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1 Executive Summary

Introduction

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.

The Problem

The most important instruments for performing research at the nanoscale are microscopes ranging from ultra high resolution instruments, capable of showing single atoms, to more mainstream instruments like scanning electron (SEM) or atomic force (AFM) microscopes and even up to classical light microscopes, which can be found in almost every laboratory or school. All these microscopes have one thing in common: only with a well-defined scale, preferably present in the picture, can the displayed objects be meaningfully interpreted.

The Solution

This project has created a new set of calibration standards for use at the atomic scale, filling a gap that was present at the start of the project. These new standards are up to 20 times smaller and 10 times more accurate than before. For the creation of these new, superior standards, a new production technology was used involving the self-organisational principles of nature. Consequently, these standards are not only better, but they are also cheaper to produce. New ways of working with these standards have also been investigated in order to simplify their application by the end-user. In summary we have produced new, better standards, which will be cheaper to produce and easier to apply.

Impact

This project was structured to investigate new technologies for the production of standards for metrological application. As one of the main objectives was to explore the options and capabilities of a new production paradigm for standards at the nanoscale, the main impact at this small scale was for NMIs and for the manufacturers of instrumentation. NMIs will use the new technologies in order to perform ground work to develop new standards and also to improve their instrumentation accordingly. For example, PTB has used the new flatness reference samples based on crystalline material to carry out a better characterisation of the LR-SPM. This led finally to the identification of one main source of uncertainty and to the improvement of the instrument based on the final uncertainty. Discussions at conferences and exhibitions with potential early adopters, such as Sensofar or Olympus, have already shown substantial interest from industry.

In the mid- to long term the results will help to promote the application and the acceptance of standardisation and calibration in larger parts of the industry. This impact will be achieved by three elements which have been provided by the project: the provision of standards with improved features and simplified application by end users. Finally, a massive reduction of the overall costs for dimensional calibration at the nanoscale will simulate the application of calibration, especially in the non-regulated economy.

2 Project context, rationale and objectives

2.1 Project context and rationale

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.

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.

2.2 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.

3 Research results

The use of self-organisation during the production of standards is offering new options according to the accuracy and the feature size of the calibration standards. Furthermore it gives the opportunity to establish a direct linkage of the artefact and its values to an invariant of nature. Besides the technical benefits of this approach, i.e. producing better standards with improved features, this new approach will also have a positive impact on the price of these standards i.e. they will get cheaper.

The project has addressed three new ways to produce dimensional standards for nanotechnology, which are based on self-organisation principles. First the use of crystalline material, such as silicon, to produce lateral and vertical standards on a small nanometre and sub-nanometre level. Second, the self-assembly of organic molecules, such as diblock- copolymers, was applied to create lateral standards, which are intended for the lateral calibration of microscopes between 10 nm and 50 nm. Finally, as a look to the future, the capabilities and assets of DNA nanorigami, for the production of next generation standards for dimensional nanometrology, were investigated.

3.1 Objective 1: Development of prototype samples for step height measurement with sub-nanometre (10x smaller than the existing ones) step heights and an expanded uncertainty of $u(h) = 10 \text{ pm}$ (50x smaller) for UHV-STM application

These prototype standards make use of the highly accurate spacing of the lattice planes in a single crystal. Silicon is a very good starting point for the research. Creating perfect single crystals from silicon is a well-established technology, however it is still a challenge to transfer this highly reproducible, fundamental ruler to the surface of the solid sample. Only the surface of the samples of this “standard of nature” can be used for calibration purposes for the majority of microscopes that are applicable to nanotechnology. These standards are specific to the needs of AFM or optical microscopes.

Unfortunately, the surface of the single silicon crystals forms in such a way that the surface roughness is in the order of 0.5 nm (or more) and additional surface features are present on the sample. Consequently, the surface of this material, after creation by sawing or polishing, is not suitable to host step height calibration features of the size of the lattice spacing. The lattice spacing of Si crystals ranges from 0.3 nm to 0.5 nm, approximately, for the low indexed lattice planes.

The technical challenge in creating steps of a single lattice plane height is therefore twofold:

1. An atomically flat surface must be created and
2. Steps from one lattice plane to the next must be created on the surface.

To perform this creation process, a self-organised process must be applied to the samples, in order to create the discussed features on the silicon surface. To initiate this self-organisation process, Si samples with (111) surface orientation will have been prepared with an initial lithographic structure, thus providing a lateral limit for the following process. Since the layout of this lithographic pre-structuring will have an additional impact on the usability of the intended calibration artefacts, the specific design of the layout was initially discussed with all partners, including the REGs, in order to also provide find-me functionality and practical measurement aspects. These samples are transferred to an ultra high vacuum (UHV) chamber, where the self-organisational step takes place. During the complete pre-processing of the sample, i.e. the required processing steps before transferring the sample to the UHV chamber, all necessary processing steps must be very carefully maintained in order to ensure a reproducible result for the main step, which is to create the atomically flat surface with defined atomic stepping.

The processing in the UHV chamber consists of a thermal treatment of the specimen with defined heating ramps and holding times. The first part of the annealing is a final cleaning of the surface from residual contamination, such as carbonaceous contaminants. This step is followed by the final self-organisation step, where the temperature is held at a defined value. Through the thermal activation in the first step, elementary Si is created by the sublimation of the initial SiO_2 , which is present on the sample. The second step is the deposition and lateral diffusion of the Si atoms on the surface. By holding the temperature in a very narrow range around the critical temperature of the self-organisation process, the Si atoms are mobilised, to move along the surface. With this lateral diffusion, the Si atoms are transferred to a crystal step and they integrate

themselves into the surface lattice. The temperature or the energy of the atoms, respectively, is not sufficient to re-mobilise the Si atoms once they have been bound to the crystal.

The self-organisational process required some initial seeds, which in this case are vacant crystal places on the surface. Without preconditioning the process has a variation bandwidth about the shape and the lateral position of the atomic step structure. In order to achieve a predictable result, the lithographical preconditioning of the samples, as mentioned above, was developed and optimised during the project. With this structure the localisation of the self-organised steps can be realised and furthermore the structure of the steps can be manipulated on a larger scale.

The manufacturing process is now, after the end of the project, well established for creating three reproducible types of reference structures:

1. **Atomically flat areas**

Atomically flat areas up to 200 μm , which can be used as flatness reference planes, are used for example to investigate the guiding errors of the AFM scanner. This is one prerequisite for improving the performance of such microscopes in order to meet the upcoming demands of future applications.

2. **Staircase structures**

A larger number of single atomic steps (up to 20) on a length scale of $l \approx 60 \mu\text{m}$. With this structure a calibration can be realised on a larger z-range with atomic resolution. Additionally the measurement of a larger number of step heights will reduce the uncertainty in the calibration of a single atomic step.

3. **Amphitheatre structure**

In this case, starting at ground level at both sides of the scan, single atomic steps arise. With these structures the levelling of the samples during AFM measurement can be performed on a longer base line thus improving the uncertainty of the related step height measurement.

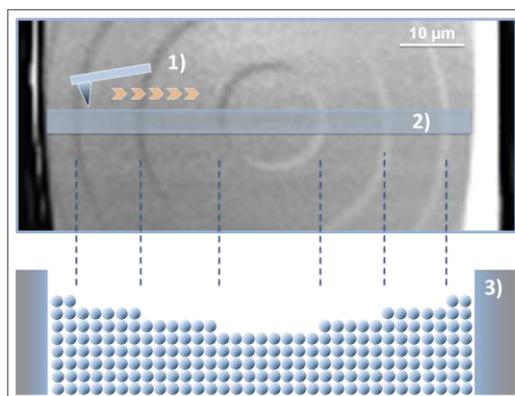


Figure 1 Example of an amphitheater structure. In the upper part a picture of a real amphitheater structure is given, which was taken with a confocal laser scanning microscope (CLSM). The lower part illustrates the arrangement of the Si atoms in this structure.

The main challenge during the development of the step height prototype standards was to control each single step in the processing chain, starting with the careful selection of the supplier for the Si wafer. Also the lithographic processing in the clean room facility of PTB needed special attention in order to identify possible sources of particle contamination, which is a very challenging issue at the nanoscale. Solutions were developed to avoid contamination in this pre-processing stage. All these topics required the implementation of an appropriate and strict quality management (QM) system. Once the QM system for the pre-processing was established, the next step was to define the critical parameter for the self-organisational step in the UHV chamber.

Unfortunately the knowledge transfer of procedures and methods from the macroscale to the atomic scale, which is used for these samples, was very limited. New phenomena, having a different physical behaviour than at the macroscale, occur at the nanoscale, leading to a different behaviour of the physical systems under development. For example, the contamination of surfaces with particles of a few nanometres

withstand classical cleaning methods (from the macroscale). The consequence is that these kinds of contaminants must definitely be avoided during development and production.

3.2 Objective 2: Stabilisation of crystalline step height samples for in air SPM measurement

After the production of the samples in the UHV process, the bare Si surface remains very reactive. As the foreseen application will take place in an air environment the surface needs to be passivated in order to minimise its reactivity. The very high reactivity of bare Si surfaces is due to the existence of non-saturated chemical bonds of the Si atoms in the crystal. Hence an optional approach to passivate the sample surface will be to saturate these dangling bonds.

For a successful passivation the dangling bonds need to be saturated and additionally the passivation layer must preserve the step height structure that is present on the sample surface. Hence, the layer thickness must be laterally homogeneous and its thickness is limited due to the covering of the edge of the atomic steps.

A second role of the passivation layer is to protect the step height samples from contamination during storage, transport and measurement. This is a very important point according to the designated application of these prototype standards for dimensional calibration of microscopes.

Different options for the passivation of the samples have been considered during the project. The most promising and almost canonical approach is the oxidisation of the Si surface i.e. an oxide layer will naturally form when the samples are exported from the UHV chamber. The native oxide layer of Si has some intrinsic features, which are well adapted to the requirements of a passivation layer as stated above:

1. Silicon oxides are very stable, they will serve as a diffusion barrier.
2. Native oxide layers are very thin ($d \approx 1$ nm).
3. The oxide growth is self-limiting and will result in a homogenous layer thickness.

According to these features the native oxide layer was formed in a controlled process during the export of the samples from the UHV production chamber. The first check of the preservation of the atomic step structures was made immediately after production and passivation with a confocal laser scanning microscope (CLSM) at PTB. Due to its specification this microscope does not have the required resolution in the z-direction to measure the atomic steps, but a special feature of the instruments is that they offer the option to detect the edges of the atomic steps in the phase image. With this feature the CLSM was used to detect the lateral position of the atomic steps. Therefore with these AFM instruments at CMI, DFM, NPL and VTT a complete screening measurement of all samples produced was performed.

The detailed investigations with AFM have proven the proper function of the native oxide layer which passivates the samples whilst preserving the step height structure for calibration purposes. As discussed later on, the uncertainty of the step height measurement on these samples, with passivation by an oxide layer, was within the targeted region of some ten picometres. Additionally, the stability of the passivation was checked by repeated measurements of the samples.

3.3 Objective 3: Stability verification for the in air application of prototype crystalline step height samples

The original plan was to store samples in a variety of environments, air, vacuum and nitrogen and to compare the stability of the samples in air with those stored in more benign environments. This should have been achieved by a regular set of measurements of the samples. Measurements of the initial samples at CMI, DFM, NPL and VTT have shown that their stability in air was only on the scale of hours. The cause of the low stability was investigated by PTB and NPL. XPS measurements at NPL revealed contamination on the sample that was consistent with the adhesive used to fix the sample to a metal disc that was used to hold the sample in an AFM. It is unclear as to whether the glue was the problem or if it was an issue with the passivation of the sample. However, after discussion between partners it was decided to use adhesive graphite sheets for fixing the sample to the mounting disc and this proved satisfactory.

For the last month of the project new samples were produced and checked by repetitive AFM measurements. These step height sample prototypes were stable under air storage for several months.

In addition, a prototype sample produced in preparation for this project was re-examined in 2014. Throughout its lifetime of several years it had been kept in air. This prototype with steps of atomic height was proven to be stable. This suggests that while the samples can be stable, care is required, both with their preparation and their handling in air.

3.4 Objective 4: Development of a software tool for the simulation of the tip-sample interactions that occur on crystalline step height standards and improved uncertainty calculations

A reliable interpretation of SPM data relies on our theoretical understanding of the physical processes that happen during scanning. In this project, the focus was on height measurements and the related uncertainties. The presence of a step can change the electronic states of the system and thus change the apparent height of the step. This must be verified with respect to the unknown chemical and structural composition of the tip apex and the setpoint of the constant force mode.

It is well-known that the van der Waals force plays a significant role in AFM experiments. Also the unknown radius of the tip smears the image of the tip. This can result in systematic errors and these should be taken into account when setting up an uncertainty budget.

Typically, theoretical AFM simulations consist of calculations of the short-range forces acting between the tip and the sample, as function of their distance. The resulting force-distance curves calculated over different characteristic surface sites can be compared directly or indirectly to experimental evidence. The character of the short-range force is determined by the chemical composition of both the tip and the sample. Typically, on metallic or semiconductor surfaces, the short-range forces reflect the chemical bond established between the outermost atoms on the tip and the sample. Therefore, only simulations employing quantum mechanics can properly describe the mechanism of formation of the chemical bond. On the other hand, precise quantum mechanical calculations are computationally very demanding, which strongly limits the size and the complexity of the modelled systems. From this point of view, simulations based on Density Functional Theory (DFT) seem to be the optimal choice as DFT provides the optimal ratio between the accuracy and the size of the model systems.

Typically, we carry out a series of DFT calculations simulating a tip approaching a surface that includes several hundreds of atoms. Here a small cluster of atoms represents a probe and a supercell model including slabs and vacuum is the more efficient choice to simulate the solid surface. The slab in the supercell is infinite and periodic in the directions parallel to the surface, but it is finite in the direction perpendicular to the surface. Subsequently the tip model is statically shifted towards the surface slab and selected atoms are relaxed to their optimal position until the residual forces acting on the atoms are smaller than a threshold value.

From the variety of different DFT packages available, the tight-binding software Fireball was chosen. Fireball is being developed by FZU in collaboration with other institutes and it is particularly well suited to large-scale DFT simulations.

First, a model for a monoatomic step on Si(111)-7x7 was created in a collaboration between CMI and FZU. The most typical features of the 7x7 structure are the existence of the two different halves of the unit cell (faulted vs. unfaulted) and the existence of the adatoms and the rest atoms. The somewhat smaller structure 5x5 has the same features. Three 5x5 unit cells were assembled into a monoatomic step model.

The DFT calculations were performed on the supercomputer at CMI. The force-distance curves for three different tips (reactive and non-reactive) were calculated for various positions. The positions of the tip were aligned along the scan lines across the step in order to create two-dimensional force maps. These force maps are a useful tool for the study of the details of the interaction of the tip and the surface.

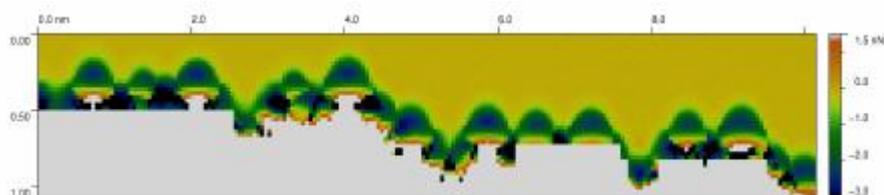


Figure 2 Typical 2D force map across a step

The 2D force maps can be easily used to simulate height measurements in the constant force measurement mode. First constant value profiles are extracted and then the height difference between maxima corresponding to adatoms are calculated. For too low setpoint values it is not possible to extract a profile due to the noise. For too high setpoint values structural changes may occur on the tip/surface.

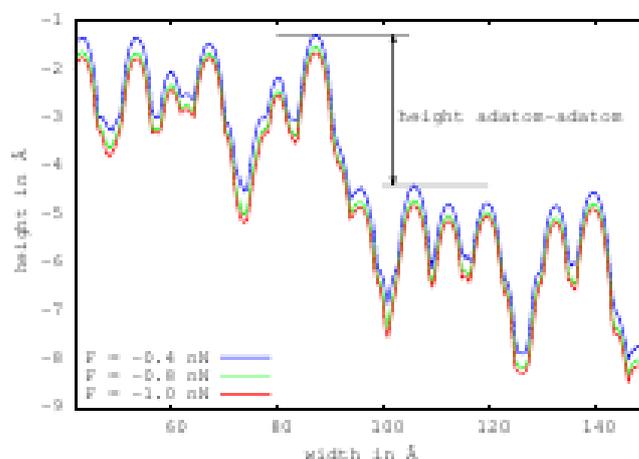


Figure 3 Example height profiles for a reactive tip

The 2D force maps reveal the different behaviour of tips. The nonreactive tip interacts with the surface when approached very closely and the interaction is weak. The reactive tip interacts at larger distances and up to large force values. It was also shown that the orientation of a tip with a dimer ending had almost no effect.

Heights were evaluated for different tips and different setpoints in order to study the effect of the tip apex and the setpoint. The values cannot be compared directly as the setpoints at which profiles can be obtained differ for each tip. A higher setpoint value reduces the influence of noise and should be preferred. However, in real experiments there is no way to tell what the maximal safe force setpoint is.

The uncertainty due to the unknown apex was estimated to be 0.04-0.07 Å. The estimate of the setpoint due to the unknown apex is 0.02-0.05 Å. However, this can be further reduced if measurements can be performed at different setpoints.

A classical model of the van der Waals forces was used. It is not possible to evaluate the interaction analytically in this situation but it must be evaluated numerically. Maps and profiles were created for several different tip radii. It was found that the smearing of the edge becomes significant at a radius around 20 Å. In order to avoid an artificially too low height value, heights should be compared at distances at approx. 2-3 multiples of the tip radius.

The uncertainty associated with the unknown tip radius can be up to 0.08 Å. If the tip radius is smaller than the distance of the adatoms from the edge, this drops below 0.005 Å.

3.5 Objective 5: Provision of a guide line for the measurement of crystalline step height samples

The scientific objective was to provide a guide for the measurement of crystalline step height prototypes describing the intended use as a new reference material. Through the preparation and later dissemination of such a good practice guide, the knowledge capacity from the project will be widely distributed to other NMIs/DIs. The guide shall also be used to ease the implementation of calibration services and the wider industrial use in sectors such as micro engineering where it will assist users and scientists in the setup of a traceability chain for their own instrumentation and measurements.

The research undertaken shows that a few symmetric step heights with a symmetric topography as an amphitheatre (described in section 3.1 to 3.4) can be used to calibrate the height sensitivity in the sub-nanometre range of an atomic force microscope. This can be done in a robust and reliable way quantifying an upper limit for the influence of possible sub-nanometre hysteresis, creep, tip-sample interaction and other sub-nanometre influence parameters. The measurement assessment is typically done over a small segment of the lateral scanned profile. The guide describes the results from this project and how the task can now be done more easily. In the very near future this will improve the measurement capability of the partners and later on other NMIs and industry.

The guide describes the fact that in some areas many amphitheatre structures were present whereas in other areas only few full amphitheatre structures were identified. The identification of the position of the amphitheatre structures was easily done from optical microscopy images. Analysis was typically done from profiles averaged over 30-100 lines.

Different mathematical approaches for measuring a single step height are described including the distance fitted to the centre part of the plateau, i.e. similar to the approach in ISO 5436, and the distance fitted near to the edge, which is not as invariant from a scientific point of view. The steps of the measured AFM profiles are described as being best detected by means of an optimal edge detection algorithm that convolves the derivative of a Gaussian kernel with the measured data. The detection algorithm can be adjusted depending on the quality of the measured profiles. A new approach was to fit a piece wise function to deduce and correct for non-linearity image errors in the atomic force microscopy (AFM) used.

The key technical insight gained in the project was that the calibration based on the prototype step heights is strongly correlated to the AFM microscope's other imaging errors, in particular the non-linear guiding of the probe along the horizontal direction (flatness). For the commercial microscope used these sub-nanometre nonlinearities and crosstalk are difficult to deduce from the parameters found on larger steps, gratings and flat surfaces and they would have been very difficult, if not impossible, to measure without the symmetric amphitheatre prototype step heights.

The *description* of the use of the amphitheatre atomic steps progressed beyond the state of the art as they have not been available for this purpose previously and only a few samples were produced. There has been a close collaboration between the producers of the amphitheatre atomic steps (PTB) and the partners doing measurements with different systems with complimentary features (DFM, NPL, CMI and VTT).

3.6 Objective 6: Provision of an uncertainty budget related to the SPM measurement of step height prototypes

The scientific objective was to develop and provide an uncertainty budget related to the SPM measurement of the step height prototypes. The analysis and accuracy level matched the target level for the expanded uncertainty of the prototype samples for the step height of $U(h) = 10$ pm. This is 10x smaller than the existing uncertainty level for step heights of 6 nm.

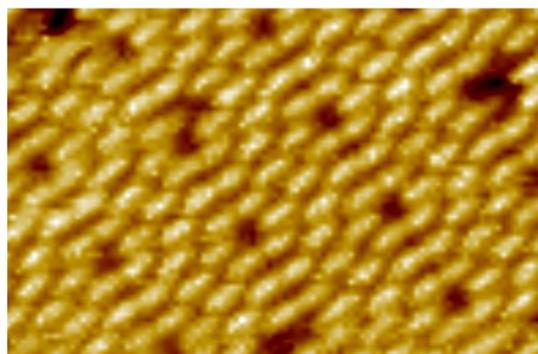
The research analysed the measurement process and found that the surface of the centre of the steps has an invariant distance independent of e.g. SiO_x properties and microscope settings. Near the edge, however, the height is not quite as invariant and the measured height is not quite as robust due to the SiO_x layer's uneven thickness, different mechanical properties, hysteresis, creep, feedback settings and the friction of the probe. Levelling is crucial and a method based on histograms is not always as useful. The project has delivered specific uncertainty budgets with combined uncertainties in the range below 10 pm.

The scientific and technical progress beyond the state of the art included the mathematical modelling of the measurement process of the step height prototypes and the quantification of the influence parameters. This modelling was performed using special software provided by FZU. This went beyond the state-of-the-art as the step height prototypes have not been available for this purpose previously and only a few samples were produced. There has been a close collaboration between the producers of the step height prototypes (PTB) and the partners working with different uncertainty budgets based on different measuring systems with complimentary features (DFM, NPL, CMI and VTT).

3.7 Objective 7: Provision of lateral pitch sample prototypes for high resolution applications in UHV, based on the unit cell of crystalline Si

For the complete calibration of a microscope in all dimensions (x, y, z) crystalline step height standards are needed as well as lateral calibration standards. One approach was again based on the Si crystal. In this specific case the surface reconstruction of Si surfaces, such as the 7x7 reconstruction of the (111) lattice plane are used.

U = 2V



U = -2V

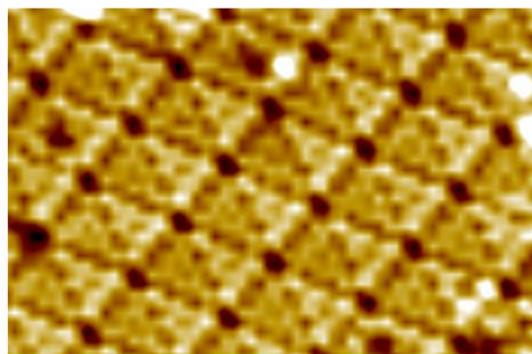


Figure 4 STM image of the 7x7 reconstruction of the Si (111) surface. Both images show the same reconstructed Si surface. The difference in the visualisation was due to the different polarity of the voltage between surface and tip. In the right image the regular structure of the reconstruction is displayed.

The 7x7 reconstruction of the Si surface has a trapezoidal shape surface unit cell. This surface cell parquets the complete surface in a highly reproducible way, having a very accurate lateral spacing. This model of the surface unit cell and the surface was in full analogy to the systematics used in 3D crystallography. Again the crystal provides a periodical structure, which should be used to create a metrological ruler of the highest quality. The 7x7 reconstruction forms a natural regular grid of approximately 5 nm spacing. A precise and traceable measurement of the Si surface unit cell are still pending. However, this project prepared the required equipment (metrological UHV-STM). Results should be obtained in due course.

As these surface unit cells are only measureable with special equipment in UHV the objective for the project was to use a self-organised process to create a topographical enhancement surface unit cell creating a super grid structure with a reproducible spacing. In particular the super grid structure was formed by a Palladium (Pd) cluster, which was strictly localised to the grid of the 7x7 reconstruction.

For this purpose, an Si wafer with a residual native oxide layer (approximately 1 nm) was used to create an Si surface with 7x7 reconstruction. The thermal annealing process was undertaken in the UHV chamber of PTB. In this case a lithographic pre conditioning of the Si wafer was not required. For this objective the QM system implemented for the processing of the step height standards could be reused. Once the reconstructed surface had been created, the decoration of the unit cells with Pd clusters was carried out. During the project the required processing parameters, such as the deposition rate, deposition time and sample temperature were optimised to increase the yield of the process.

To assess the resulting samples, a so called coverage factor η was defined. This factor ranged from 0 to 1, with 1 having exactly one Pd cluster in every unit cell of the surface at the correct place. The coverage is

zero, if no 7x7 reconstruction is available, if no Pd clusters are present or if the clusters are too large etc. During the process development, samples were processed and afterwards analysed with the UHV-STM of PTB. For this assessment the samples were constantly handled in UHV condition. By repeating the preparation and assessment it was possible to define the processing parameter in order to create samples with a covering factor of $\eta \approx 0.3$ (see **Figure 1**).

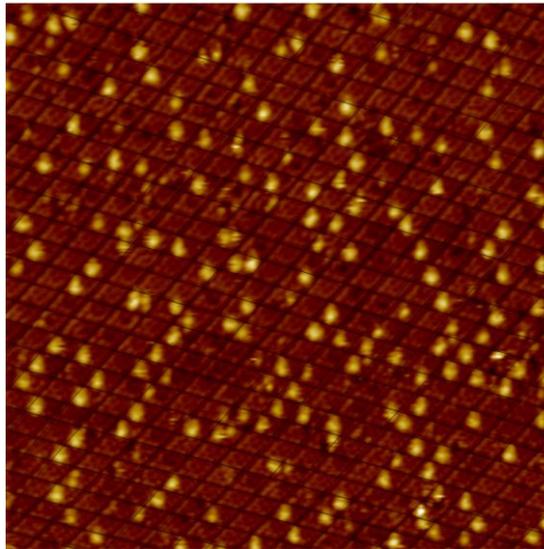


Figure 5 STM image of the 7x7 reconstruction of the Si (111) surface covered by Pd clusters in the surface unit cell. The coverage factor is $\eta \approx 0.3$.

With this result a proof of principle was made i.e. topographical enhancement was demonstrated with the self-organised process of localised Pd clustering. The lateral position of each Pd cluster was strictly defined by the metrological grid of the underlying Si crystal. The coverage factor could be increased up to $\eta \approx 0.3$, which was already sufficient for a successful development of numerical calibration methods, which use reciprocal space approaches.

On the basis of this result the next steps can be defined: i.e. the fine tuning of the processing parameters for a further increase in the coverage rate. Unless a realisation of a full coverage seems unlikely, due to fundamental principles of physics, a realisation of a coverage factor up to 0.8 should be possible. Within the range of $\eta \approx 0.3 \dots 0.8$ it should be possible to realise a numerical method for the lateral calibration of microscopes.

3.8 Objective 8: Provision of self-aligned Pd:Si(111)-7x7 lateral pitch prototypes with $p = 5$ nm (10x smaller than existing) for SPM application in air

The production of the Pd:Si-7x7 lateral pitch prototypes was delayed and started in the last period of the project. This was due to the delay of the process development for the step height standards described in Section 3.1. The work on these standards required more time and effort regarding the enhanced QM requirements for processing samples at an atomic level. Since both processes were assigning the same UHV production chamber, the initial delay had a knock-on effect on this objective.

The boundary conditions, as stated in Section 3.2 for the stabilisation or passivation of step height samples, also have to be applied for the Pd samples, but the challenges for obtaining operational passivation are somewhat higher. Compared to the step height samples, in this case, two different materials must be passivated. Once again the passivation by the native oxide layer of the samples was used as the first approach for passivation and measurement in air.

Due to the delay in sample production, the first samples with an accountable coverage factor only became available towards the end of the project. Therefore, CMI and DFM could only perform initial screening measurements with AFM on samples provided by PTB. Unfortunately the result was negative. The Pd cluster that was present during STM measurement, after production in UHV, could not be resolved by the AFM

during in air measurement. According to current knowledge, there are a number of different reasons for this negative result. The lateral pitch of 5 nm was already at the limit of current state-of-the-art AFM. Hence one possible interpretation is that the microscopes could not resolve the Pd cluster. Alternatively, it is also possible that the native oxide layer did not conserve the topography created by the Pd cluster and as a consequence a flat surface arises. More investigations to explain these results and to illuminate possible passivation strategies must be carried out.

3.9 Objective 9: Stability performance testing of crystalline prototypes under UHV, N₂ and air conditions

Unfortunately, the analysis of sample stability could only be performed in UHV for a limited time i.e. on the scale of a few days. This was due to the fact, that the storage capacity in the UHV chamber of PTB is very limited. In fact, storage of a sample in the chamber will prevent its use for the production of additional samples and sample analysis with LEED and AES, which is also available in the UHV chamber. After the longest storage period of 5 days, there was a slight degradation of the surface, which could be detected by STM measurement. However, this change of the sample during storage did not affect the intended use of the Pd:Si(111)-7x7-Samples as lateral length standards. To understand this maybe confusing finding, two facts must be kept in mind:

1. STMs have a very high sensitivity, both in lateral and vertical resolution. Hence, additional single atoms that are attached to the surface can be detected. However, single atoms do not affect the position of the Pd-cluster and
2. the lateral position of the Pd-cluster is not changed i.e. the functionality of the Pd clusters as ruler is still valid.

The stability of the samples in UHV is furthermore only important for a very short time scale (hours to days) as the application of these standards is planned for instrumentation operated in Air (or being more precise: in non UHV ambient conditions). Therefore, the experimentally determined UHV stability is already sufficient in order to have enough time to perform a passivation of the samples for in air application. Due to the negative result from measuring the first sample in air (see section 3.8), a stability check of these samples in air and N₂ could not be carried out.

3.10 Objective 10: Use theoretical calculations, based on DFT, to investigate the influence of air on tip-sample interactions

The project's samples are intended to be used by a wide range of users with different kinds of instruments. Most of these instruments operate in air, which makes it indispensable to study the influence of air. It is well-known that in air the clean Si(111) surface gets covered by a silicon oxide layer of about 2 nm thickness. The layer is highly homogenous in the horizontal directions and it covers both terraces of the step homogeneously thus not changing the measured step height. The presence of this native oxide layer presents a formidable challenge for DFT simulations. Firstly, this layer increases the size of the model required. For DFT simulations in vacuum, reasonable results could be obtained with a model that has a thickness of approx. 1.5 nm. Secondly, DFT is not very well suited for amorphous materials since periodic boundary conditions are used. There are several possible approaches to this. One approach is to use a very large supercell which would capture most of the amorphous structure. However, the computational cost would allow us to study only the geometric structure, not further interactions with the tip. A second approach is to use one of the crystalline models of SiO₂. Ignoring nonmatching periodicities, this would lead to an additional 2 nm layer which would add another approximately 500-600 atoms to the already existing 700 atoms of the step structure. This amounts to a total of over 1200 atoms, which makes a full study very demanding / costly for DFT.

Apart from the oxide layer, the presence of air requires special treatment as well. Molecules of O₂, N₂ and H₂O should be randomly present. The random nature requires large sets of different initial conditions to be calculated. Since, a force-distance curve of the vacuum model requires roughly 5 days to be calculated, it is not feasible to perform hundreds, or more likely thousands, of these calculations. Additionally, we can expect the calculations to become more demanding when we add more atoms.

Instead of performing a large number of calculations on systems with random components CMI took an alternative approach as FZU had created a model of the first stage oxidation of the Si(111)-7x7 structure in the past. This model adds oxygen and hydroxyl groups to the surface by inserting oxygen atoms between the adatoms and its neighbouring silicon atoms and hydroxyl groups pointing up to the adatoms. Making this modification increases the number of atoms by almost 20 %. The computational demands grow even more, due to the nature of the added atoms: oxygen and hydrogen. Oxygen is very reactive and requires more basis functions for its description. Charge transfer is usually quite large which also makes it very sensitive to numerical instabilities. Hydrogen with its low atomic weight requires very small time steps in relaxations. In total, one relaxation of this system can take up to 24 hours (compared to approx. 8 hours for a clean surface).

This model does, however let us study the exact interaction of the hydroxyl groups with the tip. First the structure was relaxed. This relaxation leads to a small shift of approx. 0.8 Å of the silicon adatoms into the vacuum. This is due to the insertion of oxygen. Force distance curves were calculated for a reactive tip (Tip25) and a non-reactive tip (Tip25H). With a reactive tip numerical instabilities occur often and when the tip is at a relatively large distance from the surface. These indicate strong interactions between the tip and the sample. The tip can pull an atom from the surface, usually a hydrogen atom. After retraction, this atom remains bonded to the tip. Since the short-range chemical interaction is not much larger than noise it is very difficult to avoid contamination of the tip. This leads us to the conclusion that a reactive tip is extremely prone to contamination and measurements with a clean, reactive tip will be very rare. On the other hand, with a non-reactive tip, the short-range chemical interaction was so small it is essentially lost in the noise. This means that there is almost no atomic contrast in an AFM measurement. These results are in accordance with the experimental finding that atomic contrast on a silicon surface is not possible in air.

Calculations were performed on the supercomputer at CMI. Data interpretation was a joint process between CMI and FZU.

3.11 Objective 11: Provision of an uncertainty budget for lateral pitch measurement, based on experimental results and quantum mechanical modelling

The project's samples are intended to be used by a wide range of users with different kinds of instruments. Most of these instruments operate in air, which makes it indispensable to study the influence of air. The results of experiments in UHV should be compared to the results obtained in air and also verified by theoretical calculations. Due to delays, only a few samples were produced and only one sample could be characterised in more detail. These samples were first measured by STM (PTB) and by AFM in air (PTB). After that they were shipped to CMI and DFM and measured by AFM in air. Independently DFT calculations were performed at CMI. The measurement by STM revealed areas of Si7x7 with Pd clusters, as well as areas of Pd:Si islands and areas with a disordered surface. The Pd clusters are mostly on the faulted half of the 7x7 unit cell. The 7x7 reconstruction remains undisturbed. These findings are in agreement with the literature. The areas with Pd clusters were a few ten to hundred nanometres wide.

The measurements undertaken by AFM (CMI and DFM) did not find any Pd clusters, only Pd:Si islands. No difference could be found between the surface of this sample and a typical sample. As "find-me" structures were not used during production, and the areas of interest are fairly small and require high magnification, we cannot rule out that they were simply not found by the AFM. This would have to be tested further using "find-me" structures to ensure the correct area is measured.

DFT simulations were performed independently at CMI. In order to obtain meaningful answers by DFT, atomistic models of the cluster structure are indispensable (the DFT code was provided by FZU). Unfortunately, due to the delays and resulting lack of time, there was only very little information available to create these models. Therefore, only preliminary calculations could be performed with a single Pd atom and two types of Pd clusters (4 atoms and 13 atoms) which were chosen by taking symmetry considerations into account.

It was verified that the preferred position for a Pd atom is the basin along the main diagonal between the faulted centre adatom and the faulted restatom.

It was found that the 13-atom Pd cluster has a significant dependence on the alignment of the cluster with respect to the silicon structure. The structures obtained by relaxing initial structures varied significantly e.g.

even for rotations of 10 deg. We conclude from this, that for meaningful simulations of AFM FD curves, it is crucial to start with the correct lowest-energy configuration.

Force-distance curves were computed for a single Pd-atom and a 4-atom cluster. The force distance curve above the corner adatom was not changed due to the presence of the Pd atom. This was in agreement with the literature, where it is stated that the Si7x7 structure is not disturbed. For the 4-atom cluster we could see structural changes in the inner structure.

The computations are quite demanding, ranging from approx. 12 hours per configuration for a single atom to approx. 24 hours for a 13 atom cluster. The number of possible configurations is in the order of hundreds for only these three clusters (we must take into account not only the horizontal position but also its rotation and inner structure). The demands of computational time require us to limit the number of configurations which should be calculated. However, it is impossible to do this using current knowhow. Since it is very difficult to acquire information about the three dimensional structure of a sample from STM, it would probably be necessary to use a different technique, either AFM in UHV or one of the x-ray related techniques.

3.12 Objective 12: Development of lateral and step height sample prototypes using the self-assembly power of diblock copolymers with tenable feature size. Lateral pitch between 10 nm and 50 nm and step heights in the range between 3 nm and 20 nm

In the field of lateral length measurement at the nanoscale, before this project started, no commercial standards were available under 70 nm. Correspondingly, no technology solutions were available to meet the requirements of the International Technology Roadmap for Semiconductors (ITRS) for manufacturing devices with feature sizes of 15 nm and below (termed the 22 nm technology node). The use of self-assembling materials has emerged as a significant option for microelectronic patterning strategies.^{1,2,3} By combining “bottom up” self-assembly of BCPs with “top-down” patterned templates, it is possible to register the periodic domains of the nanostructured film with the underlying topographically defined structure and to improve the long-range order of the nanostructures, thereby simultaneously reducing defect formation and increasing size uniformity.⁴⁻⁸

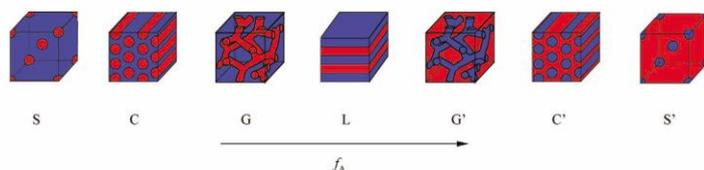


Figure 6a left: Mean-field prediction of the thermodynamic equilibrium phase structures for conformationally symmetric diblock melts. Phases are labelled as: L (lamellar), C (hexagonal cylinders), G (bicontinuous cubic), S (body-centred cubic spheres). f_A is the volume fraction. Figure 6b right: the RTP treatment.

Depending on their composition and molar mass characteristics lamellae, cylinders and gyroids morphologies (Figure 6a) with typical sizes in the 50 nm to 10 nm range were obtained, which were dependent on the chain length and molecular weight of the polymers (Figure 7)⁹.

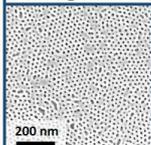
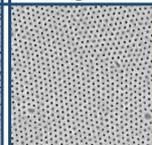
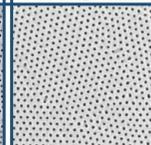
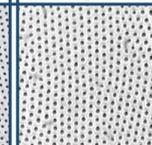
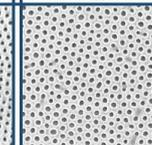
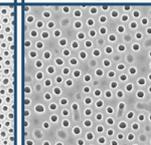
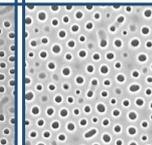
39 kg mol ⁻¹	54 kg mol ⁻¹	67 kg mol ⁻¹	82 kg mol ⁻¹	102 kg mol ⁻¹	132 kg mol ⁻¹	205 kg mol ⁻¹
						

Figure 7 SEM analysis of BCP over a large area with different molecular weights.

Usually, the organisation of a block copolymer microdomain is promoted by annealing the polymeric film at a temperature well above the glass transition^{10,11} or by plasticising the BCP via exposure to solvent vapours^{12,13}. In the framework of this project,^{14,15} the self-assembly of cylindrical polystyrene-b-

methacrylate (PS-*b*-PMMA) structures oriented perpendicular with respect to a silicon substrate was obtained on flat surfaces and in trenches predefined by Electron Beam Lithography (EBL) in as few as 10 s using the Rapid Thermal Processing (RTP) technique (Figure 6b). This new self-assembly process reduces the annealing times from days to seconds and it allows higher annealing kinetics without degrading the polymers.

In order to obtain reference samples for the lateral length at the nanoscale, the graphoepitaxy approach has been exploited, combining conventional top-down methods like EBL and Reactive Ion Etching (RIE), performed by INRIM, and BCP self-assembly, prepared and carried out by REG(PMO). The in-plane geometrical parameters characterising these structures (i.e. trench width and distance between two adjacent trenches) were selected taking into account the issue of commensurability between the topographic structure and the natural lattice spacing of the asymmetric PS-*b*-PMMA BCP.^{16,17} A detailed and systematic investigation of the dynamics of BCP ordering has been performed as a function of the in-plane geometric parameters and processing conditions.

The geometric parameters characterising the EBL-RIE trenches are illustrated in Figure 8, the BCP film has been deposited on the silicon surface neutralised with a hydroxy-terminated P(*S-r*-MMA) RCP schematically depicted by the red layer in the figure.

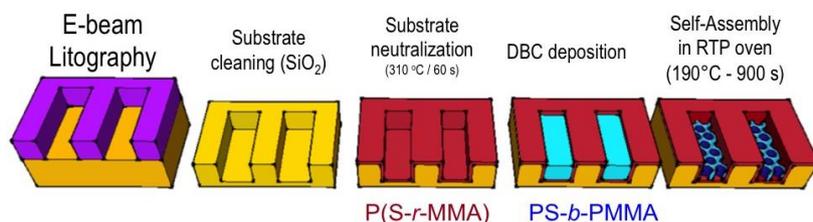


Figure 8 Scheme of the periodic topographic structures. RTP preparation with substrate neutralisation using a RCP (left) or onto the bare SiO₂ (second from left). For both substrates, the deposition of the block copolymer was performed via spin-coating and the directed self-assembly of the BCP was promoted by RTP annealing at 250 °C.

A systematic study of the geometrical parameters of the trenches and the RTP annealing of the BCP self-assembly has been performed¹⁸, achieving a very low defectivity and BCP monodomain for lateral lengths up to 100 micrometres (Figure 9). A detailed AFM study of the reference structures has been performed during the entire fabrication process and on the final delivered samples, demonstrating that the periodicity of the BCP on the major x axis is never affected by the geometrical boundaries constraint and it reflects the natural dimensions determined by BCP lengths and molar mass.

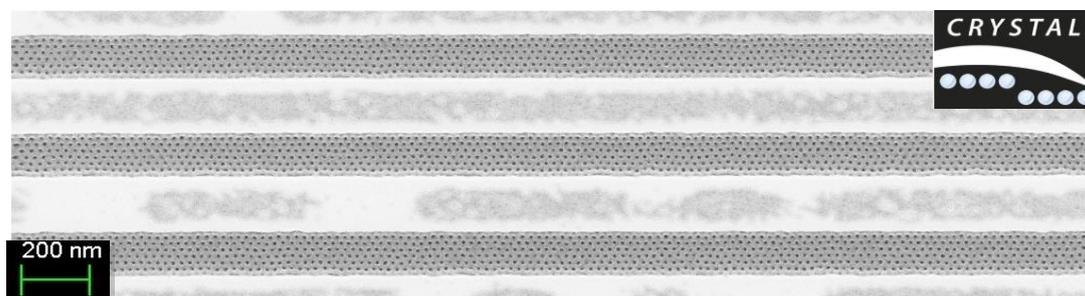


Figure 9: The final monodomain arrangement of BCP into the final layout of trenches 100 µm long.

In the shorter confinement direction (y axis) the period is strongly dependent on the boundaries with a general law allowing a priori selection of the number of rows in the trench¹⁹. AFM measurement by DFM and CMI confirmed the validity of the BCP graphoepitaxy self-assembly for AFM calibration in the range of 10 nm - 50 nm and in the analysis of the non-linearity of the x-axis scanning stage of the AFM (Figures 5, 6).

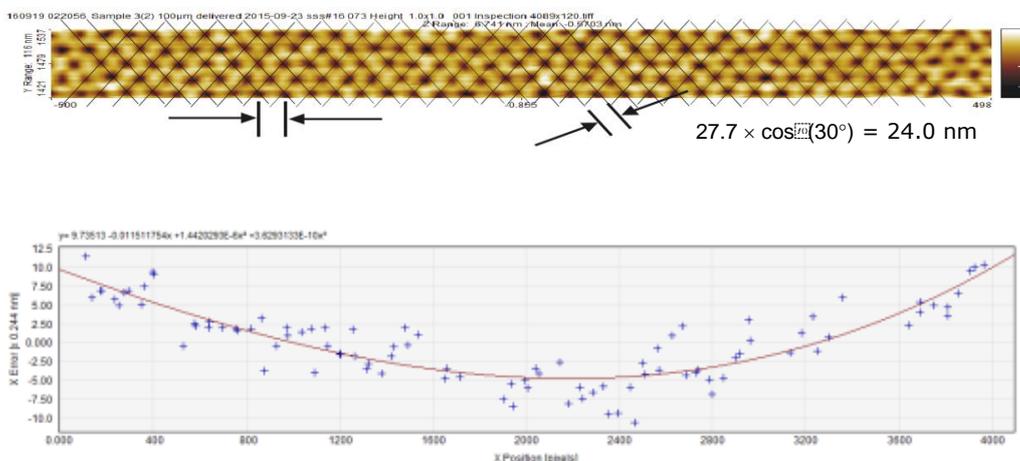


Figure 10 (top), and Figure 11 (bottom): AFM analysis of a BCP in a trench of 100 micrometres containing more than 3000 cylinders. With a 25 μm range scan along the x-axis, the dominating period of the BCP has been measured, $P = 27.473 \text{ nm} = 27.5 \pm 0.3 \text{ nm}$ ($u \pm 1 \%$). In Figure 11 the cross-correlation data of the same measurement, evidencing the non linearity of the x axis stage scanner on the whole range of 25 μm .

3.13 Objective 13: Provision of “find-me” structures for the identification of regions of interest on the sample prototypes

In the framework of graphoepitaxy parameter optimisation, INRIM produced a series of samples of 100 nm SiO_2 patterned substrates with families of trenches 130, 140, 150, 160 and 170 nm in width and 100 μm in length, filled by PS-b-PMMA BCP 54 kg/mol. “Find me” structures (two arrows and two logos) were defined using the Focus Ion Beam (FIB) method to show the best trench group. The proposals for the setup of the “find-me” structures were discussed with all partners according to the requirements of potential end-users.

Each family comprises 10 trenches with 100 nm spacing. Thirty-six different electron beam doses were performed to select the optimum process condition.

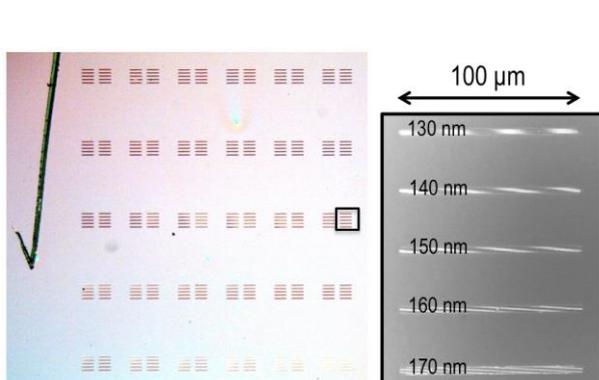


Figure 12 Graphoepitaxy layout with different trench widths

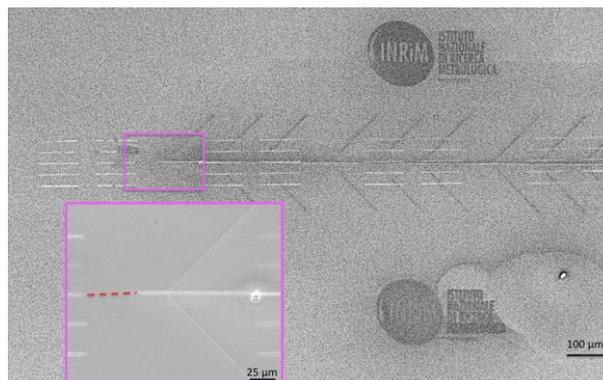


Figure 13 SEM images of the final layout for 3(1) sample

It was fundamental to search the right electron beam dose to define the best topographical structures avoiding defects which act negatively on the DBC ordered lattice.

Five cylinder rows were chosen to perform the best AFM measurement on the centre-to-centre BCP distance (L_0). For this reason a layout with different wide trench families was performed. The trench widths (130, 140, 150, 160 and 170 nm) were chosen starting from the BCP free energy plot built as a function of the trench width. The best values of electron current and width were selected after a SEM analysis on the structures. The 150 nm wide trenches perfectly accommodate the DBC in five cylinder rows showing no lattice defects.

Figure 14 below shows a SEM image of the hexagonal close packed (HCP) BCP lattice within a trench 150 nm wide. The Figure 14 also shows a schematic representation of the centre-to-centre distance L_0 on the cylinder structures. “Find me” structures were defined by FIB on the samples to identify the best trench family for the AFM measurements. For sample 3(1) one arrow indicates the right trench family 150 nm wide and two INRIM logos were placed on the top and at the bottom of the arrow. For sample 3(2) arrows indicate the right one trench family and several Crystal and INRIM logos are present beside the two arrows. Figure 15 shows the final layouts for 3(1) and 3(2) samples respectively.

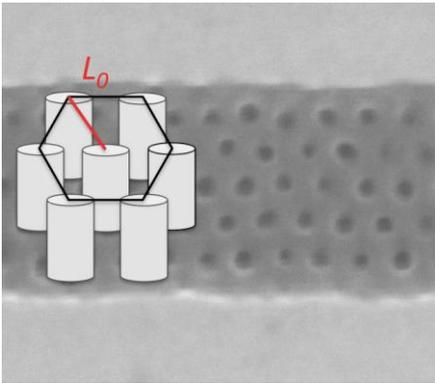


Figure 14 SEM image of the hexagonal close packed (HCP) DBC lattice within a trench 150 nm wide. The inset shows a schematic representation of the centre-to-centre distance L_0 on the cylinder structures.

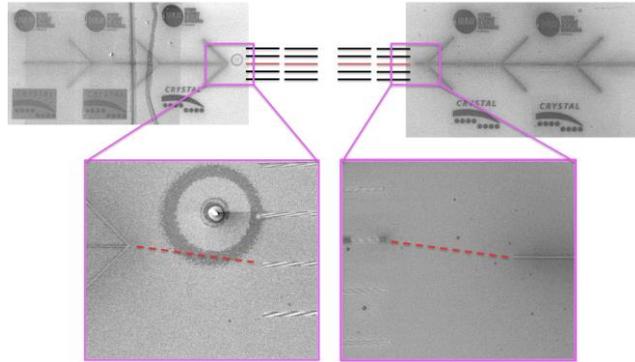


Figure 15: the final layouts for 3(1) and 3(2) samples respectively.

In the final layout of the new sets of samples, defined in the month 24 project meeting, only two optimised trenches of 100 μm have been produced, in L-shape, to allow x and y calibration with no need for “find me structures”, as in Figure 16.

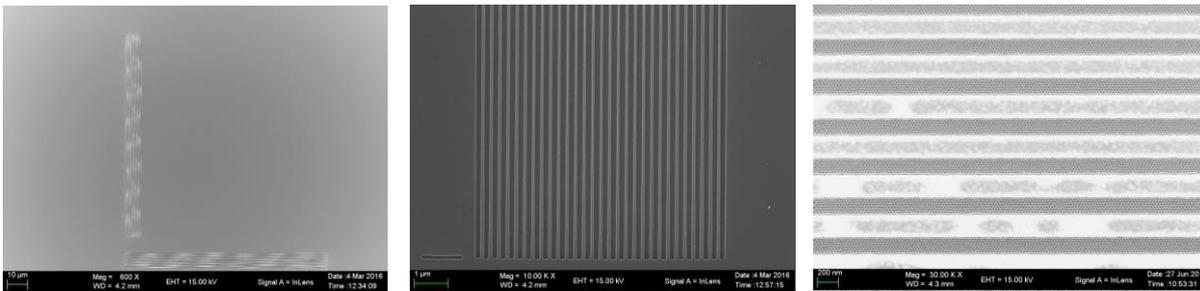


Figure 16: The new L-shape layout agreed in month 24, from left to right different magnification of the trenches.

Also in the patent²¹ deposited on the 23/05/2016 with title: „DISPOSITIVO CAMPIONE DI RIFERIMENTO PER LA CALIBRAZIONE DI MISURE DI LUNGHEZZA E RELATIVO PROCEDIMENTO DI CALIBRAZIONE“ - Italian Application No. 102016000052889, a square pattern of vertical and horizontal array of trenches has been designed without the need of “find me” structures.

3.14 Objective 14: Propagation of the BC mask to silicon dioxide over the regions of interest (ROI) which are 1 x 1 μm^2 to 10 x 100 μm^2 in area

Although the RIE pattern transfer at micrometric and submicrometric level has been widely investigated, the extension of the RIE processes to the nanometric features presents several critical issues that have to be carefully addressed, starting from the etch process feasibility, the control over the sidewalls and even the

influence of RIE effects on small structures. The final step of propagation by RIE is accomplished through a residual hard mask of SiO₂ of 10 nm, followed by dipping in HF, so releasing a flat silicon chip with holey silicon stripes in correspondence with the graphoepitaxy areas, as shown in Figure 17.

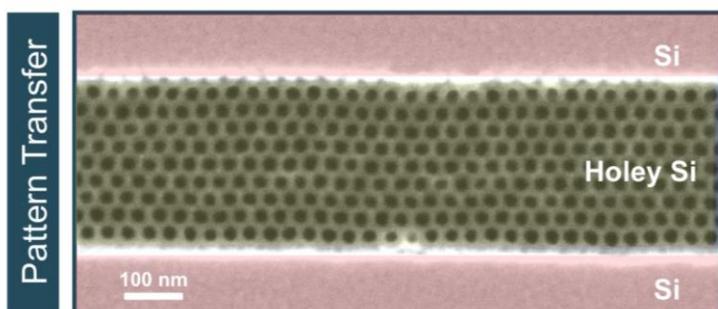


Fig. 17: Holey silicon as the final result of graphoepitaxy in a trench of 100 μm .

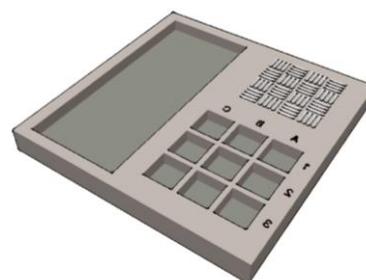


Fig. 18: Layout of the standard for AFM and X ray techniques as described in ref. 21

Before the CRYSTAL project, there were no extended studies of RIE etching on pore diameters in the sub 20 nm scale, so INRIM systematically investigated the influence of DBCs mask's pore diameter on the silicon etch rate and the final aspect ratio to study the etch behaviour. Moreover, we illustrated the feasibility of using a simple polymeric mask to transfer the pattern into a silicon substrate for low aspect ratio applications. Three different PS-*b*-PMMA perpendicular-oriented cylinders with the same thickness of 30 nm and different pores' diameters between 18 nm and 13 nm were obtained by tuning the DBC molar mass (M_n). A direct pattern transfer from the DBC mask into a silicon substrate was performed by reactive ion etching (RIE) using a cryogenic mixing mode of SF₆ + O₂. The results of this study have been submitted to the journal Nanotechnology²⁰. Also a Patent²¹ has been deposited on 23/05/2016 from the title: "dispositivo campione di riferimento per la calibrazione di misure di lunghezza e relativo procedimento di calibrazione" - Italian Application No. 102016000052889. This intellectual property covers an entire family of standards of lateral length at the nanoscale based on BCP technology, with other applications to other spectroscopy and X-ray areas (Figure 18).

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3.15 Objective 15: Fabrication of nano objects using DNA nano-origami

Aalto has successfully produced 2 nano-origami structures; cross like Seeman tiles and brick like 60-helix bundles. One of the designed structures, a large lattice structure of Seeman tiles attached together, was found to be too difficult to produce defect free and that structure was found to be unsuitable for calibration purposes. The Seeman tile and 60-helix bundle samples were handed over to VTT for checking their application according to certification. Aalto provided instructions for sample preparation for VTT measurements.

Aalto has designed DNA origami structures by caDNA software and accordingly purchased the DNA strands needed for the structure formation (scaffold strands and synthetic staple strands). The design of the structures was done in close cooperation with VTT. The optimal conditions for folding the above-mentioned nanostructures has been developed and the folding quality has been verified by using agarose gel electrophoresis, UV-Vis spectroscopy and TEM imaging. Furthermore, the excess staple strands have been efficiently separated from the folded structures by spin-filtering resulting in the purified high-quality samples containing DNA origami nanostructures. Finally Aalto was able to produce DNA-nano origami in a liquid phase with a high level of purification.

3.16 Objective 16: Testing of nano objects produced by DNA nano-origami with different SPM instrumentation for their possible application in AFM based shape measurement

Two different types of DNA nano origami structures were studied by Aalto and VTT; cross like Seeman tiles (ST) and brick like 60-helix bundles. In this feasibility study the ST were found to be suitable for calibration purposes. The 60-helix bundles were found to be unsuitable for use as a calibration standard because the multilayer structure is too soft and the dimensions were strongly affected by the measurement force.

The focus of this feasibility study was:

- preparation of the samples for measurement (Aalto)
- stability of the molecules during AFM measurement (VTT)
- identification of wrong molecules (VTT)
- statistical variation of the DNA-nano origami (VTT)
- stability during storage (VTT)

The preparation of the ST sample was easy. One of the criteria for calibration samples was that samples should be easy to prepare with written instruction and without special instruments, and without any specific knowledge of nano origami techniques. The deposition routinely yields well-separated and intact DNA origami structures on the mica surface.

The same ST structures were measured repeatedly. No changes were seen in the dimensions of the nano origami structures after 20 measurements. In this work, the studied ST structures were found to be relatively stable during storage. The prepared dry samples can retain their shape at least for 12 months. The differences between measured dimensions after 6 and 12 months were smaller than the standard uncertainty of the measurements. No degradation was observed in the measured samples when stored in temperature and humidity controlled laboratory conditions.

The sample uniformity was high; the number of defective structures was very low (< 10 %) and these structures were easy to detect. In addition, the cross-like structure is partially self-referring. It can be easily observed if the arms do not have the same width. Improper folding of the DNA origami structures may yield

defective structures, but most probably the observed deformations are caused by the interaction between the flexible structure and the substrate.

Both lateral and vertical dimensions of the ST structures were characterised. The ST structure has two steps of different height. Only the first step (2.0 nm) was found to be suitable for calibration. The standard uncertainty of the measurement was 0.2 nm. The second step was a double step and therefore not suitable for calibration. The width of the ST structure and arms of the ST were measured to be 88 nm and 28 nm, respectively, with a standard uncertainty of 3 nm. Standard deviations of the lateral dimensions were 3.5 nm, and it was mainly caused by deviations to the ST structures.

The lateral calibration of microscopes is usually carried out using large periodic structures. The average pitch can be used to calibrate large scales, and the non-linearity of the scale can also be detected. Single structures do not allow decent averaging, which limits their use in the scale calibration of the instrument. Despite the quite large standard deviation of the lateral dimensions (errors in the dimensions are 10 % or less), ST samples could be used in rough calibrations, as the scale errors in non-calibrated instruments can be as high as 30 %.

In addition to the scale errors, there are several other errors which affect the measurement accuracy and which are difficult to detect and correct from the measured image, especially the effect of drift. One solution is to mix the known origami structures with unknown samples, and to measure these samples simultaneously. Then the origami structures could be used to calibrate the scales, detect the drift and also correct the drift from the measured image. The ST is easy to distinguish from other structures, which makes it an especially suitable structure for calibration purposes.

In this study, DNA nano origami structures were found to be promising for calibration standards with some limitations. The maximum sizes of the structures are limited by the current production methods. Also multilayer structures were found to be too soft for proper characterisation and they are therefore not suitable for use as calibration standards.

In general, the fabrication of DNA origami nano-objects is relatively expensive (1 gram costs roughly 100 000 €), but for calibration purposes, the sparse coating of small substrates can be considered as a low-cost method. Coating of the substrates can be furthermore enhanced by spray-coating, resulting in a price of ~10 euros / square metre (with coating densities relevant for calibration purposes).

4 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 particular 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.

5 Website address and contact details

A public website is available at: www.ptb.de/emrp/sib61-home.html

The contact person for general questions about the project is Ingo Busch. (ingo.busch@ptb.de)

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6 List of publications

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