Final Publishable JRP Summary for SIB61 CRYSTAL Crystalline surfaces, self-assembled structures, and nano-origami as length standards in (nano)metrology

Overview

Nanotechnology covers materials with dimensions less than 100 nm, and includes the manipulation of individual atoms and molecules. The nanotechnology industry, manufacturers and accredited calibration laboratories require reliable and suitable measurement length standards for the exploitation of this technology. The fundamental quantities that are used to characterise a nano-material are step height and lateral pitch. They are measured using ultra-high resolution microscopes, but before the project the standards were not small or accurate enough i.e. on the same scale as the nano-objects being measured. This project developed new length standards which enable the calibration of ultra-high resolution microscopes, used to characterise nanomaterials, to less than 0.3 nm, or up to 20 times smaller length scales and 10 times better accuracy than previously possible. The length standards were tailored to the needs of the semiconductor industry, and will also enable the traceable measurement of nanoparticles and carbon nanotubes, which are of great interest to the environmental and health sectors. In addition, these new reference length standards will be cheaper to purchase, due to the development of new low-cost production technologies by the project.

Need for the project

Nanotechnology is one of the most promising technologies for developing novel materials that have unique properties, such as functionalised surfaces, particularly for electronics. However, to promote the sustainable development of the nanotechnology market and to foster the implementation of traceable measurement capabilities, new types of reference samples for length metrology at the nanoscale are needed.

Simple improvement of existing technology is not sufficient because it will not give the required accuracy to keep pace with the new manufacturing techniques. Instead, a new method for the production of nanoscale length standards is required using references such as the lattice spacing, which is a fundamental constant, or self- assembled principles at the nanoscale. Currently there are no strict definitions of the terms ‘self-assembly’ and ‘self-organisation’. In this project ‘self-organisation’ is the more general term, describing the formation of structure in a system, without external organisation. ‘Self-assembly’ is more specific and is used to address the formation of nanostructures of diblock-copolymers into regular patterns which have properties that can be used as length standards.

The most important instruments for nanotechnology are ultra-high resolution microscopes capable of viewing single atomic steps, such as specialised scanning electron microscopes (SEM), scanning probe microscopes (SPM) or atomic force microscopes (AFM). Each of these microscopes needs precise calibration standards on the same scale as the nano-objects being measured. But prior to this project, the size of the objects to be investigated were far smaller than any available calibration standards. For example the smallest calibration standard for measuring the height of an object in an AFM was 6 nm. Therefore, this standard was unsuitable for measuring the height of DNA, which is about 0.5 nm. The same issue was found in nearly every area of nanotechnology, including the semiconductor industry or material science.

"Nano-origami" is a new technique that allows nanoscale materials to be folded into simple 3-D structures which can be used as motors and capacitors, potentially leading to better computer memory storage, faster microprocessors and new nanophotonic devices. The project used the nano-origami technique to fabricate nanoscale structures to be used as reference standards to validate AFM and other nanotechnology measuring instruments. The project also used DNA to build nanostructures and as a structural material in self-assembling nanostructures.

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EMRP
European Metrology Research Programme
Programme of EURAMET

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This project aimed to develop new types of length standards in the nanometre and sub-nanometre range to allow traceable measurements with an uncertainty of 0.01 nm for step heights in surfaces, and to characterise the flatness of surfaces. The project developed techniques for the dimensional calibration of nano-structures, using the self- organising characteristics of crystalline materials, the self-assembly of organic materials and nano-origami.

Scientific and technical objectives

The scientific and technical objectives fell into four areas:

1. New standards by self-organisation of crystals
This objective aimed to provide prototype next generation length standards based on the lattice parameters of crystalline materials, such as silicon. This should result in step height standards in the sub-nanometre range with a target uncertainty of 0.01 nm, a reduction of more than a factor of 10 than currently available. This will be achieved by using improved laser-interferometry and using the self- organising nature of crystalline materials made up of multiple step heights.

2. Standards by self-organisation using the surface unit cell of Silicon
This objective addressed the production of lateral pitch samples based on the lattice parameters of single crystals. Samples with large atomic flat surfaces of up to 100 µm in diameter were used for lateral standards for high resolution instrumentation like SPM. Palladium (Pd) can then be evaporated onto this flat surface and its self-organisation used to produce structures with a known pitch height.

3. Self-organisation using diblock copolymers

This objective investigated the self-organisation of diblock copolymers (long molecular chains made up of two monomers, which organise themselves). With this technique, the existing structure of the substrate surface becomes the origin for the formation of laterally structured patterns, made by self-assembly with a lateral pitch between 10 nm and 50 nm and step heights in the range between 3 nm and 20 nm.

4. DNA-nano-origami: An option for future standards?
This objective investigated the use of DNA nano-origami methods for the future development of 3D nano objects, and its implementation as standards for shape measurement at the nanoscale using SPM instrumentation.

Results

New standards by self-organisation of crystals

Using the crystalline structure of silicon, the project was able to create new step height standards with single steps with a spacing given by the lattice constant of the silicon crystal. This step height standard is available for calibration measurements which are approximately 20 times smaller than any previously available. The related standard uncertainty for step height measurement was also reduced by a factor of 10, hence a standard uncertainty of 20 pm can now be estimated.

These uncertainties can be reached by fabricating not only a single atomic step, but a series of up to 20 atomic steps over a distance of 100 µm in so called staircase structures. These structures enable the end user to also calibrate the z-axis (i.e. 3D vertical axis) of an instrument with the smallest possible resolution.

Most high resolution microscopes operate in ambient conditions, but their calibration standards are manufactured in ultra-high vacuum conditions. This means that the calibration standards must be stabilised by forming an oxide layer on the step height samples. However, regular measurements during the project have proved the stability of the project's crystal step height standards during application and storage in ambient conditions, thus demonstrating their practical use for typical microscopic experimental conditions.

The project also produced a good practice guideline for the application of these calibration step height standards, which was made available to stakeholders, and is available on the project website (http://www.ptb.de/emrp/sib61-home.html).

In addition to the project's experimental work on crystalline standards, theoretical groundwork was carried out and simulation software was developed to investigate the interactions of the tip (the main imaging part of an AFM) and the sample surface. The results of the modelling provided further understanding of the factors influencing the measurement uncertainty of step height calibration standards.

For the calibration of the lateral dimensions of the microscopes (i.e. the x-(horizontal) and y-(vertical) axis of the instruments) self-organised silicon lattices were used. After heating, the surface of the silicon reconstructs and forms a lattice, with a very precise and reproducible spacing of approximately 5 nm. This lattice was used as a metrological basis to create samples for the lateral calibration of ultra-high resolution microscopes. The reconstructed surface could only be measured in ultra-high vacuum with scanning tunnelling microscopes (STM) or very special AFMs. Thus to make this lateral structure measurable with typical AFM instrumentation, methods were developed to enlarge the height of the regular pattern in the z-axis.

In conclusion, the project developed reference length standards based on the self-organisation of a crystalline material for the sub-nanometre calibration of ultra-high resolution microscopes. This included a step height standard for calibration measurements which are approximately 20 times smaller than any previously available and with a reduction in measurement uncertainty by a factor of 10. The project also produced an associated good practice guide and simulation software for AFM.

Palladium can be used to create clusters of atoms in specific regions, and make lateral pitch reference samples for AFMs. The project developed prototype samples and demonstrated the feasibility of this concept, however further work is required to transfer these samples to AFM instrumentation.

Self-assembly of polymer standards and self-organisation of diblock copolymers

By combining self-assembly of block copolymers with patterned surface templates, it is possible to link a nanostructured film with its underlying topographically defined structure and thus to improve the order of the nanostructures, by simultaneously reducing defect formation and increasing size uniformity.

Using this technique, the project developed prototype polymer standards for lateral calibration of AFM (and related ultra-high resolution microscopes). These polymer standards provide self-assembled, monodomain calibration for areas of 100 µm length and a width of 100 – 200 nm. The standards can also be combined at different orientations to fully calibrate the microscope's axes. Measurements of the project polymer standards have revealed a pitch value of 27.5 nm for the periodic structure, which is a reduction of more than 100 % compared to the standards available prior to this project. The related measurement uncertainty of this lateral pitch standard was also improved to 0.3 nm, setting a new benchmark in this field.

In summary the project has developed new ways to produce polymer standards for the lateral calibration of high resolution microscopes, such as AFM using the self-assembly of polymers.

DNA-nano-origami: An option for future standards?

In addition to providing new standards or prototype standards for industry and science, the future development of nano-origami standards was investigated. The project explored whether novel nano-origami objects, such as folded DNA structures, could be used to create stable metrological calibration artefacts. The experiments proved that DNA nano-origami has the potential to create standards, but new procedures for application, measurement and data evaluation need to be developed further.

Actual and potential impact

Dissemination of results

The project generated 12 articles in peer-reviewed journals and 30 presentations at conferences on nanotechnology. This included Nanoscale 2016 in Worclaw, Poland which is a key conference and brings together experts and scientists working in the field of AFM and related microscopy. A session was organised to present the results of the project and included scientists, stakeholders from industry and experts from standardisation bodies. A good practice guide on crystalline step height standards has also been published and is available on the project website.

Impact on standards

The project produced a calibration artefact based on the step height, and worked with the ISO and national standards to make this part of the standardisation process. The project worked closely with the standards bodies for nanotechnologies, in particularly length through EURAMET's technical committee for length (TC-L), 'SPM and surface metrology' and 'Surface metrology on micro- & nanoscale'. Additionally, direct communication between standardisation institutes, such as ISO, DIN, etc., and the project played an important role in preparing for the standardisation process.

Actual impact

This project demonstrated how self-organisation and standards can work together to produce prototype standards, artefacts and regulations, which are available for stakeholders to use for nanomeasurements. It developed a new type of dimensional standards on a smaller scale than had previously been possible, for step height and lateral resolution measurements for AFM and interference microscopy. It addressed the demands of stakeholders from the semiconductor and nanotechnology industry as well as in biophysics and surface science. These standards will fill the gap at the nano- and subnanoscale, and provide the metrological framework for further research in these materials.

The new calibration standard prototypes, particularly the step height standards, are already being used by research and instrumentation manufacturers such as:

- A German SME, specialising in the development of high tech technologies for medicine and engineering, is using the sub-nanometre step height of the atomic steps to certify the resolution of surface measurement technology derived from the shearography (a surface inspection tool based on interferometry). In this example the accurate and non-destructive measurement of layer thicknesses of single atomic layers is a key to the successful development of a modern new sensor in a medical application. This has the potential to make a big impact on the European health care industry.

- The flat samples, from objective 1, provided reference standards for AFM calibration. This will allow AFM to change its design and reduce its measurement uncertainty. An SME worked with PTB and is now looking to commercialise this.

- The company Sensofar from Spain, a member of the project's advisory committee, has adopted the project's step height calibration standard prototypes. Measurements of the step height samples with one of Sensofar's microscopes demonstrated that their instrumentation is capable of sub-nanometre resolution in the z-axis, and that the sample was applicable for use with optical high resolution measurement technology. This is a very important milestone, since optical measurement technology will become the dominant technology for accurate in-line measurement systems in the future, as optical instruments can combine high performance and high throughput.

Potential impact

Patents were registered for the calibration procedure for reference sample sizing of length and related measurements in Italy and in Germany. This project will allow instrument and ultra-high resolution microscope manufacturers to produce equipment for characterising new nano-materials, which is essential before they can be commercialised. The project also informed the EURAMET technical committee for length (TC-L) about its work.

List of publications

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