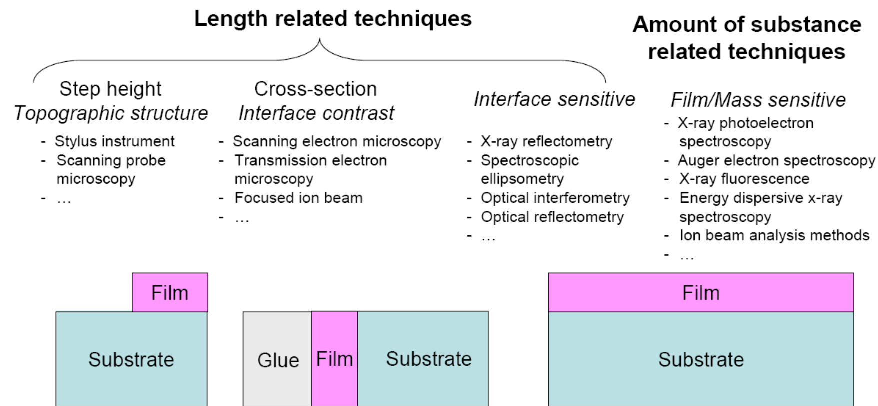


Figure 3 Classification scheme for thin film measurement methods and related techniques

Future trends in the requirements for thin films and their nanometrology are clear:

- Full compositional and structural control throughout the film.
- A range of layer/substrate material combinations, including many which have no bulk analogue and which may be metastable.
- Decreasing individual layer thicknesses.
- Atomic-level control of bonding and structure at surfaces and interfaces.
- Nanostructuring - 3D engineering of film structure (for example thin films made from nanoparticles), controlled porosity, grain structure and nanotiling.
- Measurement techniques with ever-higher spatial resolution and sensitivity.
- Full understanding of probe-sample interactions, perhaps at a quantum mechanical level, and very likely including simulation and comparison.

Key nanolayer requirements for nanoelectronics include the gate dielectric, gate metal and silicon-on-insulator substrate for CMOS transistors, in each case from 1 nm to a few nanometres. The gate dielectric material is evolving from silicon oxide to higher dielectric constant materials. Very close control of thickness, composition and purity are needed in all cases.

The following additional specific challenges and measurement gaps have been identified:

- Measurement of functional organic thin films (as surface monolayers or multilayers). In particular the characterisation of molecular structure and quantification of surface functional groups.
- Techniques for measurement of porous thin film parameters such as surface area, pore size and pore size distribution.
- Techniques for 3D imaging of nanostructures. These may require the development of new parameters for structure definition as well as for measurement.
- Rapid non-destructive large area measurement of film thickness and other parameters. Optical techniques (for example SE and interferometry) are particularly attractive for this, being non-contact and non-invasive. Refractive index determination of thin and ultrathin films is necessary for optical thickness measurement.
- Further development of TEM methods, to achieve improved confidence and industrial throughput in measurement of film thickness and other parameters.
- There is an identified need for more physical and specification standards. For example standards of certified thickness may be used for direct comparison against samples with similar film type and thickness.

Mechanical Nanometrology

Mechanical nanometrology is a key technology for the support of the important industrial sector of thin films and coatings in industrial applications. It is also important for the development of micro and nanotechnology devices and components. The most advanced areas are nanoindentation and AFM indentation measurements, with a range of institutes working on the subject and a series of commercial companies selling instruments.

Nanoindentation, or nanoscale instrumented indentation testing is one of the very few techniques that can measure both the elastic and plastic properties of very small volumes of

materials and so is one of the most useful test methods for determining the mechanical properties of nano-sized elements of materials or coatings [30-33]. Nanoindentation allows for the measurement of other properties such as modulus, creep and visco-elasticity as well as hardness. Besides applications in material research, nanoindentation is now widely used for quality assurance in industry, mainly in the microelectronics industry and microsystems technology. Nanoindentation is also applied to the investigation and testing of biological matter and for medical diagnosis.

Although nanoindentation is better developed for mechanical property evaluation than AFM, considerable care is still necessary for good mechanical property evaluation, with the calibration of force, displacement, frame compliance and tip shape all being essential requirements.

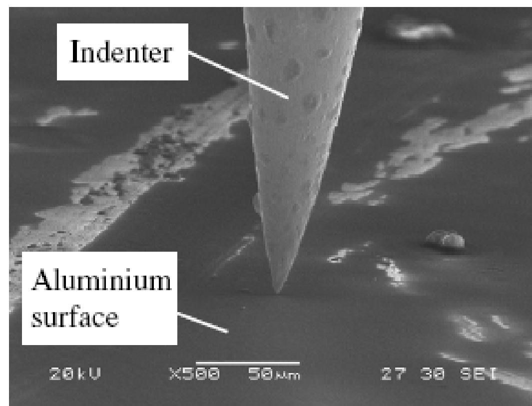


Figure 4 Indentation of sharp tungsten probe into aluminium in nanomecahnical AFM

The AFM is now also being developed for mechanical testing at low load ranges (piconewton to micronewton range) [34-37]. With the close control of displacement and measurement of force that is inherent in AFMs, the mechanical response of surfaces can be evaluated with high spatial resolution (see Figure 4). A simple modification that is often employed for mechanical testing is to use a cantilever that has increased stiffness by comparison with conventional AFM cantilevers.

The AFM can also be used to produce lateral force, or friction force maps that derive their signal from the torsion (lateral twist) of the cantilever. Other modes of operation can measure the adhesion forces between the tip and the surface under examination, and give elastic property measurement.

There are issues with the accuracy of many of the mechanical property measurements with the AFM due to lack of traceability or calibration. Meeting the need for accurate and traceable low force measurement is difficult for AFMs and tip size evaluation is a particular problem as the tip size is extremely small and in some case, only a few atoms may interact with the probed surface.

Nano-tensile testing for free-standing films is being carried out but is not straightforward due to issues such as alignment and grip of thin film specimens, realization of the test force with necessary accuracy, determination of the corresponding uniaxial deformation of the specimen and preparation of the freestanding film sample.

A number of groups are exploring the use of compression testing of pillars of materials that have been nano-machined out of solid blocks of material [38-40]. These tests are often carried out in a high resolution SEM and provide stress-strain behaviour information of materials with confined spatial dimensions showing significantly different behaviour on the nanoscale than on the macroscale.

Direct measurements have also been made of the mechanical strength of carbon nanotubes (CNTs) and other similar structures [41]. This is normally carried out in electron microscopes or FIB systems. Many of these results are not traceable with problems such as fixation of nano-sample, directionality of applied and measured forces and calibration of small forces.

Another method of nano-mechanical testing is to build nano-mechanical elements directly into nano-devices, so that mechanical testing is built into the same environment that is inherent in the devices themselves [42]

Nanotribology is an expanding area of measurement that has relevance to the function of contacts and sliding elements in micro- and nano-mechanical elements [43-45]. As stated earlier, the AFM can be used to make high resolution friction measurements, but care is needed to ensure accurate calibration of the lateral force measurement of the devices, and also that cross talk between the topographical and lateral force measurement is not significant.

Many other nanotribology measurement systems have also been developed in the USA and Europe that target a load range higher than that available for the AFM. These systems all require good control and calibration of small forces and displacements for good measurements to be made. Nanoindentation systems can also be used to make these measurements.

Control of the surrounding environment is particularly important for nanotribology tests as it can have a significant effect on the results that are obtained. One of the main metrology issues with these measurements is again the measurement of the probe shape and size.

All nanomechanical testing relies on the calibration of low forces. Existing traceable low force measurement methods can be divided into two groups: mass based and electrical force based methods. The mass based methods use mass compensation balances to measure forces down to nanonewtons [46].

For low force calibration and generation, electrostatic techniques have been developed by the NMIs of the USA, UK and Germany. NIST and NPL have developed devices with the electrostatic force acting on an electrode suspended from a vertically oriented uniaxial spring suspension [47,48]. PTB´s system is based on a horizontally oriented disc pendulum and a variable electrostatic stiffness reduction system [49].

The exact knowledge of probing force is important for stylus instruments, SFMs, nanoindenters, hardness instruments and CMMs. A variety of different spring-type force stiffness transfer artefacts have been developed. The simplest are silicon cantilevers with marks on their surface to indicate the calibration locations of [50-52]. Probing forces from 1 μN up to 500 mN can be calibrated.

Initial standardization activities in low force metrology are taking place in the field of AFM cantilever spring constant determination in ISO Technical Committee 201. Standardization of transfer artefacts and the use of balances for the calibration of stiffness are now required.

Nanometrology of Structured Materials

Nano-structured materials have specific features with at least one dimension less than 100 nm. The core constituents or building blocks of such materials are nano-sized components such as spherical particles, rods, wires, tubes and plates. The route to a full understanding of these materials lies with first characterizing these nano-sized components in terms of their dimensions and structure and then determining their position in the enabled material. It is hoped that through measurement of the nano-sized components their behaviour and influence on the macroscopic properties of the material can be predicted.

The major roadblock preventing the large-scale adoption of nanomaterials is the lack of reliable large-scale processes for producing large amounts (often many trillions) of individual components that all meet a tight specification. The characterization of materials is an important part of the development process and it serves two broad purposes. Firstly, as part of the research and development into new processes, materials and products, and secondly as quality control and assurance during the pilot plant and manufacturing stages. By developing new characterization tools a greater degree of control can be achieved. It is likely that research into nanoscale materials will lead to new measurement methods.

Nanoparticles is the other class of materials that is very important for nanotechnology products. Similar to ultrafine particles, nanoparticles are sized between 1 nm and 100 nm. Some of the properties of nanoparticles can be strongly dependent on their size, for example the colour of quantum dots [53]. There are numerous techniques used to determine the dimensional properties of nanoparticles [54]. However, the techniques can be broadly broken down into three groups. The first group are ensemble techniques where a large number of particles are analysed simultaneously, examples include DLS [55] and small angle x-ray scattering [56]. These are fast, well-established and produce large statistical datasets but are

prone to errors where changes in the nanoparticle sample go undetected. The second group are imaging techniques that analyse individual particles using high-powered microscopic techniques (such as SPM or electron microscopy [57]), where a large amount of information can be obtained on small numbers of particles (typically 200 to 1000) out of a sample size of many millions. The second group of measurement techniques can suffer from non-representative sampling and also tend to be slower and more expensive than their ensemble counterparts. The third group covers the methods that perform a classification of the nanoparticles in terms of their (apparent) size. Examples are centrifugal liquid sedimentation or field-flow-fractionation.

HAR nanoparticles, nanoplates, nanotubes or nanowires are still a challenging topic for accurate measurement technology [58]. Currently the only commonly used techniques capable of measuring the shape of HAR nanoparticles are based on SPM or electron microscopy, for an example see Figure 5a. These techniques require high-level investment in capital equipment and personnel. Small angle x-ray scattering has also been used to determine nanoparticle shape and accurate measurements benefit from access to synchrotron radiation sources [59]. More cost effective solutions for assessing the aspect ratio of particles in relatively short amounts of time are needed.

Increasingly companies, research groups and institutes are generating nano-sized components with complex physical and chemical structures designed across all three dimensions. Examples include coated nanoparticles and filled nanotubes. Many of these companies lack the capability or expertise to verify their structure. Bulk chemical analysis of nano-sized components reveals the overall structure, but not any variation across or within the components. Surface analytical techniques (for example, XPS [60] and ToF-SIMS [61]) have been used to investigate the surface structure of nanoparticles deposited onto a substrate but lack the resolution to detect individual particles. Electron microscopy and SPM are the only techniques currently in widespread use that can resolve the structure of nano-sized components [62]. The major issues with both of these methods are sample preparation and, again, obtaining a representative sample.

The way in which nanomaterials interact with their environment is determined by their interface and transport properties. For example, the zeta potential of a suspension of nanoparticles determines whether they will agglomerate or disperse in a particular liquid [63]. A full understanding of transport at the nanoscale or through nanostructured materials is at present lacking and is essential for many promising applications of nanomaterials such as advanced materials for the transport, aeronautics and communication sectors [64]. New metrology is required to study and understand such phenomena, ideally on a single particle basis. This new metrology should be conducted under conditions that mimic the actual working conditions of the material as closely as possible.

As stated earlier, all these nano-sized components are produced to form parts of an enabled product, whose final properties are determined not only by these core constituents but also by their position within the final material. The poor dispersion of nanoparticles has been identified as one of the major causes of their related product failure. Electron microscopy (Figure 5b) and x-ray diffraction have both been widely used to study such dispersions, but are either too specialized, costly or time consuming for widespread use. Rheological methods have been proposed for rapid assessment of the dispersion within polymer composites [65]. In the future nanostructured materials will be produced where the components are positioned in predefined positions. In order to achieve this new production routes will have to be devised, possibly based on self-assembly. In turn this will require new metrology, such as those based on SPM (Figure 5c) to test the feasibility of such interactions and to ensure the correct assembly of the final product.

In summary, the metrology capability that is currently lacking and needs to be developed to enable the full exploitation of nano-sized components and their related structured materials is given by:

1. Determination of nanoparticle size and shape with better than 1 nm accuracy.
2. Dimensional characterization of 3D structures with 1 nm resolution.
3. Characterization of interfaces.
4. Transport at the nanoscale or in nanostructured materials.
5. In-situ measurements.

All of these issues need to be addressed using methods and procedures that can be accessed by the largest number of internal people possible. Ideally relatively low cost

instrumentation that can be used by non-specialist personnel is required. New reference materials with certified size, shape, composition and materials properties need to be made generally available to verify these new procedures. This is particularly true as it is very unlikely that a single method will be able to supply all the required information. New reference materials are required to allow comparison between techniques.

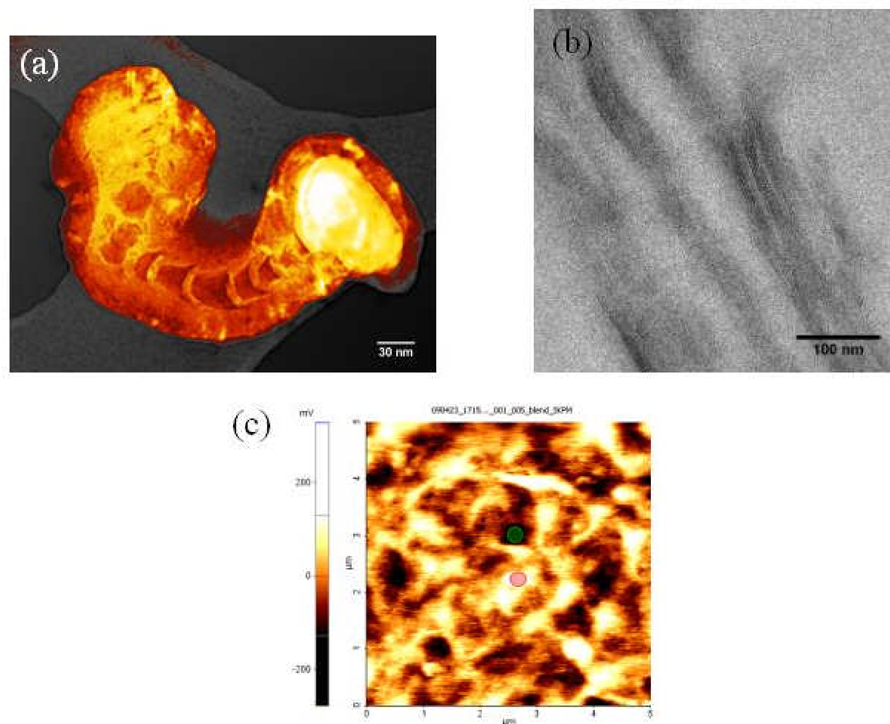


Figure 5 The metrology challenges presented by nanostructured materials: characterising the core components (e.g. (a) TEM image of a nanotube grown from a nanoparticle catalyst, a non-spherical particles causes defective growth of the tube), their position within the final material (as indicated by (b) a TEM image of the dispersion of nanoclays in a polymer matrix) and their affect on the overall properties (as highlighted (c) an AFM image showing the distribution of contact potential of a organic electronic blend).

Electrical Nanometrology

Only a small number of NMIs and other institutes have significant work in the field of electrical nanometrology. Electrical nanometrology activities can be divided in to the following:

- Support of the metrology for the semiconductor industry. Activities for semiconductor devices have to take into account the International Technology Roadmap for Semiconductors (ITRS) [66].
- Metrology for the electrical quantum triangle related to measurements or improvements on quantum based measurands such as the quantum Hall effect, circuits based on Josephson junctions to define voltage over larger ranges and single charge or electron transistors (SETs) to define electric current.
- Investigation into new or improvements to methods to reduce the measurement uncertainty and the traceability to support electrical measurements of nanoparticles/aerosols, for example providing traceable femtoampere measurements for nanoparticle counting, of thin films, of nanostructures, of organic materials and CNTs.
- Use of nanotechnology to setup improved devices for the quantum Hall effect (QHE) or SETs based on new materials, for example graphene or organic materials.
- Use of the AFM to measure the magnetic properties of nanostructures, for example bits on hard discs.
- Measurements to support spintronics.

Mask metrology is an area of relevance to semiconductor manufacturing with nanometre-sized functional structures. The main topics for the metrology on masks are overlay, registration and linewidth, or CD. However, following the introduction of double patterning lithography schemes these parameters are now more strongly interrelated [68]. The semiconductor industry group SEMATECH is the main driver in elaborating and regularly updating the ITRS, where one section deals with the projected accuracy of the measurement equipment for mask metrology.

For the increasingly complex optimization of the semiconductor manufacturing processes it is necessary, not only to determine a single parameter, such as a linewidth, but additional information such as edge angles, line edge roughness and other topography details [68,69]. For example, the ITRS roadmap [66] requires for the 32 nm half pitch node in 2011, a CD metrology tool uncertainty for isolated lines of 0.48 nm (for EUV reflection lithography) and of 0.30 nm (for 193 nm transmission lithography double patterning).

In addition to topography the optical parameters of the mask structures become important. For CD measurements different methods are used: SEM, AFM, scatterometry and optical microscopy. All these techniques have in common that the influence of material and structure topography, and the interaction of the different kinds of probes on the signal generation, must be understood and modelled to assure comparable results using different measurement equipment. For most of the above listed measurement principles it is beneficial to have prior information of the structure shape by AFM measurements to allow for adequate, accurate modelling of the probe sample interaction.

Graphene is currently one of the most promising fields of research for electrical nanometrology for the QHE and SETs. Since its discovery in 2004 [70,71], there has been a great deal of theoretical and experimental research into graphene targeting, not only electronic, but also magnetic, thermal, optical, structural and vibrational properties [72]. However, there are many relevant questions still to be answered, for example the effect of strain, defects and of boundary conditions of the graphene flakes on the electronic bands. The understanding of the limiting factors of electronic mobility as short range scatterers, ripples, charge impurities, the conditions for the appearance of the fractional QHE in graphene, and understanding why the QHE is not observed in suspended graphene with contacts in the Hall bar geometry, are still important, open questions. Improved experimental methods to control the size, shape and degree of roughness in graphene ribbons are needed.

Biological Nanometrology

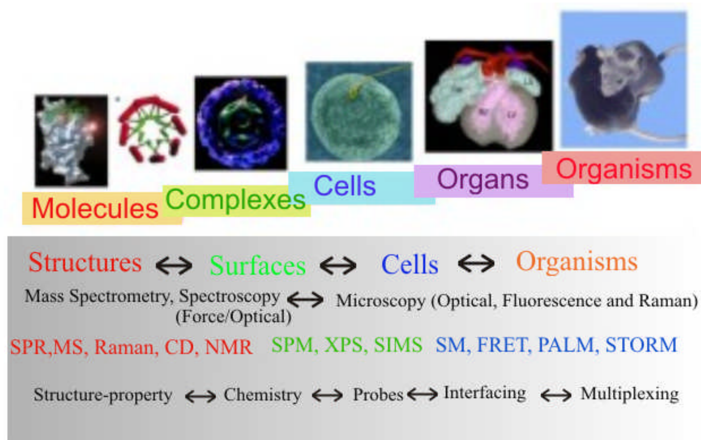
Bio-nano is defined as the cross section of life science, healthcare and nanotechnology, which includes the use of nanotechnology to understand and develop biological science and biotechnology, and vice versa (see Figure 6). Bio-nano may be considered from two sides: the benefits and risks. The risks of bio-nano such as nanotoxicology are very important, and are described in detail elsewhere [73].

There are three main areas where development of bio-nano is currently taking place, namely (a) medical devices and implants, (b) nanomedicine and personalised medicine, and (c) biological superstructures and engineered bio-nanomaterials. The first two are expected to be of particularly high impact in the next two decades.

Bionanotechnology (bio-nano) is an emerging technology area that requires interdisciplinary cooperation and novel metrology tools to facilitate its development. There is no single technique applicable for bio-nano metrology. Often a set of techniques is used together for reliable measurements. The responses to the Co-nanomet survey [3] clearly highlighted three important measurands/methods that are currently being addressed:

- characterisation of chemical, structural and mechanical properties of engineered bio-nano structures and bio-surfaces at ambient conditions;
- quantification, distribution, structure and activities of biological materials;
- quantification and distribution of nanoparticles in biological systems.

Imaging and characterising biological structures and surfaces at the nanoscale at ambient conditions or in buffer solution are very challenging as such structures are extremely soft and susceptible to deformation and damage. Examples of such structures include living cells, tissues, neurons, membranes and protein surfaces. Novel SPM-based techniques such as scanning ion-conductance microscopy [74] with electrochemical microscopy, tip-enhanced Raman spectroscopy (TERS) [75] with total internal reflection fluorescence microscopy, scanning near-field microscopy [76], super-resolution optical microscopy, extremely sensitive optical spectroscopy such as coherent anti-Stoke Raman scattering and stimulated Raman scattering will be required for such characterisations [77,78].



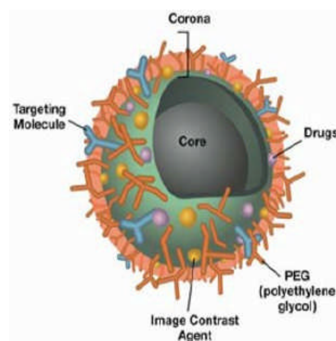


Figure 6 Upper Image - Molecules can be organized in different forms starting from single molecules, complexes and organized in macroscale structures. Lower Image- Schematic diagram of molecules on a nanoparticle surface with core, drug layer and targeting molecules. Such complex structures are being used in nanomedicine and targeted drug delivery

Traceable quantification and distribution of biological substances on surfaces and interfaces are very important for a wide range of industrial applications including sensors, implants, drug delivery and regenerative medicine. Vacuum based techniques such as SIMS and XPS are often used for the measurements. Surface plasmon resonance, quartz crystal microbalance, radio labelling, Raman and infra-red spectroscopy are used at ambient condition or in buffer solution. Novel techniques such as TERS can perform measurements at spatial resolutions of less than 50 nm. More techniques are required for quantification and distribution at high spatial resolution at ambient conditions.

Single molecule measurements are extremely powerful techniques in biology [79]. These allow direct probing of molecules, in some cases one by one and, therefore, very small amounts of sample are required for the measurements. There are several issues with spatial resolution of single molecule imaging. New techniques such as photo-activated localisation microscopy and stochastic optical reconstruction microscopy can improve spatial resolution beyond the diffraction limit.

The need for reliable, accurate and traceable methods of quantification and distribution of nanoparticles will grow as the use of nanoparticles in nanomedicine, nanobiodiagnostics, as contrast agents in MRI, drug delivery and medical devices expands [80]. It is also very important for regulations on nanoparticles for health and environmental safety. There is no single technique that can provide the information related to nanoparticle uptake and localisation. Most of the current techniques such as DLS, field-flow fractionation, AFM, SEM and TEM adopt physical characterisation methods before or after the nanoparticles are loaded into the biological systems. Confocal fluorescence microscopy (involving fluorescent marker labelling), video-enhanced differential interference contrast microscopy, inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectroscopy have been commonly used for estimating uptake of nanoparticles by biological systems. However, quantification of nanoparticle uptake, their aggregation/agglomeration, chemical and structural stability and distribution of such particles/agglomerates need to be measured both in-vitro and in-vivo.

From the Co-nanomet survey of activities of NMIs and other related laboratories, it is clear that the NMIs have started to respond to the measurement needs in bio-nano metrology. Since bio-nano has developed very rapidly in the last few years, it requires immediate measurement infrastructure support to enable safe, reliable and high-quality commercial products. In particular there are urgent needs for development of multi-parameter

measurement methods at ambient conditions with high spatial resolution in real time within the next five to twenty years.

The bio-nano area is extremely cross-disciplinary, involving different scientific cultures. Whereas most of the measurement technology development is carried out by physicists, chemists and engineers, the end-users of the technologies to be developed are usually from the biomedical field. From contacts with stakeholders, it has become clear that the awareness and level of priority of metrology is traditionally very low among the latter. (Notable exceptions are the extensive biological standardization work carried out by WHO, and the area of clinical chemistry where measurement quality has reached a well developed level). Adding to this is the fact that much of the technology development is (with a few exceptions) carried out outside the NMIs, i.e. at universities and in small, specialised companies that also have a relatively low awareness of the importance of metrology. Taken together, these circumstances have led to a relatively low level of awareness about metrological aspects among important players in the area. A top priority must therefore, be to strengthen the contacts between key players in the field. Scientists from the biomedical fields and relevant industrial players need to be more closely engaged in the metrology development, and the NMIs need to intensify their efforts to establish such contacts and to disseminate metrology knowledge.

From the foresight review it is also clear that the measurement and other nanotechnologies used, or being developed, in the field span over a wide range of techniques and applications. To advance the metrological aspects of all of these technologies would be a very large effort. The different techniques are at different stages of metrological development and it seems appropriate that the techniques that are most highly developed and offering the highest biomedical and industrial impact are selected as “cases” for focused metrological development efforts. Such efforts should involve development of suitable reference materials, best measurement practices, standards and establishing traceability to relevant measurement standards.

Nanometrology Policies

The OECD recently carried out a review of targeted policies for nanotechnology across Europe and beyond [81] and nanometrology policies are addressed in the Co-nanomet foresight review [3]. Of twenty-two European countries reviewed, all except Belgium had nanotechnology related policy in place. However, nanometrology policy documents at government or related agency level were not readily accessible across the European countries sampled, but have often been developed within the national structures of government, state agencies and institutes for internal use only. Further sampling is required to confirm the existence or otherwise of such nanometrology policy documents. Such sampling might be carried out through the EURAMET forum. In this way, the nature and organisation, challenges and opportunities of different national policy approaches may be better understood and a more common Europe-wide understanding developed.

Summary

An extensive review has been completed, addressing the field of nanometrology through seven discipline areas, namely: i) dimensional, ii) chemical iii) thin film iv) mechanical iv) structured materials v) electrical, vi) biological and vii) European policies.

Within dimensional nanometrology, SFMs continue to be an essential tool for the development of nanotechnology products and applications. Several SFM areas of research have been highlighted as critical to support future nanotechnology development. The lateral scanning range of SFMs needs to be increased, to several tens of millimetres, to allow the measurement of, for example, large area structured surfaces, wafers and optics. Conversely, the resolution of SFMs, both metrological and non-metrological, needs to be improved to allow the measurement of smaller structures with higher accuracy. Strategies need to be developed to enable 3D probing and scanning. Fuller understanding of probe-sample interactions, perhaps at a quantum mechanical level, is also required. All of the highlighted SFM research areas need to be supported by an appropriate traceability infrastructure.

The AFM is now also being developed for mechanical testing at low load ranges, to produce lateral force, friction force maps or adhesion forces to give elastic property measurement. Issues with the accuracy of many of the mechanical property measurements with the AFM occur due to lack of traceability or calibration.

In the field of electron microscopy, the interaction of internationally recognized laboratories with complementary expertise should be supported.

Chemical nanometrology faces the challenge to provide traceable quantification of functional groups in monolayers and multilayers nano-scaled in one or two dimensions. Imaging techniques that preserve molecular structure whilst depth profiling are required. An increasing need to determine the composition of very small quantities of matter or chemical species without prior replication, for example DNA, demands new and improved techniques in terms of better spectral and spatial resolution, contrast and sensitivity for elements and molecular species.

Within the thin films area, specific challenges and measurement gaps exist for functional organic films, porous films and the rapid, non-destructive large area measurement of film thickness and other parameters.

A full understanding of transport at the nanoscale or through nanostructured materials is at present lacking and is essential for many promising applications of nanomaterials such as advanced materials for the transport, aeronautics and communications sectors. New metrology is required to study and understand such phenomena.

Looking to the growing commercial application of nanoparticles, methods are required for quantification of uptake, their aggregation/agglomeration, chemical and structural stability and measurement of the distribution of such particles/agglomerates both in-vitro and in-vivo.

Since bio-nano has developed very rapidly in the last few years, it requires immediate measurement infrastructure support to enable safe, reliable and high quality commercial products. A top priority is to strengthen the contacts between key players in the field. Scientists from the biomedical fields and relevant industrial actors need to be more closely engaged in the metrology development, and the NMIs need to intensify their efforts to establish such contacts and to disseminate metrology knowledge.

Techniques that are most highly developed and offer the highest biomedical and industrial impact should be selected as “cases” for focused metrological development efforts. Such efforts should involve development of suitable reference materials, best measurement practices, standards and establishing traceability to relevant measurement standards.

From the above review, it can be seen that nanometrology, like nanotechnology and nanoscience, crosses multiple disciplines, each of which today face some key challenges and opportunities.

The ‘2008 Nanoscale Materials and Markets’ report by Nanoposts is one of many examples analysing nanoscale technology companies across the globe, by region (Europe, Asia-Pacific, and the US). This report cites Europe as leading the way in terms of such companies, with numbers in 2007 estimated at 1100. US companies are estimated at 900 and the Asia-Pacific region at 700, with China and Japan in first and second positions with 154 and 136 companies respectively.

According to the above report, the focus of the $1.4bn invested in 2007 in Europe was on ICT and electronics, life sciences and healthcare, and chemicals. Twenty-five per cent of European nanoscale technology companies were developing applications for healthcare and life sciences.

By pro-activiely addressing the nanometrology challenges set out above, the European metrology community will provide vital support to the further growth of these and future nanoscale technology companies and the promotion of Europe’s leading position.

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