Budapest University of Technology and Economics
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INVESTIGATION OF THE LOCAL MECHANICAL PROPERTIES WITH ATOMIC FORCE MICROSCOPY TECHNIQUES

Summary of the Ph.D. dissertation

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Motivation and background of the research

The atomic force microscope (AFM) was invented in1986 by Binnig and Quate for scanning the surface topography, extending the family of scanning probe microscopes. The advantage of the AFM lies in the simplicity of its imaging technique: it uses a tip mounted on a flexible cantilever to follow the surface changes, which makes possible even 0.05 nm lateral and 0.2 nm horizontal resolution [1].

After the invention of AFM, the need for measuring local material properties (besides topography) from the tip-sample interaction appeared quite early. The competence of the AFM had expanded. From the new application fields, the investigation of mechanical properties has a significant role. In the last few years, every AFM manufacturer developed different tools, packages, or modes to measure mechanical properties (Bruker: QNM and Force Volume modules, Asylum Research: Bimodal Dual AC Imaging module, Park AFM: PinPoint nanomechanical mode, etc.). These modules use different physical approaches and models to get specific mechanical properties, and their development continues even today. The most widely used parameter is Young's modulus since it can be measured by a common AFM without any special hardware requirements. The modules need several parameters given by the user (e.g., the type of the mechanical model for the fitting, starting point of the fitting, how much part of the curve is used to the fit, etc.) which seriously affect the obtained Young's modulus; sometimes they are already built in the module, but the actual implementation is concealed due to the industrial secret.

The motivation of my work was to contribute to the standardization of Young's modulus measurement with AFM, to obtain more reliable results and enable the quantitative comparison for the scientists working in different research fields and laboratories.

The addressed problems of the research field – Objectives

Most AFMs use the optical-lever technique for the detection, where a laser beam is reflected from the backside of the cantilever and collected by a multi-segmented photodetector, which produces a voltage signal proportional to the cantilever deflection. Therefore, the first step of every AFM measurement is the conversion of the voltage signal into the natural unit of the deflection: nanometer or micrometer. The standard determination method is that before any measurements, a contact-mode point-spectroscopy is implemented on an ideally hard and flat sample (e.g., on a silicon wafer) when all of the deflection occurs on the cantilever without the indentation of the hard sample. The slope of the obtained curve yields the conversion factor, the so-called inverse optical lever sensitivity (InvOLS).

After the rescaling the raw deflection-curve, the real mission is to determine the Young's modulus of the sample obtained from the fit of a contact-mechanical model to the data of the so-called force curve.

The determination of Young's modulus is also based on the point-spectroscopy. During the contact-mode point-spectroscopy, the tip is pushed into the sample and then withdrawn; the deflection of the cantilever is measured in relation to the absolute position of the piezoceramic, which drives the sample vertically. During this process, the tip deforms the surface, and it can be assumed that one of the known contact mechanical models [3] –chosen to the measurement settings– is valid in the elastic range of the deformation and gives the value of the Young's modulus. For the fitting, the measured point-spectroscopy curve has to be transformed into the so-called force curve. This transformation is so essential that the point-spectroscopy curve is often referred to as force-curve in the literature. The force-curve shows the interaction force between the tip and the sample, concerning the tip-sample distance, or as it is often called tip-sample separation. The first step of the transformation is the conversion of the voltage signal of the cantilever deflection to nanometer, as it was mentioned above. The next step is the determination of the contact point, the point where the tip jumps to contact with the sample. This will be the starting point of the fitting. Then the Young's modulus can be calculated from the fitting parameter using some constants describing the geometry of the tip.

For the right measurement setup, it is particularly important to choose the spring constant (k) of the cantilever appropriately; it has to fit the elasticity of the investigated sample. The measured curve is the result of the elastic deformation of the sample and the deflection of the cantilever. The obtained curve can be evaluated if the deformation of the cantilever and the sample are in the same order of magnitude. If the spring constant is too small compared to the sample, the cantilever will deflect without indentation (sample deformation), it is the case of the calibration. If the cantilever is too stiff, the sample could be deformed without the deflection of the cantilever, and the curve will not contain information about the elasticity of the sample.

Here it is the brief summary of the critical steps of the evaluation (*):

- choosing the cantilever with proper spring constant
- determination of the inverse optical lever sensitivity (InvOLS)
- choosing the fitting model and the range of the fitting

The above-presented evaluation method has several unsolved problems that I will demonstrate in the order of (*).

The AFM manufacturers occasionally give a recommendation for their packages about the **spring constants** and the related measurable range of the elasticity; however, these are valid for some techniques more special than the contact mode point-spectroscopy. From my best knowledge, there is no method which says, how to find the proper spring constant for a sample with unknown elasticity; or even which measured curve is proper for the evaluation and can give relevant Young's modulus value.

In the case of the **InvOLS** determination, the user does the standard or recommended calibration method (e.g., by AFM manufacturers) before the measurements according to the way as mentioned above. Henceforward, the obtained value is used, although some parameters can change during the measurements (e.g., laser position, the topography of the sample, tip-sample incident angle, etc.). There is no study about the size of the error that can be caused by the change of these parameters. However, its presence has a direct impact on the results in the case of every type of evaluation. Hence, there is a strong need for a new calibration method, which provides an adaptive InvOLS factor according to the real-time geometrical arrangement.

In the case of the **fitting**, the determination of the contact point for the different types of the curves and the algorithmization issues are the subjects of a large number of studies, but there is no widely accepted method for the determination of the endpoint. The choice of the endpoint is a significant problem since the contact-mechanical models are valid theoretically in the elastic region; thus the determination of the endpoint equals the determination of the validity region of the models. It is not known that in case of a given model and a given contact point, how does the calculated value of the Young's modulus depend on the choice of the endpoint. Furthermore, it is also a question of how much error can be caused by leaving the validity region of the model and how it can be recognized.

My dissertation aims to solve the problems of Young's modulus measurement that are independent of the method, the instrumentation, and the applied model. Since I study these problems through the most common methods; thus, the solutions are valid independently of the AFM instrumentation and the AFM manufacturers.

Considering the experienced incompletenesses of the common methods, I endeavored to find a solution primarily for the following issues:

1. Developing a method which helps to distinguish the different type of the measured curves and helps to find the cantilever with the proper spring constant, which is inevitable to obtain a trustable value of the Young's modulus.
2. Developing a method, which implements the calibration and the measurement in parallel, and gives an adaptive InvOLS factor. This InvOLS value is characteristic to the actual setup and the local topography of the sample at a given point-spectroscopy.

The steps in (*) are closely linked, which makes difficulties. For example, to decide whether the chosen spring constant of the cantilever is right, we have to analyze the measured curve, which is required knowledge of the conversion factor. Accordingly, the implementation of the measurement is following the order of the steps in (*), the keys to the solution are the analyses and the classification of the point-spectroscopy curves. Thus, I will present my theses following this logic.

New Scientific Results

Thesis I.

I have developed a new method for the optimization of endpoint selection during contact-mechanical model fitting on force-curves measured by AFM point-spectroscopy, for the evaluation of elastic sample deformation. Explanation

a.) The method is based on the proven observation that two dominant regions can be separated on the AFM force-curves: a region characteristic to the elastic deformation of the sample and another region which characterizes only the deflection of the probe.

b.) The method helps in the identification of the proper endpoint (opposite to the contact point) for Hertz, Hertz-Sneddon, and DMT contact-mechanical models.

c.) To separate the two dominant regions, the method uses the slope of the deflection-curve, which is a series of linear regressions (or differentials) between last point of the obtained curve and each point of the curve. The region which characteristic only to the cantilever deflection can be identified as a definite plateau on this slope.

d.) The proper endpoint for model fitting is defined at the end of the region which is characteristic to the elastic deformation of the sample, namely, the point on the normalized slope curve which belongs to 95% of the plateau value can be assumed as the endpoint for fitting.

e.) It was shown that any deviation from the proposed optimal endpoint can cause significant errors (more than 20 %) in the value of Young's modulus which was obtained from the fitting.

Related publications: [L1], [L3] – [L5], [K3] – [K5]

Thesis II

I have proved that for a sample with given elastic properties it is possible to select a probe with an adequate spring constant in order to obtain force-curves suitable for the optimized endpoint selection method, described in Thesis I. I have shown that the method can also be used to assess the range of sample elasticity in which probes with different spring constants can be used to measure the Young's modulus of samples with AFM point-spectroscopy.

Explanation:

a.) It was shown that the AFM force-curves can be classified into three categories based on how many of the two characteristic domains are present in the curves. In the two simpler cases the curve only contains the range either where the elastic deformation of the sample is dominant or purely the deflection of the cantilever, while in a third case both regions are present.

b.) It was demonstrated that the force-curves fall into these three characteristic categories according to the relation between the Young's modulus of the elastic sample and the spring constant of the cantilever.

c.) It was shown that by the proper selection of the cantilever's spring constant for a given elastic sample such force-curves can be obtained which contain both characteristic regions and thus can be used for the optimal endpoint selection method for contact mechanical model fitting, as described in Thesis I.

d.) Based on the series of proton beam irradiated PDMS samples it was found that for the evaluation of the elastic properties of materials based on AFM force-curves a cantilever with 0.2 N/m spring constant can be used in the 4 MPa – 830 MPa elastic range, while a cantilever with 5 N/m spring constant was found to be applicable in the 830 MPa – 16.7 GPa range.

Related publications: [L1], [L3] - [L5]

Thesis III

I have proved that the standard calibration method of InvOLS for AFM point-spectroscopy measurements (which uses an ideally hard and flat surface) can introduce significant errors during force-curve evaluation because the actual InvOLS (which is valid at the time and place of sample measurements) can differ significantly due to experimental conditions (position of the laser spot on the back of the cantilever, surface/probe incidence angle). I have introduced a new, adaptive InvOLS calibration method which successfully eliminates these problems.

Explanation:

a.) It was shown experimentally and with simulations that the relative dependence of the obtained InvOLS values during calibration (on an ideally hard and flat surface) on the position of the laser spot is around 1.5 %/μm (measured on a silicon wafer with a probe of 5 N/m spring constant).

b.) It was shown experimentally, that the inclination of the surface (e.g. the variation in the surface/probe incidence angle) in the 10-15^{o} range can cause a 10 % variation in the measured InvOLS during calibration (measured on a hard (~30 GPa), proton beam irradiated PDMS with a probe of 0.2 N/m spring constant).

c.) The effect of improper InvOLS calibration on the determination of Young's modulus during force-curve evaluation was implicitly expressed and it was found that a ±20 % error in the InvOLS could lead to relative errors in the calculated Young's modulus in the -40%/+60% range.

d.) It was proven that the AFM force-curve classification method presented in Thesis I can be used for an adaptive InvOLS calibration as well. By using a cantilever with adequate spring constant (defined by Thesis II) the linear terminal part of the force-curve provides an InvOLS value, which is characteristic for the actual measurement parameters (including laser spot position and sample/probe incidence angle) and provides a reliable scaling factor for each obtained deflection-curve independently.

Related publications: [L2], [K1], [K2]

Applications

The method introduced in my theses I-III has proven to be a useful tool in the investigation of the following material systems.

PDMS (polydimethylsiloxane) is an optically clear, hydrophobic, non-toxic, and non-flammable material. It is often applied for the fabrication of micro- and nanoscale devices, such as Micro-Electro-Mechanical Systems (MEMS), lab-on-a-chip (LoC) or microfluidic devices. However, PDMS also has some significant limitations, for instance, low hardness and low Young's modulus, which prevents the creation of e.g. high aspect ratio microstructures. Joining the research of Róbert Huszánk Ph.D. (from the HAS-ATOMKI), the PDMS system irradiated by a proton beam with different fluences was investigated. With the developed method, I managed to determine the Young's modulus of the PDMS polymer as a function of the ion fluence. The problem was not trivial, since the Young's modulus varies in a wide range (from few MPa to about 50 GPa) and the presence of the diverse surface structures.

I joined to the cooperation of Institute of Physics at the University of Debrecen with HAS-ATOMKI in the research on chalcogenide thin films using my developed method. There are several applications of the chalcogenides such as memory devices, optical devices and optical fibers, or it has a role in the manufacturing of various sensors. Thus, the photo-induced changes in the chalcogenide semiconductors are highly important, as the change of the refractive index, the optical edge or the volume. The photo-induced change can be crystalline or a change keeping the amorphous phase. It depends on the material, the wavelength and the intensity of the light and the temperature. During our cooperation I investigated changes of the volume and the elasticity of laser-induced and electron beam induced structures in case of chalcogenides with various compositions. The obtained results can help to determine the atomic mechanism which forms the surface structures. This research keeps going.

Besides these applications, the method can help to develop a reliable algorithm that can automatize the following steps:

- it can help to decide whether the measurement was done with a proper tip. If the answer is yes, it does the followings
- determine the adaptive InvOLS
- gives the Young's modulus from the fit

This program can be beneficial in the research fields, where the elasticity of nanostructures is needed.

Publications

Publications related to the thesis points

International, peer-reviewed journal papers, written in foreign (English) language

[L1] **Judit Kámán**, Róbert Huszánk, Attila Bonyár, "Towards more reliable AFM force-curve evaluation: A method for spring constant selection, adaptive lever sensitivity calibration and fitting boundary identification", **MICRON** 125: pp. 102717**.** (2019) (IF=1.53, Scimago: Q3)

[L2] Ágoston Gábor Nagy, **Judit Kámán**, Attila Bonyár, Róbert Horváth, "Spring constant and sensitivity calibration of FluidFM micropipette cantilevers for force spectroscopy measurements", **SCIENTIFIC REPORTS** 9(1): pp. 10287. (2019) (IF=4.011, Scimago: D1)

[L3] Róbert Huszánk, Attila Bonyár, **Judit Kámán**, Enikő Furu, "Wide range control in the elastic properties of PDMS polymer with ion (H+) beam irradiation", **POLYMER DEGRADATION AND STABIILITY,** 152: pp. 253-258 (IF = 3.78, Scimago: D1)

[L4] **Judit Kámán**, Attila Bonyár; „Investigation of the Local Mechanical Properties of the SAC Solder Joint with AFM", **MATERIALS SCIENCE FORUM** 885: pp. 269-274. (2017) (IF: -, Scimago: Q3)

[L5] **Judit Kámán**, „Young's Modulus and Energy Dissipation Determination Methods by AFM, with Particular Reference to Chalcogenide Thin Film", **PERIODICA POLYTECHNICA-ELECTRICAL ENGINEERING AND COMPUTER SCIENCE** 59(1): pp. 18-25. (2015) (IF: -, Scimago: Q4)

International, peer-reviewed conference papers, written in foreign (English) language

[K1] **Judit Kámán**, Attila Bonyár, Róbert Huszánk, "The effect of surface inclination on AFM force-curve calibration and evaluation", In: Proc of the 41th International Spring Seminar on Electronics Technology. Zlatibor, Serbia, (IEEE) (2018) (WoS, Scopus).

[K2] **Judit Kámán**, Attila Bonyár, "Investigation of the AFM contact-mode force calibration with simulation", In: Proc of the 40th International Spring Seminar on Electronics Technology. Sofia, Bulgaria, (IEEE), pp. 1-4. (2017) (WoS, Scopus).

[K3] **Judit Kámán**, Attila Bonyár, Tamás Hurtony, Gábor Harsányi, "Investigation of Surface Mechanical Properties of the Copper-Solder Interface by Atomic Force Microscopy" In: Proc of the 38th International Spring Seminar on Electronics Technology. Eger, Hungary, (IEEE), pp. 425-430. (2015) (WoS, Scopus)

[K4] **Judit Kámán**, Attila Bonyár, István Csarnovics, Csaba Cserháti, "Investigation of mechanical properties of the generated surface structures on a chalcogenide thin film with AFM", Proc of the 21st International Symposium for Design and Technology in Electronic Packaging. Brasov, Romania, (IEEE), pp. 31-34. (2015) (WoS, Scopus)

[K5] Attila Bonyár, **Judit Kámán**, István Csarnovics, "Elastic modulus and energy dissipation measurements with AFM on chalcogenide thin films", Proc of the 20th International Symposium for Design and Technology in Electronic Packaging. Bucharest, Romania, (IEEE), pp. 31-34. (2014) (WoS, Scopus)

Additional publications

International, peer-reviewed journal papers, written in foreign (English) language

[L6] A. Bonyár, I. Csarnovics, M. Veres, L. Himics, A. Csík, **J. Kámán**, L. Balázs, S. Kökényesi, ” Investigation of the performance of thermally generated gold nanoislands for LSPR and SERS applications”, **SENSORS AND ACTUATORS B: CHEMICAL 255,** pp. 433-439 (2018) (IF=5.401, Scimago: D1)

[L7] A. Bonyár, I. Csarnovics, M. Veres, L. Himics, A. Csík, **J. Kámán**, L. Balázs, S. Kökényesi, ”Investigation of the performance of thermally generated Au/Ag nanoislands for SERS and LSPR applications”, **PROCEDIA ENGINEERING 168**: pp. 1152-1155. (2016) (WoS, Scopus)

International, peer-reviewed conference paper, written in foreign (English) language

[K6] Attila Bonyár, Attila Géczy, Olivér Krammer, Hunor Sántha, Balázs Illés, **Judit Kámán**, Zsolt Szalay, Péter Hanák, Gábor Harsányi, "A review on current eCall systems for autonomous car accident detection", In: Proc of the 40th

International Spring Seminar on Electronics Technology. Sofia, Bulgária, (IEEE) pp. 1-4. (2017) (WoS, Scopus)

[K7] Attila Bonyár, **Judit Kámán**, István Csarnovics, László Balázs, "Characterization of the shape of gold nanoparticles prepared by thermal annealing", Proc of the 22nd International Symposium for Design and Technology in Electronic Packaging. Oradea, Romania, (IEEE) pp. 25-31. (2016) (WoS, Scopus)

[K8] Peter Martinek, Zsolt Illyefalvi-Vitez, Oliver Krammer, Attila Geczy, Balazs Villanyi, Balazs Illes, **Judit Kaman**, Slavka Tzanova, "Building a Cloud Platform for Education in Microelectronics", In: Proc of the 40th International Spring Seminar on Electronics Technology. Sofia, Bulgária, (IEEE), pp. 1-4. (2017) (WoS, Scopus)

Hungarian paper, written in Hungarian language

[M1] **Kámán Judit**, „Felületek lokális mechanikai tulajdonságainak mérése AFM-el”, **ELEKTRONET** XXV(1): pp.36-38. (2016)

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[2] L. G. Rosa, J. Liang "Atomic force microscope nanolithography: dip-pen, nanoshaving, nanografting, tapping mode, electrochemical and thermal nanolithography", *Journal of Physics: Condensed Matter*, **21**, 483001, (2009)

[3] H. J. Butt,B. Cappella, M. Kappl, "Force measurements with the atomic force microscope: Technique, interpretation and applications", *Surface Science Reports*, **59**, pp. 1-152 (2005)

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