Final Publishable JRP Summary for NEW05 MechProNO
Traceable measurement of mechanical properties of nano-objects

Overview

The mechanical properties of nano-objects are increasingly attractive for industry, since nano-objects can be used to improve the properties of everyday materials. Several methods of mechanical measurement using atomic force microscopes (AFMs) have been developed but suffer from not being verified and traceable to the SI units. This project improved the force measurement of AFMs by developing the instrument's cantilever stiffness calibration, reducing the uncertainty of AFM elastic modulus (Young's modulus) measurements from several hundred per cent to only 30%. It also developed a new technique for the mechanical property measurement of nano-objects inside a DualBeam Focused Ion Beam (FIB)/Scanning Electron Microscopy (SEM)-device with a cantilever type force probe and provided validated reference methods that will help to develop new materials with improved mechanical strength.

Need for the project

Nano-objects are used in industry to improve the mechanical properties and functionality of advanced materials, for instance to reduce weight and increase stiffness in aerospace or automotive applications or for biological applications. In the longer-term as costs come down they have the potential to be used in everyday products like glass, steel, cement, coatings and easy-to-clean ceramics. Whether the nanostructure is a layer or particles of a specific shape (nanowire, nanotube or nanoparticle) embedded in the material, it is important to know the mechanical properties and be able to measure them reliably.

Several measurement methods using AFMs have been developed to assess mechanical properties but they have not been verified and are not traceable to the SI units and therefore there is no guarantee that measurements made by different instruments, or at different times or places are comparable. One of the key parameters to determine is the Young's modulus or stiffness of nanomaterials, which requires knowledge of the indentation force applied by the measurement instrument. However this can be affected by the stiffness of the AFM cantilevers, the AFM tip radius and shape, and the dimensions of the nano-objects.

Due to their small size and smaller volume compared to their surface, the mechanical behaviour of nano-objects is sometimes completely different from macroscopic objects. The smaller volume leads to a reduced stiffness of the nanostructures and the relatively large surface leads to large interaction forces between the AFM tip and the surface. These factors must be taken into account during measurement of the mechanical properties of nanostructures.

Several papers on AFM methods of measuring the Young's modulus of nano-objects have been published in the past 10 years, but the scatter and deviation of the results is more than 100%. A particular issue is the lack of reliable methods to fix the nano-particles to the substrate, so that they do not slide away during the force application by the AFM tip. Furthermore the interaction forces between tip and sample can be affected by the humidity.

Nanoscale measurements are particularly difficult to make accurately, so by supporting experimental results with modelling and simulation the behaviour of the material can be understood and optimised. Macroscopic Finite Element Modelling (FEM) is used for macroscopic simulations and Molecular Dynamic Calculation (MDC) for the nanoscopic simulations. By extending the former towards smaller dimensions (1 µm) and the latter towards larger dimensions (100 nm) it is possible to compare the results. Instrumented indentation technique (IIT) is widely used and understood, but is not able to measure objects smaller than 500 nm. However comparative measurements between IIT and AFMs on the developed test samples, along with the modelling techniques, mean that measurement uncertainties at the nano-scale for indentation and bending can be quantified.

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Scientific and technical objectives

The overall objective of the project was to develop measurement traceability for the mechanical properties of nano-objects such as nanoparticles, nanowires, nanoscale structures and composite materials through the development of test samples and techniques, as well as improved instruments. It focused on the key measurement tools used by the developers of nano-objects and advanced materials – AFMs and IITs.

The project developed preparation methods to fix nano-objects to substrates in order to make mechanical measurements, and developed well-defined test samples and measurement methods to verify the instruments. This was done in objectives 3 and 7.

Objectives 1 and 2 developed force calibration techniques for AFM and instrumented indenters for traceable measurement of the mechanical properties of nano-objects.

Objective 4 developed modelling of the mechanical properties to support experimental results.

Objectives 6, 8 and 9 investigated the Instrumented Indentation Technique (IIT) and AFM techniques for the measurement of mechanical properties for real nano-objects, including the effect of humidity.

Objective 5 compared measurement results from different NMIs, as the first step of establishing reference samples.

1. Development of traceable stiffness calibration of AFM cantilevers in the force range of 10 pN to 1 µN
2. Provision of a method for easy-to-use in-situ calibration of AFM cantilever stiffness and a method for instrumented indenters
3. Provision of three test structures with arrays of structures for a qualification of instrumented indentation technique (IIT) and AFM
4. Provision of new Finite Element and Molecular Dynamic simulation tools to model the deformations of nano-objects from the molecular level up to object sizes of 100 nm to support experimental data
5. Performance of an interlaboratory comparison on a set of test samples to reveal their mechanical properties as a first step towards the creation of new types of reference materials
6. Provision of a guideline for the measurement of the geometrical parameters, e.g. length, diameter, width and height of nanostructures and nano-objects and to establish correction factors considering tip–sample effects
7. Provision of a guideline for the preparation of nano-objects attached to hard substrates, like nanoparticles, and nanowires
8. Provision of a guideline for the measurement of the mechanical properties of small nano-sized objects by AFM and IIT
9. Provision of uncertainty budgets related to the measurement of mechanical properties, such as elastic modulus.

Results

1. Traceable stiffness calibration of AFM cantilevers in the force range of 10 pN to 1 µN

Working with NanoWorld Services GmbH, who specialise in nanotechnology product development, PTB improved the widely used thermal vibration method for the traceable calibration of the bending stiffness of AFM cantilevers with stiffnesses ranging from 0.01 N/m to 5 N/m from 20 % to 10 %. NanoWorld used calibrated reference cantilevers to calibrate their thermal vibration method. PTB calibrated the stiffness of these cantilevers with an uncertainty of 4 %. NanoWorld states an uncertainty of 10 % for their improved thermal vibration method which can be used by material developers. By having an easier, more accurate way to work out the stiffness of the cantilever, better measurements of the nanomaterials are possible.

2. A method for easy-to-use in-situ calibration of AFM cantilever stiffness and as a method for instrumented indenters

A single method for both in-situ stiffness calibration of AFM cantilevers and IITs has been developed. The method is based on the well-known cantilever on reference spring method. Meander springs with a stiffness of 15 N/m were developed. The linearity deviations up to 1 mN force are smaller than 0.2% and more importantly, the influence of the loading position on the stiffness is strongly reduced (<1%) compared to cantilever type reference springs (10 – 20%). The reference springs are available from CiS GmbH and an AFM force uncertainty of 7% is possible with these reference springs.

3. Test structures with arrays of structures for a qualification of IIT and AFM

The project partners provided nano structures (pillars, cantilevers and particles) to compare AFM and IIT techniques. Pillars of two different materials were fabricated using microtechnolgy, silicon and photo-resist. IIT measurements on high aspect ratio silicon pillars revealed that the equivalent stiffness of the pillars has to be taken into account [1] in order to prevent systematic errors of the measured Young's modulus. The equivalent stiffness is proportional to the square of the pillar radius and inversely proportional to pillar height. Both pillar diameter and height were measured using NPL's traceable dimensional AFM. No change of Young's modulus with decreasing size (size effect) was observed for nano-pillars or nano-beams using various measuring methods including IIT and Dual Beam Focussed Ion Beam (FIB) / Scanning Electron Microscopy (SEM).

Two commercially available materials, amorphous silicon oxide and amorphous silicon nitride, have been identified as suitable as future reference materials [2, 3]. BAM developed a new technique for in-situ bending in a Dual Beam FIB/SEM-device based on a micromanipulator with piezoresistive cantilever force sensor for force application and measurement, as well as a digital image correlation software for the evaluation of beam displacements. This meant that at least two independent methods could be used for Young's modulus determination of the same material. The measured Young's moduli agreed to within 20% [4] and no size effect was observed.

4. Finite Element and Molecular Dynamic simulation tools to model the deformations of nano-objects from molecular level to object sizes of 100 nm to support experimental data

Finite Element (which models at the macroscopic level) and Molecular Dynamic modelling (which models at the nanoscale) were both compared with gold nanorod test materials and a diamond AFM tip with 5 nm radius [5]. There was agreement between the different techniques giving confidence to the modelling techniques.

5. Interlaboratory comparison on a set of test samples to reveal their mechanical properties as a first step into the creation of new types of reference materials

An interlaboratory comparison was performed with FIB fabricated silicon nitride beams made of membranes. The thickness was measured with an uncertainty of 3% at BAM using the in-situ FIB bending test and IIT. PTB used the MEMS-based bending method [6]. The Young's modulus of the two bending methods agreed to within 6% and the Young's modulus measured by IIT is 20% higher [4].

6. Guideline for the measurement of the geometrical parameters of nanostructures and nano-objects and correction factors considering tip–sample effects

NPL has set up an AFM for studying the tip-sample interaction, for different shapes and sharpness ie the effect of wear. It was found that measurements were affected by the deformation of the tip as well as that of the particle itself. Different tip materials were also found to have an effect on the measurements [7], [8].

7. Guideline for the preparation of fixed nano-objects on hard substrates, like nanoparticles, and nanowires

In order to carry out reliable nanomechanical measurements the particles need to be fixed to the substrate, without influencing the measurements. Two methods were developed: one used drops of fluids with dissolved nano-objects on samples which were then dried [9], and the second tightly fixed nano-particles to a substrate by embedding them into a 40 nm thin PMMA layer [10]. The second method was the most successful. Guidelines were published on the project webpages.

8. Guideline for the measurement of the mechanical properties of small nanosized objects by AFM and IIT

An introductory guide on the measurement of the mechanical properties of nano-objects using AFM was published [11]. It covers AFM cantilever stiffness determination, force-displacement measurement, cantilever bending, indentation of nanoparticles, keeping them in place and the measurement of contact area using a polycarbonate reference sample.

9. Provision of uncertainty budgets related to the measurement of mechanical properties, such as elastic modulus

BAM developed a new method for the measurement of the elastic modulus of small micro-sized beams using the in-situ bending method inside the vacuum chamber of a Dual Beam FIB/SEM-device. The uncertainty for the measurement of the elastic modulus was less than 10% using the new device.

In summary, the objectives were fully achieved. The accuracy of a range of techniques for measuring the mechanical properties of nanomaterials have been significantly improved. Forces can now be measured with AFM more accurately, with an uncertainty of 7 %. The mechanical properties of materials can also be measured more accurately, with an uncertainty of 10 %, using a new technique for in-situ bending tests in a DualBeam FIB/SEM device. A new method for IIT measurement of the Young's modulus of silicon nano-pillars was developed which removed the size effect. Two future reference materials were identified: amorphous silicon oxide and amorphous silicon nitride.

Actual and potential impact

This project enables NMIs to perform and provide traceable calibration of the mechanical properties adhesion, stiffness and elasticity of nano-objects, such as nanoparticles, nanowires and nanoscale structures and composite materials. The impact of the project is directly related to the new methodologies, calibration and test tools, and improved analytical tools for modelling and simulation.

Dissemination

Project results were also publicised by a tutorial at TU Dresden, presentations are available online, which was primarily attended by NMIs. Micro- and nano-object samples developed during the project are now available to interested scientists.

Impact on metrological and scientific communities

The following best practice guides for improved measurement of size, shape and mechanical properties of nanoscale objects were developed and made available via the project web page:

- Guideline for the preparation of fixed nano-objects on hard substrates, like nanoparticles and nanowires
- Good Practice Guide for the measurement of the cantilever normal spring constant using a MEMS device
- Good Practice Guide for nanoindentation of nanoparticles embedded in a layer using an SEM in situ technique
- Good Practice Guide "Elastic property measurement of nanobeams by cantilever force measurement inside a Scanning Electron Microscope"
- Introductory guide to measuring the mechanical properties of nano-objects/particles with AFM on flat surfaces
- Introductory Guide on the determination of geometrical properties of nano-objects under different adhesion levels

Dissemination of the instrumented indentation results was incorporated in the revision of the ISO standard 14577 Metallic materials - Instrumented indentation test for hardness and materials parameters by the project partners. Project results have also fed into the ISO standard 11775 Surface chemical analysis -- Scanning-probe microscopy -- Determination of cantilever normal spring constants.

Early impact

Micro- and nanoforce metrology with AFM and IIT is now possible with lower uncertainty. With AFM it is possible to buy cantilevers whose stiffness is calibrated with an uncertainty of only 10 %. Newly developed meander or MEMS reference springs allow AFM and IIT to reduce the uncertainty further. Thus measurement techniques for the mechanical properties of nanomaterials are now more accurate and traceable. Several companies and NMIs are able to provide reference samples and services, which are essential for all measurements of nano-objects.

- Cantilevers are now available from NanoWorld with stiffness uncertainties of only 10% [14]. Using these, calibrated cantilevers can reduce force measurement uncertainty from 20% using the thermal vibration method. AFM users can also calibrate their own thermal vibration method on their instrument by using a reference cantilever with known stiffness from NanoWorld.
- BAM is offering a new service for the calibration of elastic modulus via FIB in-situ bending measurements of nano-beams [4]. A good practice guide describing the method is available [15].

A new calibration service for cantilever stiffness (U = 5%) based on calibrated MEMS [19] is being offered by PTB and is based on calibrated MEMS reference spring actuators [6] which are fabricated by TU-Ch.

- Cantilevers with stiffness ranging from 0.01N/m to 1000N/m can be calibrated by PTB with an uncertainty of 5% [20]. A good practice guide describing the method is available from the project website [21]. The calibrated stiffness of one cantilever (PPP-CONTR, stiffness 0.12 N/m) has been compared with PTB's nanonewton force facility, which offers an uncertainty of only 0.6% [22]. The deviation of the stiffness value measured by the MEMS was less than 1% [23].
- New meander type reference springs with a very big loading area (1 mm x 0.7 mm) for force application were developed and are now commercially available from the CiS Forschungsinstitut für Mikrosensorik GmbH for the improved in-situ cantilever on reference cantilever calibration method of AFM cantilever spring stiffness with reduced uncertainty [24].
- A new MEMS reference spring was developed for AFM offering separate calibrating force and deflection of the AFM [25]. It consists of two springs in series and the stiffness shows no dependence on the loading position, and the temperature dependence of stiffness, force and deflection is below 1% for ambient conditions. TU-Ch plans to offer these MEMS double springs to customers in the near future.
- TU-Ch developed new approaches for encapsulation of the sensitive MEMS devices. The technology provides an open platform for further MEMS fabrication and delivery to interested partners, and the stiffness parameters can be easily adapted to customer requirements.

Potential impact

Traceable calibrated AFM cantilevers and reduced uncertainty in stiffness will, in the long term, lead to further investigations of mechanical properties of nano-objects using AFM and help to build confidence in AFM mechanical property measurements and performance. Reliable data, combined with modelling, will allow nanomaterials to be exploited in new applications and to replace existing components. Nanomaterials have the potential to be used in the development of new materials with better mechanical properties and new functionalities, this will be facilitated by easier and more accurate mechanical property measurements. The techniques developed during the project are already being used in universities and some companies.

List of publications

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