Welcome!

As the organizers we take great pleasure in welcoming you to the “2nd International Workshop on Advanced Atomic Force Microscopy Techniques". The workshop will again be a forum for stimulating discussions and the exchange of new ideas which will help to explore the nanoworld in more detail. We especially thank our Invited Speakers and all of you, who contribute to the talks, the posters and the discussions. On the following pages please find the conference program.

The workshop will take place at the lecture hall of the Institute of Nanotechnology on Campus North of the Karlsruhe Institute of Technology (KIT). A map of the Campus and travel instructions how to reach the Campus are also included in this booklet.

We acknowledge financial support for this workshop from the KIT, the Institute of Microtechnology (IMT), the Institute of Nanotechnology (INT), and the Karlsruhe NanoMicro Facility (KNMF) as well as generous sponsoring by the companies SPECS Surface Nano Analysis GmbH, Omicron Nanotechnology GmbH, Atomic Force F&E GmbH, Zürich Instruments, and Bruker AXS GmbH.

We hope that you will enjoy the workshop and have a wonderful time in Karlsruhe, and we are looking forward to seeing you.

Hendrik Hölscher

Thomas Schimmel

Monday, February 28, 2011

10:00	Shuttle bus from the Renaissance Hotel Karlsruhe to the Institute of Nanotechnology (INT) located at the Campus North of the KIT
10:30	OPENING COFFEE & REGISTRATION
	Chair: Hendrik Hölscher & Thomas Schimmel
10:50	WELCOME *Hendrik Hölscher & Thomas Schimmel, Karlsruhe Institute of Technology*
11:00	Probing Magnetic Exchange Interactions and Forces on the Atomic Scale *Roland Wiesendanger, University of Hamburg*
11:40	Atom-Specific Interaction Quantification and Identification by Combined Scanning Tunneling and Atomic Force Microscopy *Udo D. Schwarz, Yale University*
12:20	LUNCH
	Chair: Roland Bennewitz
13:20	AFM-based bionanotools to locate, quantify and manipulate the molecular machinery of the living cell *Daniel Müller, ETH Zürich*
14:00	Quantifying cell adhesion forces with AFM *Christine Selhuber-Unkel, Christian-Albrechts-Universität zu Kiel*
14:15	Magnetic Resonance Imaging with Nanomechanics *Martino Poggio, University of Basel*
14:55	Nanomechanical coupling enables detection and imaging of 5 nm superparamagnetic particles in liquid *Christian Dietz, Instituto de Microelectronica de Madrid*
15:10	POSTER SESSION including COFFEE BREAK
	Chair: Bernd Gotsmann
17:10	Using higher flecural modes in noncontact atomic force microscopy *Thilo Glatzel, University of Basel*
17:50	Reversible charge-induced switching of a single redox molecule *Sebastien Gauthier, Cemes/CNRS, Toulouse*

18:05 Toggling bistable atoms via mechanical switching of bond angle
Adam Sweetman, University of Nottingham

18:30 Shuttle bus from the KIT Campus North to Campus South

19:00 DINNER at the Gastdozentenhaus “Heinrich Hertz”
located at the Campus South of KIT

Tuesday, March 1, 2011

8:45 Shuttle bus from the Renaissance Hotel Karlsruhe to the KIT Campus North

Chair: Roland Wiesendanger

9:30 Infrared Nanoscopy done by coupling AFM and IR Laser: application to microbiology
Alexandré Dazzi, Université Paris-Sud

10:10 Trimodal Tapping-Mode AFM: Simultaneous Topographical, Phase, and Frequency Shift Contrast
Santiago D. Solares, University of Maryland

10:50 COFFEE BREAK

Chair: Udo Schwarz

11:20 Atomic friction experiments under electrochemical control
Roland Bennewitz, Leibniz Institute for New Materials, Saarbrücken

12:00 Novel aspects of angle and temperature dependence of atomic-scale friction
Alexis Baratoff, University of Basel

12:15 LUNCH

Chair: Santiago Solares

13:15 Direct measurement of deep traps in single silicon nanowires using Kelvin probe force microscopy
Yossi Rosenwaks, Tel-Aviv University

13:45 Electronic structure of grain boundaries of solar cell materials
Sascha Sadewasser, Helmholtz-Zentrum Berlin für Materialien und Energie

14:00 Atomic force microscopy using heated tips
Bernd Gotsmann, IBM Research Zürich

14:40 NC-AFM in the surface science approach to model catalysis
Markus Heyde, *Fritz-Haber-Institut, Berlin*

15:00 Sub-molecular resolution imaging and force spectroscopy of adsorbed and on-tip C_{60} using dynamic STM and qPlus AFM
Christina Chiutu, University of Nottingham

15:15 BEST POSTER AWARD & CLOSING REMARKS

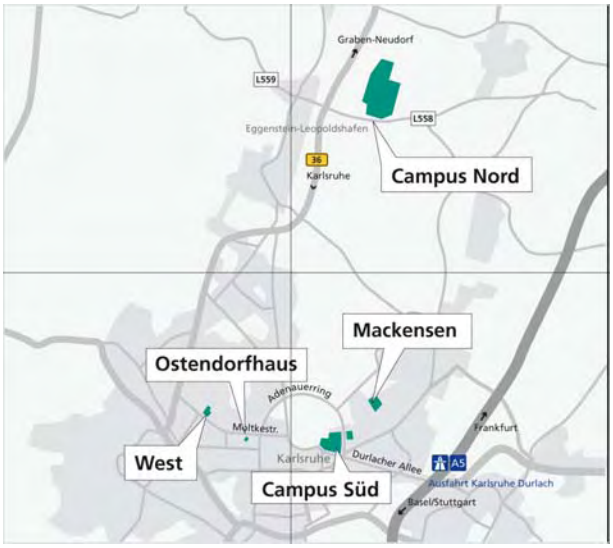
15:25 COFFEE BREAK & DISCUSSIONS

16:00 Shuttle bus to Karlsruhe Hauptbahnhof (main station)

How to Reach the Karlsruhe Institute of Technology

The Karlsruhe Institute of Technology is distributed over several locations. While the Campus North is situated in the administrative district of Karlsruhe near Eggenstein-Leopoldshafen, the Campus South is about 10 km away in the heart of the city of Karlsruhe.

The AAFMT Workshop 2011 takes place at the Campus North (Campus Nord) in seminar room of the Institute of Nanotechnology. You will be asked for your identity card at the front gate of the research centre.



How to Reach the Campus North by Car

The Campus North is located in Eggenstein-Leopoldshafen (about 12 km north of Karlsruhe). The address for your GPS is: Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

Coming from North: Frankfurt and Heidelberg (A5)

- Leave the motorway at the exit of Bruchsal and go in the direction of Karlsdorf-Neuthard / Germersheim / B35.
- Stay on this road for some 4 km, and then turn off on the B36.
- Leave the B36 after some 12 km, at the exit of Eggenstein-Leopoldshafen / KIT Campus Nord
- After about 1 km, you reach the entrance road to the Campus North on your left.

Coming from Northwest: Landau (A65)

- Leave the motorway at the Knielingen exit and go straight ahead on the road (Rheinbrückenstraße) for another 3 km as far as to the Neureuter Straße junction (after having passed the premises of Siemens AG).
- Then turn left in the direction of Mannheim (B 36). Go straight ahead at all following junctions.
- After some 10 km, turn right at the exit of Bruchsal / Stutensee / KIT Campus Nord.
- Go ahead for another 1 km until you reach the entrance road to the Campus North on your left.

Coming from East: Munich and Stuttgart (A8)

- At the Karlsruhe motorway triangle, turn off in the direction of Karlsruhe / Frankfurt (A5).
- Leave the motorway at the Karlsruhe-Mitte exit and go in the direction of Landau / Pfalz (B10).
- Stay on this road another 9 km and turn off in the direction of Mannheim (B36).
- Drive straight ahead on the B36 at all junctions.
- Leave the B36 after some 11 km at the exit of Bruchsal / Stutensee / KIT Campus Nord.

- After about 1 km, you reach the entrance road to the Campus North on your left.

Coming from South: Basel and Freiburg (A5)

- Leave the motorway at the exit No 48 Karlsruhe Süd and go in the direction of Karlsruhe / Landau-Pfalz (B10).
- Stay on this road another 4 km and turn off in the direction of Mannheim (B36).
- Drive straight ahead on the B 36 at all junctions.
- Leave the B 36 after some 11 km at the exit of Bruchsal / Stutensee / KIT Campus Nord.
- After about 1 km, you reach the entrance road to the Campus North on your left.

How to Reach the Campus North by Public Transport

The Campus North is located in Eggenstein-Leopoldshafen. There are various ways to get there by bus or tram from Karlsruhe city or Central Train Station. The exact times of departure are available on the website of the Karlsruher Verkehrsverbund (`www.kvv.de`). Information about travel data of the German Railway is provided by the Deutsche Bundesbahn (`www.bahn.de`).

Tram lines S 1 / S 11 from Karlsruhe Hauptbahnhof (Central Station) to the destinations of Leopoldshafen / Hochstetten

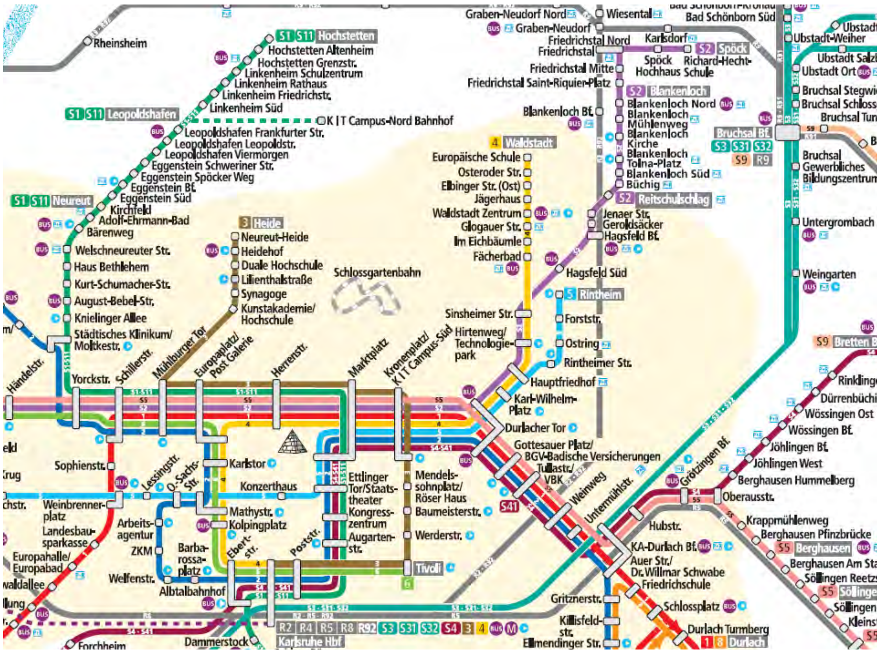
- Trams operate in 20-minute intervals; travelling time is approx. 40 minutes.
- Go by tram to stop "Leopoldstraße" at Leopoldshafen, change to bus No. 195 as far as "Forschungszentrum-Südtor" (southern entrance gate to the Campus North).

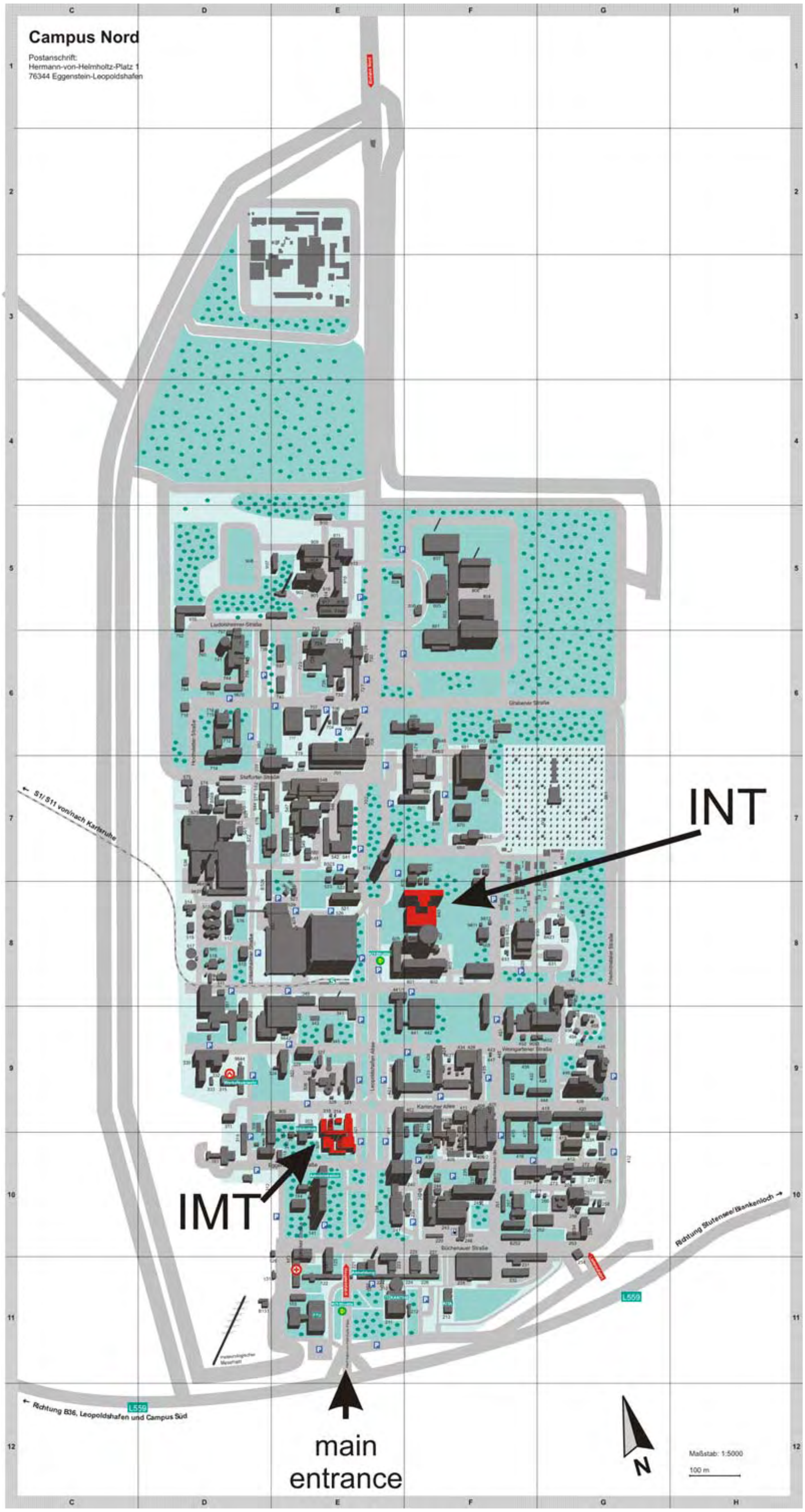
Regional train R 2 from Karlsruhe Hauptbahnhof (Central Station) to the destinations of Blankenloch Station / Mannheim.

- Trains operate in 60-minute intervals; travelling time is 25 minutes.
- At Blankenloch Station, change to bus No. 195 as far as "KIT Campus Nord"

Tram line S 2 from the Karlsruhe Central Business District (Kaiserstrasse) via Durlacher Tor in the direction of Blankenloch Nord.

- Trams operate in 20-minute intervals; travelling time is 36 minutes.
- At the "Blankenloch Nord" stop, change to bus No. 195 as far as "KIT Campus Nord"

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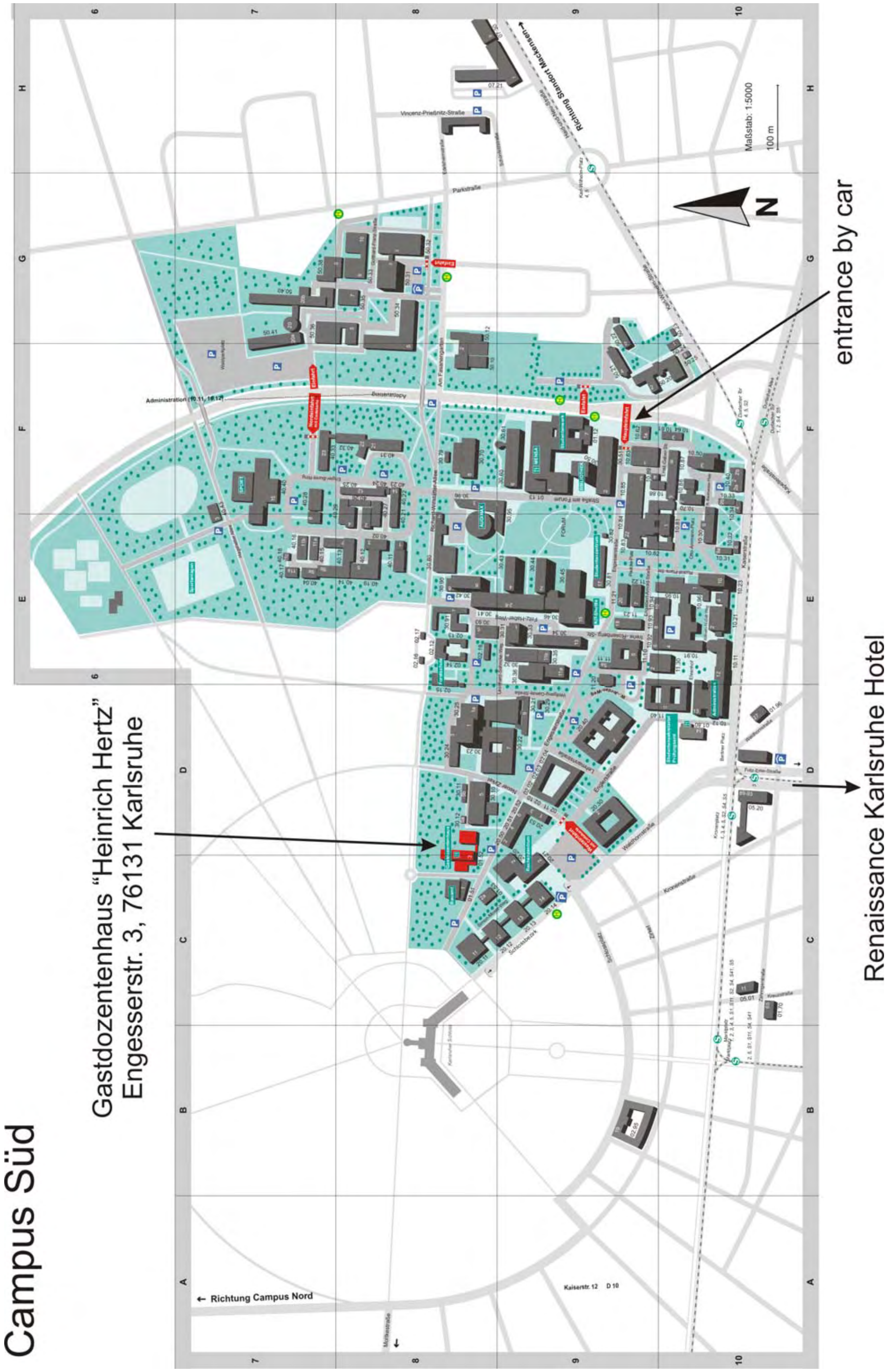

Campus Süd

Gastdozentenhaus “Heinrich Hertz”
Engesserstr. 3, 76131 Karlsruhe

entrance by car

Renaissance Karlsruhe Hotel

Probing Magnetic Exchange Interactions and Forces on the Atomic Scale

Roland Wiesendanger, Institute of Applied Physics, University of Hamburg, Germany

Atom-Specific Interaction Quantification and Identification by Combined Scanning Tunneling and Atomic Force Microscopy

Udo D. Schwarz[1,2], Mehmet Z. Baykara[1], Harry Mönig[1,2], Todd C. Schwendemann[1,3], Milica Todorovic[4], Ruben Perez[4], and Eric I. Altman[2]

[1] *Department of Mechanical Engineering and Materials Science and Center for Research on Interface Structures and Phenomena (CRISP), Yale University, New Haven, CT 06520, USA*
[2] *Department of Chemical and Environmental Engineering and Center for Research on Interface Structures and Phenomena (CRISP), Yale University, New Haven, CT 06520, USA*
[3] *Physics Department, Southern Connecticut State University, New Haven, CT 06515, USA*
[4] *Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain*

Entire scientific disciplines such as mechanics and chemistry are governed by the interactions between atoms and molecules. On surfaces, forces extending into the vacuum direct the behavior of many scientifically and technologically important phenomena such as corrosion, adhesion, thin film growth, nanotribology, and surface catalysis. To advance our knowledge of the fundamentals governing these subjects, it would be useful to simultaneously map electron densities and quantify force interactions between the surface of interest and a probe with atomic resolution. For example, in the case of a catalytically active surface, this would allow to study the role and effectiveness of surface defects such as vacancies, steps, kinks, impurities, and domain boundaries as active sites. An ability to discriminate between different chemical species on the sample surface would offer further insight.

In this talk, we will show with the example of an oxygen/copper(100) surface phase that much of this information can be derived from combining the new method of three-dimensional atomic force microscopy (3D-AFM) [1,2], a variant of noncontact atomic force microscopy, with simultaneous scanning tunneling microscopy. The surface oxide layer of Cu(100) features domain boundaries and a distinct structure of the Cu and O sublattices that is ideally suited for such model investigations. While different tips show different chemical contrasts, 3D data sets enable site-specific quantification of force interactions and tunneling currents. In order to clarify the different contrast modes data, DFT total-energy calculations and non-equilibrium Green's Function (NEGF) methods for electronic transport have been used to determine the interaction and the tunneling current for a variety of tip models. These calculations provide insight into (1) the fundamentals of contrast formation in this experimental technique and (2) the correlation between tip-sample forces and local chemical reactivity.

[1] B. J. Albers et al., Nature Nanotechnology **4**, 307 (2009)
[2] M. Z. Baykara et al., Advanced Materials **22**, 2838 (2010)

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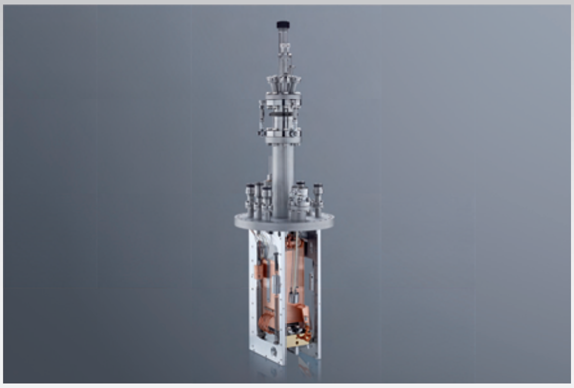

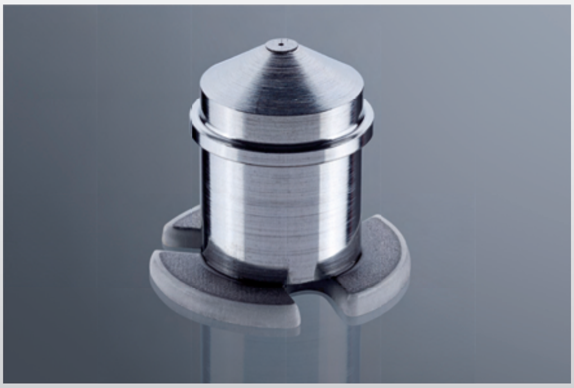

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AFM-based bionanotools to locate, quantify and manipulate the molecular machinery of the living cell

Daniel J. Müller

ETH Zürich, Department of Biosystems Science and Engineering, 4058 Basel,
Switzerland

Every process of the biological cell relies on molecular forces that are a complex interplay of chemical, biological and physical interactions. Elucidating when and where certain interactions determine cell biological processes resembles deciphering a basic molecular language. Here, I survey novel AFM-based bionanotools that can be applied to probe the functional role of individual molecular machines in living human cells. We further introduce bionanotechnological assays to identify the molecular machines as a pharmacological and medical target, to determine the functional state of the target, to structurally locate the binding of a molecular compound at amino acid accuracy, and to determine binding kinetics and the mechanisms by which a given compound modulates the functional state of the target. Recent developments of the technology enable to quantify the energy landscape of the target and to predict molecular reaction pathways. Together this information provides unique insight into how the cell controls its highly sophisticated molecular machinery and how we can use this knowledge to functionally control cells.

Reviews on the topic:

‘Five challenges to bringing single-molecule force spectroscopy into the living cell’ Y.F. Dufrene, E. Evans, A. Engel, J. Helenius, H.E. Gaub & D.J. Müller, *Nature Methods* (2011) **8**, 123-127.

‘Force probing surfaces of living cells to molecular resolution’ D.J. Müller, J. Helenius, D. Alsteens, Y.F. Dufrene, *Nature Chemical Biology* (2009) **5**, 383-390.

‘Atomic force microscopy as a multifunctional molecular toolbox in nanobiotechnology’ D.J. Müller & Y. Dufrene, *Nature Nanotechnology* (2008) **3**, 261-269.

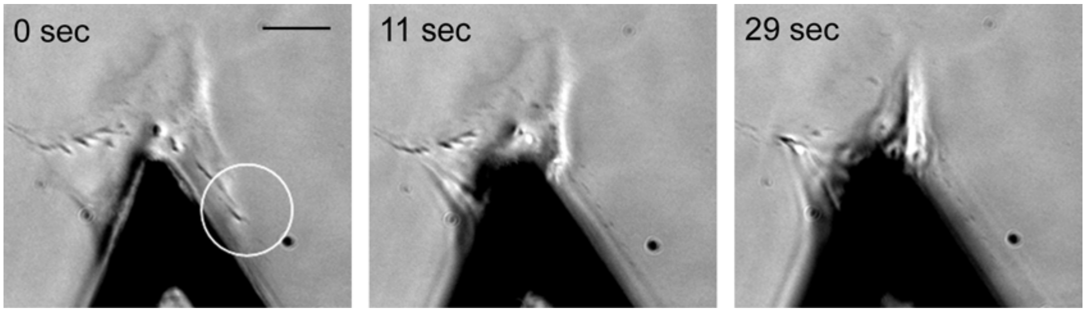
Quantifying cell adhesion forces with AFM

Christine Selhuber-Unkel

Cell adhesion is highly essential for a viable contact between cells and surfaces, as it controls fundamental cellular activities such as cell migration, cell differentiation and programmed cell death. In the body, cells are permanently in contact with nanostructures; examples include the periodic nano-grooves of collagen and nanometer-sized protein structures. Therefore, nanostructures might have significant impact on cell adhesion properties.

In order to quantify the interaction between cells and nanostructured surfaces, we are using an AFM-based method that is capable of characterizing the adhesion forces of cells to surfaces with Piconewton resolution at timescales from a few seconds to many hours. This large range of timescales is, for example, essential for characterizing cell adhesion to implant surfaces. In our experiments, we attach a cell to a tipless protein-coated cantilever. After cell attachment to the cantilever, it is retracted and the detachment force is continuously recorded. Simultaneously, cell detachment is monitored with an optical microscope in phase contrast or fluorescence mode.

We have applied this method for quantifying the strength of cell adhesion on biofunctional, nanostructured surfaces that provide anchorage points for single cellular receptor proteins in a quasi-hexagonal lattice with nanometre resolution. On these substrates, cell spreading, cell migration, and adhesion cluster formation are controlled by the nano-scale spacing between individual binding sites for adhesion receptor proteins. Using AFM-based force microscopy, we found that the intermolecular, nano-scale spacing between individual adhesion receptor proteins cooperatively controls the strength of cell adhesion, the mechanical properties of cells and the formation of adhesion clusters.



References:

Selhuber-Unkel, C., Erdmann, T., López-García, M., Kessler, H., Schwarz, U. S. and Spatz, J. P. **Cell adhesion strength is controlled by intermolecular spacing of adhesion receptors.** Biophysical Journal (2010), 98, 543-551.

Selhuber-Unkel, C., López-García, M., Kessler, H., Spatz, J. P. **Cooperativity in Adhesion Cluster Formation during Initial Cell Adhesion.** Biophysical Journal (2008), 95, 5424-5431.

Magnetic Resonance Imaging with Nanomechanics

Martino Poggio, University of Basel, Dep. of Physics, Switzerland

Can we use the same forces that cause two magnets to attract or repel each other to measure the dynamics of single spins? This is the basic question driving research in mechanically detected magnetic resonance. In conventional magnetic resonance, the dynamics of a spin ensemble alter magnetic fields inside a pick-up coil inducing currents in that coil. While this works beautifully for macroscopic samples, as samples approach the nanoscale, the scheme breaks down. Moving to a mechanically-detected technique is one solution to this problem. In such methods, the oscillating force between spins and a small magnet drive a compliant cantilever. The cantilever's mechanical oscillations are then measured using an optical interferometer. I will describe how mechanically detected techniques have been used to do nanoscale magnetic resonance imaging, achieving a billion-fold improvement in the volume sensitivity over inductively-detected methods. Could a “molecular structure microscope," whereby one could image the atomic structure of macromolecules, be around the corner?

Nanomechanical Coupling Enables Detection and Imaging of 5 nm Superparamagnetic Particles in Liquid

Christian Dietz, Elena T. Herruzo, Jose R. Lozano and Ricardo Garcia
Instituto de Microelectrónica de Madrid, CSIC, Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain
christian.dietz@imm.cnm.csic.es

We demonstrate that a force microscope operated in a bimodal mode enables the imaging and detection of superparamagnetic particles down to 5 nm. The bimodal method (Fig. 1) exploits the nanomechanical coupling of the excited modes to enhance the sensitivity of the higher mode to detect changes in material properties. The coupling requires the presence of nonlinear forces. Remarkably, bimodal operation enables to identify changes of slowly varying forces (quasi-linear) in the presence of a stronger nonlinear force. Thus, unambiguous identification of single apoferritin (non-magnetic) and ferritin (magnetic) molecules in air and liquid is accomplished using a cobalt coated cantilever.

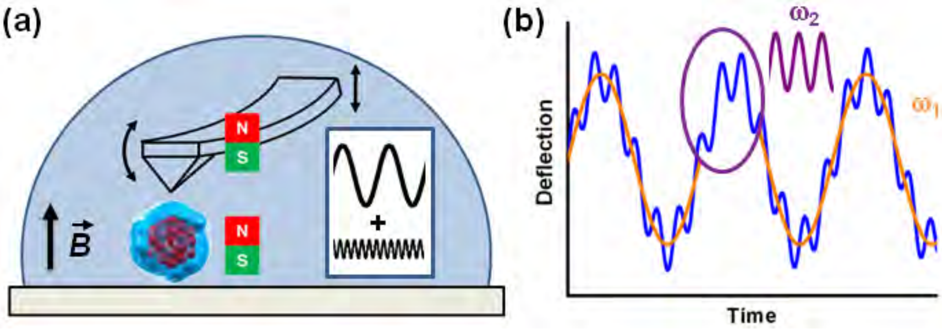


Fig. 1: Scheme of bimodal AFM operation to measure simultaneously mechanical and magnetic interactions [1-2]. (a) The first two cantilever-tip eigenmodes (ϕ_1, ϕ_2) are excited by applying a mechanical force at the cantilever base. Ferritin molecules are imaged in liquid under the presence of an external magnetic field. (b) The amplitude of the first mode is used to generate an image of the topography in exactly the same way as in amplitude modulation AFM. The phase shift of the second mode ϕ_2 is used to reconstruct the structure of the protein with its mechanical (protein shell) and magnetic (iron oxide core) contributions.

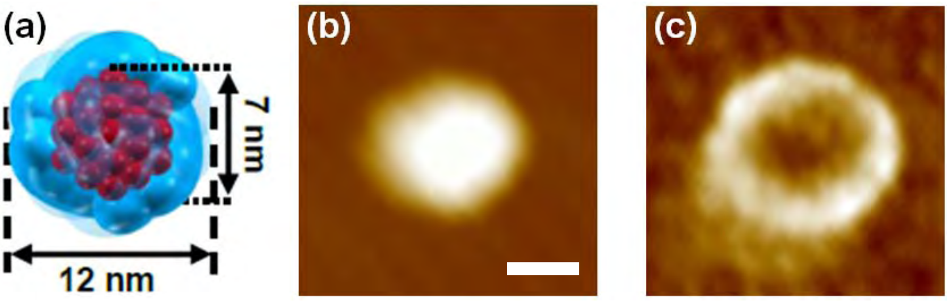
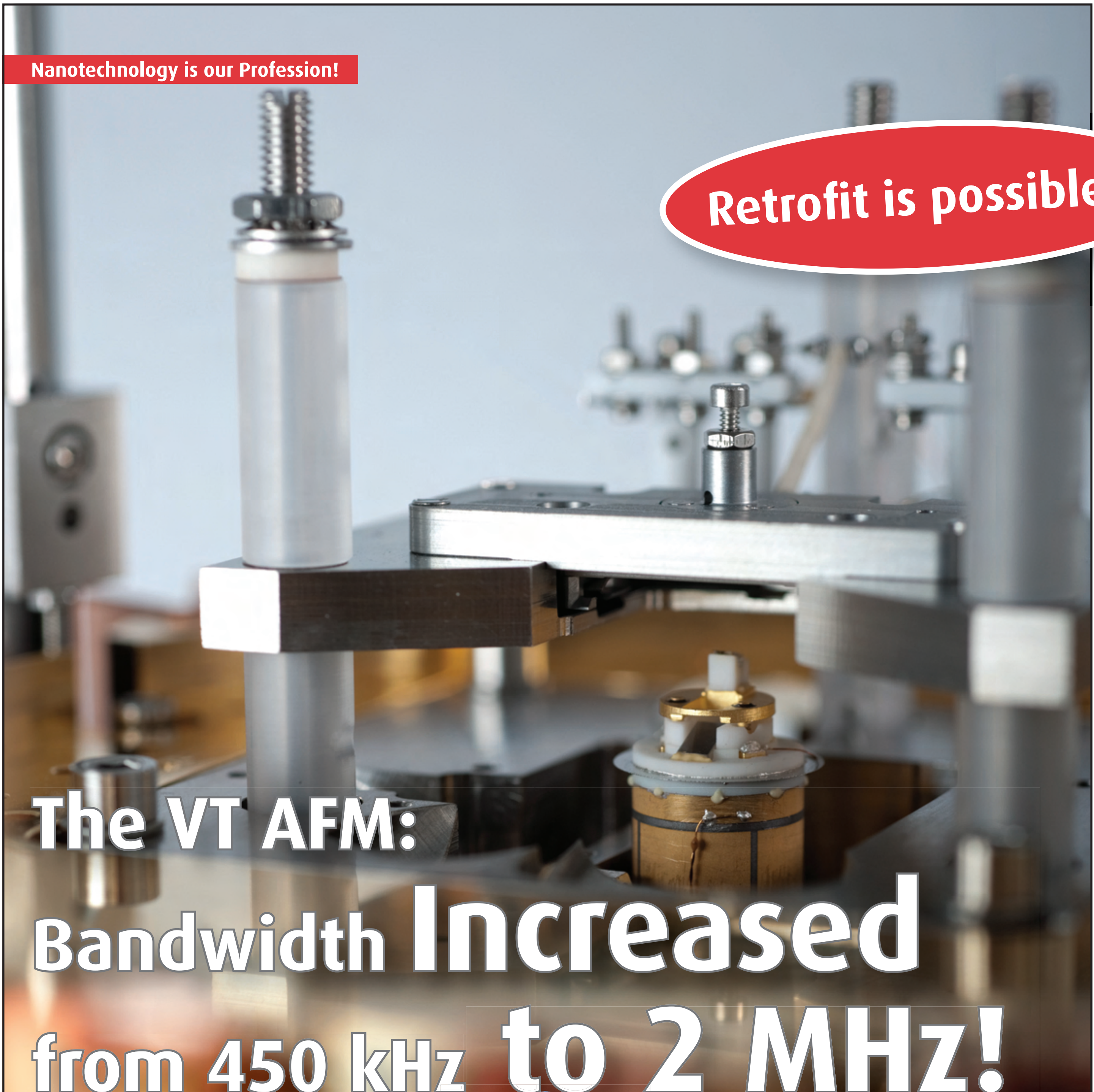


Fig. 2: (a) Scheme, (b) bimodal AFM topography image and (c) second mode phase image of a single ferritin molecule measured in water. Scale bar is 20 nm and color scales are 20 nm and 7.2° for (b) and (c), respectively.

[1] T. R. Rodriguez and R. Garcia, Appl. Phys. Lett. 84 (2004) S449.
[2] R. Proksch, Appl. Phys. Lett. 89 (2006) S113121.

Nanotechnology is our Profession!



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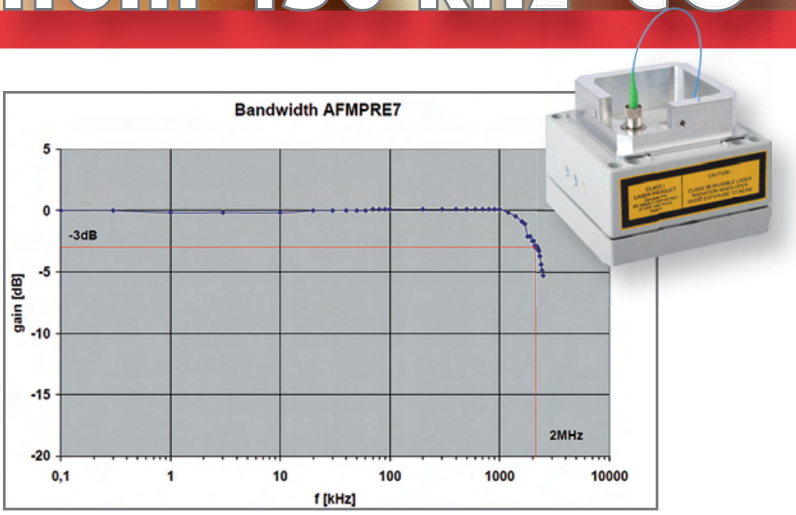

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Using higher flexural modes in noncontact Atomic Force Microscopy

Th. Glatzel & S. Kawai
Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland

Since the way to obtain atomically resolved images using noncontact Atomic Force Microscopy (nc-AFM) was established in 1995 [1] it has become a broadly used technique. The tip-sample distance is conventionally controlled by the frequency shift Δf_{1st} of the first flexural resonance of a cantilever caused by interaction forces. The simultaneous excitation of higher resonances was used up to now mainly for the separate and very sensitive detection of magnetic and electrostatic forces [2]. The increased spatial resolution enabled atomic resolution of the local contact potential difference [3] which is still discussed controversially. The atomic-scale contrast arises mainly from short- range forces while the stronger long-range interaction, which depends on the macroscopic tip geometry and the electrostatic potential, act as a background force. In order to optimize the detection sensitivity of short-range forces, as well as the signal/noise ratio, a small tip oscillation amplitude comparable to the decay length of the short-range interaction (< 0.1 nm) is desirable. The effective stiffness of higher resonance modes of typical cantilevers is high enough to achieve such small and stable amplitude operation [4] to enable the detailed analysis of the short-range interaction.

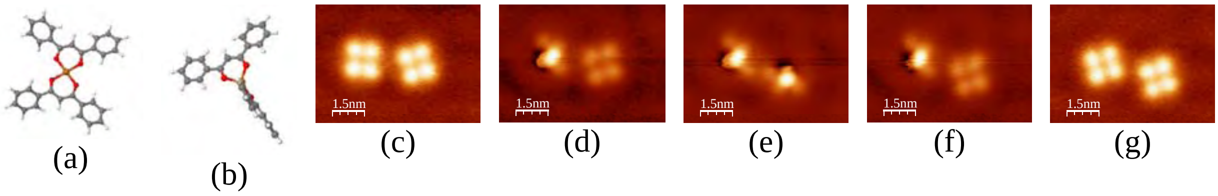
In the presentation atomically resolved Kelvin probe force microscopy (KPFM) measurements using the amplitude sensitive technique at the second resonance of the cantilever will be presented and discussed. Distance dependent measurements obtained by a quasi-constant height mode indicate that the short-range electrostatic force, arising from individual surface atoms, plays a major role in KPFM, especially at small tip-sample distances. Furthermore, bimodal nc-AFM using various flexural modes will be introduced and detailed applications using the second and the first torsional resonances will be discussed. By this technique potential tip instabilities in single-mode measurements with a small amplitude can be avoided, providing still a higher force sensitivity than conventional nc-AFM with amplitudes of 5 to 20 nm. 2D and 3D force spectroscopy allows now the analysis of normal and lateral force fields as well as the energy dissipation at atomic scale even at room temperature.

[1] F. J. Giessibl, Science 267, 68 (1995).
[2] Ch. Sommerhalteret al., APL 75, 286, (1999).
[3] S. Kitamura et al., ASS 157, 222, (2000).
[4] S. Kawai et al., APL 86, 193107, (2005).

Reversible charge-induced switching of a single redox molecule

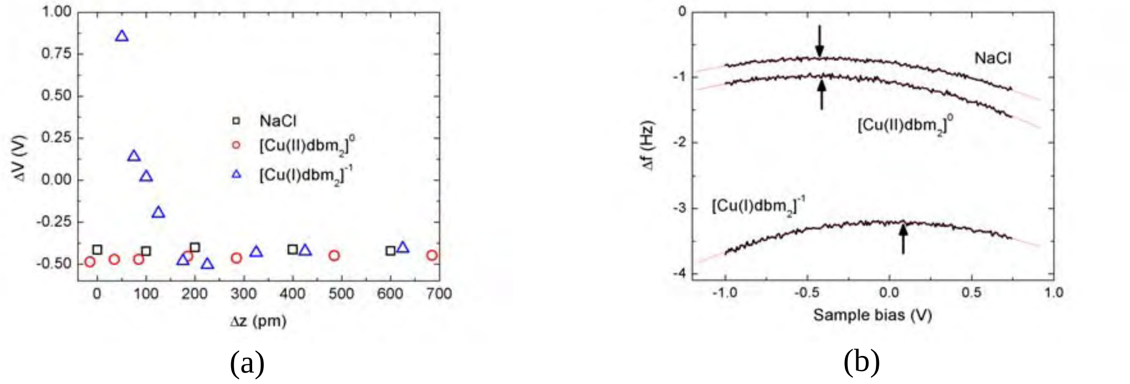
T. Leoni, O. Guillermet, H. Walch, V. Langlais, A. Scheuermann, J. Bonvoisin and S. Gauthier
Cemes/CNRS, 29, rue Jeanne Marvig 31000 Toulouse France.
e-mail: gauthier@cemes.fr

Controlling the charge state of individual nano-objects is of great importance for future atomic-scale technology. It was recently demonstrated that the charge state of atoms, molecules or point defects on thin insulating films deposited on metal surfaces can be monitored, and in some cases manipulated [1-4]. We show that the charge state of a single redox molecule adsorbed on a thin insulating film deposited on a metallic substrate can be controlled. We used a low temperature STM/AFM (5 K) to study the coordination complex bis-dibenzoylmethanato-copper ($Cu(dbm)_2$ figure 1a-b) adsorbed on a NaCl bilayer on Cu(111). By applying voltage pulses of suitable polarity, the molecule can be *reversibly* switched between two stable conformations. STM imaging (figure 1c-g) and coupled AFM electrostatic force measurements (figure 2) demonstrate that the as-deposited neutral and square-planar molecule becomes tetrahedral and negatively charged after switching. This interplay between conformational change and charge state, which is well documented in the chemistry of transition metal complexes, could be used to study fundamental phenomena, such as electron transfer between two redox centres or to develop new manipulation schemes, such as triggering mechanical movement in a molecule by electron injection.



(a) (b) (c) (d) (e) (f) (g)

Figure 1: *(a) and (b): Neutral (a) and negatively charged (b) $Cu(dbm)_2$. (c)-(g) Sequence of STM images showing the reversible switching between the two molecular forms.*



(a) (b)

Figure 2: *(a) Local contact potential difference measured on NaCl, neutral and charged $Cu(dbm)_2$. The LPCD shift toward positive values on the charged species demonstrates that it is negatively charged. (b) $\Delta f(V)$ spectra at Δz=100pm.*

[1] Repp J., Meyer, G., Olsson, F. E., Persson, M., Science 305, 493 (2004)
[2] Mikaelian, G., Ogawa, N., Tu, X. W., and Ho, W., J. Chem. Phys. 125, 131101 (2006)
[3] Gross, L., Mohn, F., Liljeroth, P., Repp, J., Giessibl, F. J., Meyer, G., Science 324, 1428 (2009)
[4] König, T., Simon, G. H., Rust, H.-P., Pacchioni, G., Heyde, M., and Freund H.-J., J. Am. Chem. Soc. 131, 17544 (2009)

Toggling bistable atoms via mechanical switching of bond angle

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The ability to manipulate matter via (chemo)mechanical interactions at the level of individual bonds is key for the development of atomic-precision circuitry and systems. A fundamental circuit element is the switch and there has been significant progress towards the exploitation of bistable atomic and molecular systems for nanoscale switching architectures. We describe a new approach to atom switching which involves mechanical, rather than electronic, activation. Individual bistable dimers at the Si(100) surface [1,2] are flipped using a non-contact atomic force microscope tip, actuating the smallest conceivable mechanical toggle switch (two atoms) via chemical force alone [3]. The response of a given dimer to a flip event depends on both the local and, critically, the non-local environment of the target atom - an important consideration for future atomic scale fabrication strategies.

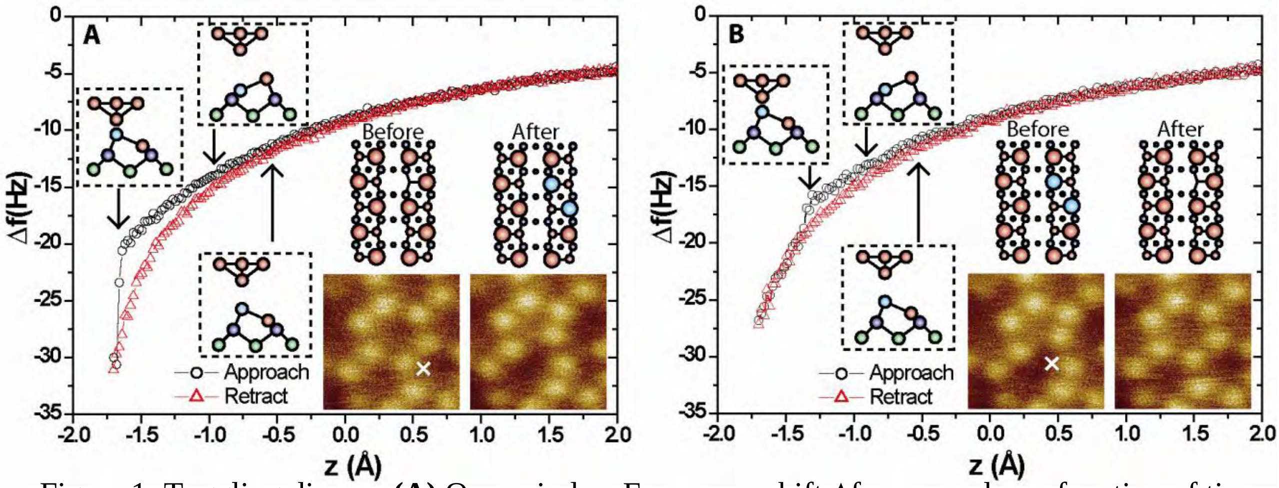

Figure 1: Toggling dimers. **(A)** Open circles: Frequency shift Δf measured as a function of tip displacement (z) towards the “down” atom of a Si(100) dimer. The cartoons illustrate the tip-sample configuration before and after the dimer flip. Open triangles: Δf-vs-z spectrum acquired during retraction of the tip. The insets show NC-AFM images, and illustrations of the atomic configurations, taken before and after the Δf measurement (acquired at the position marked with a cross) where the original zig-zag buckling of the dimers has been replaced by a phason pair structure. The dimer flipping event appears as a sharp jump in the Δf-vs-z spectrum. **(B)** A Δf-vs-z spectrum taken above a “down” atom of one of the phasons created in **(A)**, restores the original symmetry via a second correlated flip event. (Imaging parameters: A_0: 250 pm; Δf setpoint = -9.1 Hz)

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INFRARED NANOSCOPY DONE BY COUPLING AFM and IR LASER
Application to microbiology

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For 25 years, near-field techniques have quickly progressed and have taken a large place in Nanoscience microscopy. Whatever, in the infrared range, the near-field microscopes have been not so numerous to work properly. We can count up only two different way to make infrared studies : the optical technique measuring the transmitted signal coming from the nano-object and the photothermal approach using a tiny thermometer to link temperature to absorption measurements.

Considering these previous methods limitations, we have developed an innovative infrared spectromicroscopy technique, called AFMIR, based on the coupling between a tunable infrared laser and an AFM (Atomic Force Microscope). This coupling allows us to perform ultra-local infrared spectroscopy and chemical mapping at the nanometric scale. The principle[1] is based on detecting the local thermal expansion of the sample, irradiated at the wavelength of its absorption bands. This expansion is detected by the AFM tip in contact mode. As the duration of expansion and relaxation of the sample is always shorter than the response time of the cantilever in contact, the excitation transmitted to the cantilever is close to a delta function, so that it always oscillates at its own resonance frequencies. By recording the amplitude of these oscillations we can measure the corresponding infrared absorption as a function either of space or wavelength. We have validated this technique by comparing the infrared spectrum of a single *E.coli* bacterium and the corresponding FTIR spectrum, and showing the possibility to perform chemical mapping with sub-wavelength spatial resolution (50 nm)[2]. Later, similar outcomes have been obtained in nanophotonics (20 nm resolution)[3].

Our work is now mainly focused on microbiology systems[4,5,6]. The strong constraint of the biologist is often to study living samples in their common environment. To fill this condition, we have developed our technique to work in liquid (AFM liquid scanner). The first results have been really promising : we recorded the spectrum of the glycogen band (1080 cm^{-1}) of one *Candida albicans* blastospore in water and obtained the corresponding chemical mapping, despite the fact that the liquid water is absorbing in this range[7]. The next step is to perform series of measurements on one bacterium *Rhodobacter capsulatus* to follow the growth of PolyHydroxyButyrate vesicule (*figure 1*) in real time by mapping the sample on its specific band. The succeed of such experiments led us to propose to biologist users a technique suited to their thematic mixing infrared studies and “in vivo” experiments.

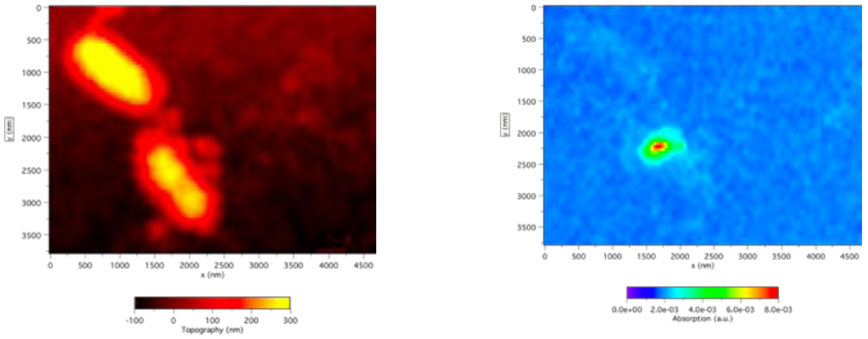

Figure 1 : AFM Topography of two Rhodobacter bacteria (left picture) and corresponding chemical mapping of PHB (right) revealing a 300 nm diameter vesicle in only one bacterium.

For four years, the AFMIR technique associated to the CLIO infrared FEL facility (http://clio.lcp.u-psud.fr/clio_eng/clio_eng.htm) is proposed to users as a standard beam line (also called AFMIR). In addition, in order to compensate the limited availability of the CLIO FEL and to complement it in the short wavelength range, we added to our experiment an infrared OPO laser tunable from 4000 to 1250 cm^{-1}.

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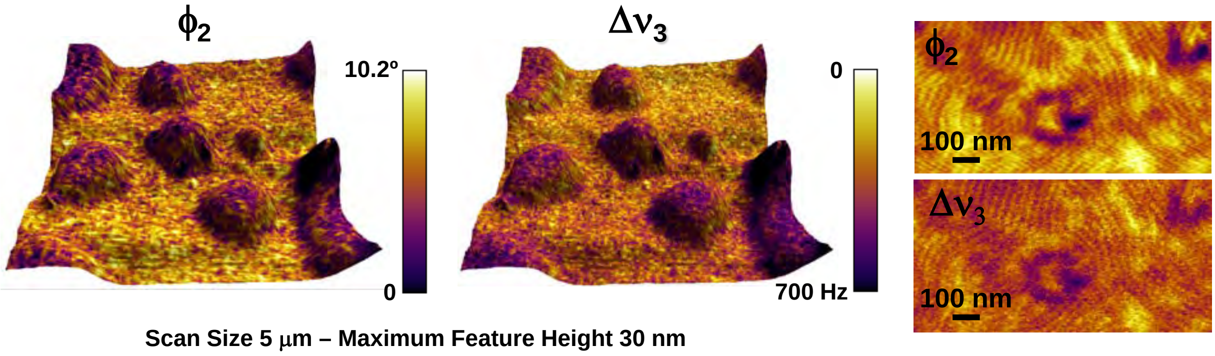
Trimodal Tapping-Mode AFM: Simultaneous Topographical, Phase and Frequency Shift Contrast

Santiago D. Solares, University of Maryland, USA

A trimodal tapping-mode AFM technique has been recently commissioned [1,2], whereby control of a third eigenmode has been incorporated into the already established bimodal tapping-mode AFM scheme [3-5]. The additional eigenmode is controlled using a phase-locked loop [6] and provides a frequency shift contrast, in addition to the topographical and phase contrast obtained with bimodal tapping-mode AFM. The figure below illustrates typical results obtained on a tri-block co-polymer sample (note that the frequency shift scale is inverted). In general, the phase and the negative of the frequency shift exhibit similar contrast, in agreement with harmonic oscillator dynamics, although deviations from this trend are often observed, such that all available sources of contrast could provide complementary information in the study of tip-sample conservative and dissipative interactions.



Trimodal AFM images of a SEBS KRATON^{TM} G-1652 thermoplastic rubber triblock co-polymer: (left) second eigenmode phase superimposed on topography, (center) third eigenmode frequency shift superimposed on topography (note that the frequency scale is inverted), and (right) close-up images of the phase and frequency shift. These images were acquired with $A_{1\text{-o}}$ = 100 nm, $A_{1\text{-setpoint}}$ = 70 nm, $A_{2\text{-o}}$ ~ 8.5 nm, $A_{3\text{-o}}$ ~ 5.5 nm and scan speed = 5μm/s.

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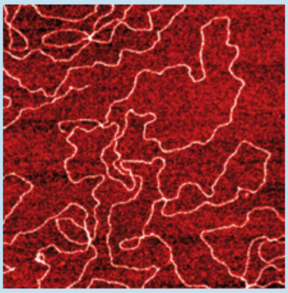

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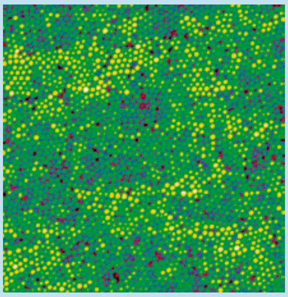

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Atomic friction experiments under electrochemical control

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INM – Leibniz Institut für Neue Materialien, Saarbrücken, Germany
Aleks Labuda, Peter Grütter, and Bruce R. Lennox
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Electrochemical methods allow for fast and reversible modification of metal surfaces through deposition and dissolution of metal films, adsorption and desorption of anions, as well as oxidation and reduction. The surface composition and structure undergo dramatic changes in these processes, which should cause significant changes in the friction on the surface. We will report on our friction force microscopy experiments, in which we study atomic friction processes in order to explore the prospects of friction control through electrochemical methods.

The resolution of atomic stick-slip events in an electrochemical cell is improved by the development of a dedicated instrument [1]. The lateral force contrast reveals the atomic structure of the Au(111) surface and its herringbone reconstruction. After deposition of one monolayer of Cu by underpotential deposition, the atomic stick-slip changes into a periodicity which indicates frictional response of a CuCl rather than a Cu layer.

Wear-less friction on Au(111) surfaces is extremely weak and exhibits almost no load dependence. Upon electrochemical oxidation of the surface, significant friction with linear load dependence is observed. The process is reversible and allows switching repeatedly between high and low friction. More subtle effects are found in the regime of anion adsorption. Here the results indicate a frictional response with threshold behaviour. The threshold depends on both applied normal load and the electrochemical potential.

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Novel aspects of angle and temperature dependence of atomic-scale friction

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Additional insights into atomic-scale lateral force microscopy (LFM), in particular on (001) surfaces of cubic crystals have been obtained in our group from critically damped 2D simulations based on a separable Prandtl-Tomlinson (PT) model [1].
The dependences of the maximum force required to initiate stick-slip motion (static friction) and of the average friction force thereafter (kinetic friction) on the scan angle and on the starting position have been derived analytically for $T \rightarrow 0$ and confirmed numerically. Simulations also allow one to interpret the predicted cusps about symmetry directions and the spread of static friction values in terms of characteristic changes in the tip trajectories.
Fits based on the 1D PT model, used earlier to extract the amplitude U_0 of the corrugation potential and the effective lateral stiffness k from scans along symmetry directions [2], are justified, provided that thermal activation is taken into account.
For typical LFM cantilevers in particular, room temperature 1D simulations based on a two-spring have revealed a significant reduction of friction (thermolubricity) up to about 3 times the $T \rightarrow 0$ superlubricity threshold [3]. For higher values of U_0/ka^2, these simulations are, however, consistent with the less demanding common model which assumes addition of cantilever and contact compliances.
Consideration of the 3D compliance tensor qualitatively explains why best agreement with most lattice-resolved LFM images of alkali halide (001) surfaces has been obtained by assuming that k is isotropic and also when the apparent bending signal is dominated by lateral forces along the cantilever axis, as assumed in early work on 2D effects.
Comparison with systematic LFM measurements of friction anisotropy on rocksalt type crystals, so far performed under ambient conditions [4], suggest that higher Fourier components of the corrugation should be detectable if anion and cation radii are substantially different. Measurements as a function of sample rotation angle will hopefully provide quantitative information about resulting deviations, already anticipated earlier [5], and also further clarify connections between LFM and dynamic force spectroscopy measurements [6].

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Direct measurement of deep traps in single silicon nanowires using Kelvin probe force microscopy

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It is anticipated that most semiconductor nanowires (NWs), commonly grown by the vapor-liquid-solid (VLS) mechanism, contain deep sub-bandgap traps induced by metal catalysts-mainly Au. To date, there is no method to measure such electronic states in single nanowires.

Here we use Kelvin probe force microscopy (KPFM) to image individual deep acceptor-type trapping centers in single undoped Si NWs, grown with an Au catalyst. The method is based on gate-biasing single NW transistors and measuring the surface potential profiles using KPFM (Figure 1). The traps are observed by peaks and dips in the KPFM profiles (Figure 1, middle), and the switching between occupied and empty traps is reversibly controlled by the back-gate potential of the NW transistors. The key in extracting the traps energy level (E_C-E_T=0.65eV±0.1V) and concentration (~2x10^{16} cm^{-3}) is deconvolution of the measured potential images. This is based on a novel algorithm which takes into account the whole KPFM probe (tip+cantilever) which will be described in details.

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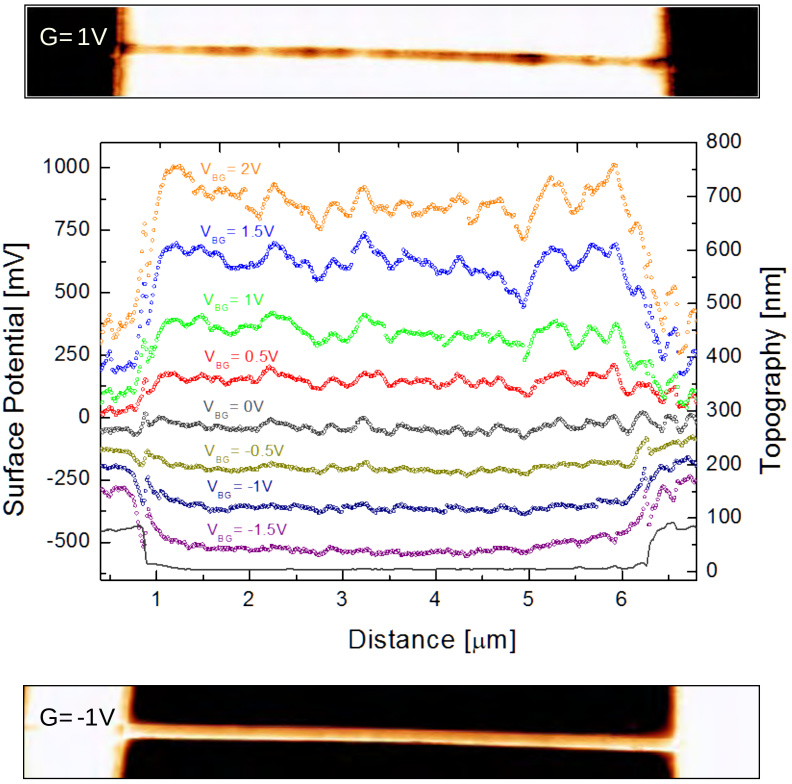

Figure 1: Surface potential measurements of intrinsic VLS grown Si nanowire under different back gate potentials. The upper and lower images are 2D potential distribution maps of the device under back gate potential of 1V (occupied state) and -1V (unoccupied state), respectively. The scale is 200 mV.

Electronic Structure of Grain Boundaries of Solar Cell Materials

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Polycrystalline p-type Cu(In,Ga)Se_2 semiconductors represent the absorber material in thin film solar cells currently reaching the highest power conversion efficiency. Efficiencies above 20% are surprising considering the high density of grain boundaries in these thin films. Their role in the solar cell as well as their electronic structure are largely investigated and discussed.

We present here a study of single grain boundaries in $CuGaSe_2$ combining microscopic and macroscopic techniques on the same grain boundary. For this purpose model samples were specifically grown, consisting in bicrystals with two millimeter-sized grains separated by a well defined grain boundary with different specific orientations. The structural properties were characterized by electron backscatter diffraction, while electronic properties were investigated by Kelvin probe force microscopy, conductivity and Hall-effect measurements. The analysis of the combined results leads to a model of the electronic structure, which depends on the atomic structure of the specific grain boundary. Common to all characterized grain boundaries is a thin (3-6 atomic layers) and high (200-600 mV) electronic barrier across which electronic transport is largely dominated by tunneling. The resulting lower probability density of majority charge carriers at the grain boundary explains the low impact of these on the recombination and the high power conversion efficiencies of the related solar cell devices.

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Atomic Force Microscopy using Heated Tips

Bernd Gotsmann, IBM Research – Zurich, Switzerland

The use of heated tips in atomic force microscopy enables exploring thermal and thermally activated phenomena or surfaces and interfaces. This talk will review several applications and give insight into relevant methods and mechanisms.

Nanoscale patterning can be done conveniently using heated tips. For this, the thermomechanical interaction between a tip and a surface is used to create patterns used for data storage and lithography.

Tribology at the nanoscale is governed by thermally activated processes. Here, heated tips (or samples) allow performing fundamental kinetic measurements identifying key mechanisms of friction and wear.

Thermal transport cannot be studied easily at nanoscale dimensions. Here, experiments using heated tips carry the hope to solve some outstanding issues in material design for thermal applications. For this, the heated tips are used to measure local thermal conductance in the so-called Scanning Thermal Microscopy (SThM). At the nanoscale, the thermal interface (or boundary) resistance becomes comparable to the thermal spreading resistance at the tip-surface contact.

In a step further from this, SThM is used to measure local temperature distributions. Technologically relevant examples include the self-heating of nanowires. Examples are discussed in relation to nanoscale thermal management in electronic devices.

For all these applications it is essential to understand the temperature distribution of a heated tip in contact with a surface. This problem is equivalent to the case of a heated sample surface in contact with an unheated tip as commonly used in variable temperature microscopes. Basic scaling laws and typical examples will be discussed.

NC-AFM in the Surface Science Approach to Model Catalysis

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Relative chemical identification [1], force determination during atom manipulation [2], visualization of the backbone of individual molecules [3] and the detailed characterization of color centers [4] have moved atomic force microscopy into the focus of the wider surface chemistry and catalysis audience.

In recent years non-contact atomic force microscopy (NC-AFM, also known as frequency modulation dynamic force microscopy – FM-DFM) has met the expectations towards its imaging capabilities. Atomic resolution has been achieved on metals, semiconductors and insulators. Currently the NC-AFM community strives to obtain accurate physical and chemical information in addition to surface topography. A development that is advantageous for the study of surface structure, its defects and possible adsorbates. With respect to insulators, the technique is most conveniently and most usefully applicable to metal supported thin films of varying thickness and chemical nature. Here the results directly complement results from scanning tunneling microscopy (STM) and other surface science techniques. Further they can be related to a wealth of data – be it experimental or theoretical. If desired, and if obstacles in sample preparation are overcome, the technique is applicable to bulk insulators as well.

My workgroup has studied the ordered alumina film on NiAl(110) [5], MgO thin films on Ag(001) [4, 6] as well as the crystalline silica film grown on Ru(0001) [7]. The use of a dual-mode NC-AFM/STM in ultrahigh vacuum at 5 Kelvin enables simultaneous recording and direct comparison of both signals.

The alumina film has been subject to a structural and work function analysis of its line defect network [8] as well as to a gold adsorption site study. On silica the first low temperature STM and NC-AFM studies were performed and NC-AFM measurements on MgO/Ag(001) allowed the characterization of charge states for individual color centers within the film. In particular it has been shown that NC-AFM gives a large difference for two types of centers on MgO/Ag(001) that are nearly indistinguishable in scanning tunneling spectroscopy [4].

All results corroborate the capabilities of modern force microscopy in the acquisition of detailed local scale information for the rigorous analysis of surface science aspects in catalysis.

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Sub-molecular resolution imaging and force spectroscopy of adsorbed and on-tip C_{60} using dynamic STM and qPlus AFM

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Sub-molecular resolution imaging is now commonplace in scanning tunnelling microscopy. Fullerene molecules have been particularly important in developing this capability and intramolecular features arising from the orbital structure of C_{60} have been repeatedly observed [1]. The elegant experiments of Gross et al. [2] showed that imaging of molecular structure with resolution significantly higher than that achievable in conventional STM is possible using qPlus atomic force microscopy. Prior to this, Giessibl's group had pioneered "sub-atomic" resolution imaging [3], where spatially localized surface orbitals are used to image tip structure.

We show that it is possible to transfer a C_{60} molecule to a dynamic STM tip and then exploit the relatively narrow spatial extent of dangling bond orbitals on the Si(111)-(7x7) surface to image the molecular orbital structure. Figs. 1(a) and (b) show the transfer of a single C_{60} molecule to the tip. Subsequent dynamic STM measurements yielded images where the silicon adatoms each have a node in their centre, arising from the charge density distribution of the transferred C_{60} molecule (Fig. 1(c)). Changes in the structure of the tip during imaging (Fig. 1(d)) produce a return to "conventional" images of the (7x7) surface, where nodes in the adatoms are not visible. This provides a very useful diagnostic for the orbital structure of a C_{60}-terminated tip.

In addition, our dynamic STM images of C_{60} adsorbed on the Si(111)-(7x7) surface in many cases exhibit an intramolecular structure and symmetry (see inset to Fig. 1(d)) which has not previously been observed experimentally but has been predicted in recent theoretical studies [4]. The implications of our observations in terms of the mechanism of dynamic STM imaging will be discussed. We have also measured the force of interaction between the tip and adsorbed C_{60} molecules using qPlus AFM frequency shift-vs-tip displacement spectroscopy.

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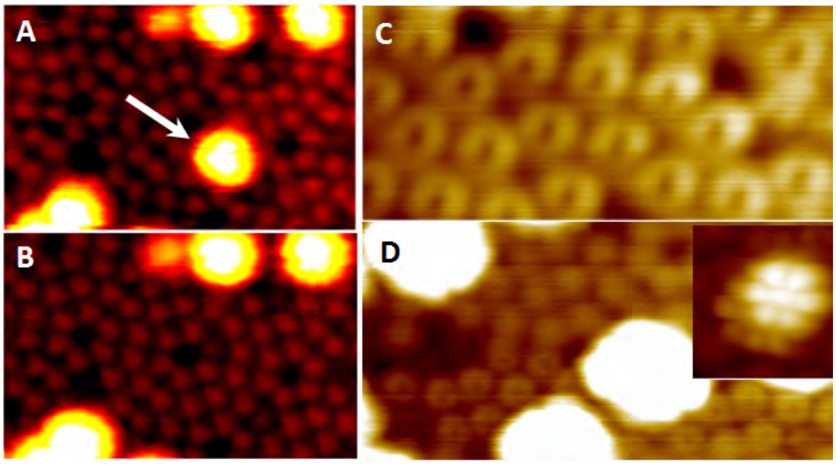

Fig.1: **(A,B)** Transfer of a C_{60} molecule from the Si(111)-(7x7) surface to the tip; **(C)** With a C_{60} molecule on the tip, Si adatoms are imaged with a node at their centre; **(D)** Change in atomic contrast during a scan (~ 1/3 from the bottom of the image); Inset: Intramolecular structure observed in dynamic STM.

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Site selective assembly of tobacco mosaic viruses: RNA-directed modular construction as smart processing tool for nanotechnology

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[‡] *Biological Institute, Stuttgart University, Germany*

Readily available nanoscaled particles are limited to such simple structures as spheres or rods. However, it is highly desirable to create smart particles more complex in shape (e.g. branched nanotubes) since such particles exhibit improved properties especially in catalysis. As biology provides a wide range of structural diversity, biotemplating is a method of choice to produce applicable hybrid or composite structures at the nanoscale. One example being readily used is tobacco mosaic virus (TMV). Here we present a novel strategy to generate TMV-derived artificial scaffolds: By tuning the assembly process of the viral coat protein via genetic modifications of encapsidated RNA strands, kinked and branched virus-derived particles have been created and are now available as biotemplates for various applications e.g. in nanoelectronics, catalysis or biosensing. Moreover, to achieve the integration of such synthetic viral architectures into technical devices at predestinated sites, concepts for the site-specific assembly of TMV coat protein with RNA immobilized on different inorganic surfaces are introduced. This is accomplished with a new approach in silane chemistry: The use of isothiocyanate-terminated silane for covalent attachment of aminofunctional biomolecules on inorganic surfaces provides a good alternative to realize bio-inorganic interfaces. Furthermore, we were able to combine this technique with a site-selective oxidation of polymer surfaces, allowing patterned assembly of TMV-like architectures. AFM investigation on surfaces with the TMV-like self assembled particles and polymer structures is proposed.

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Quantitative understanding of ink transport in Dip-pen Nanolithography

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The Dip-Pen Nanolithography (DPN) process uses a chemically coated scanning probe tip (“pen”) to directly deposit a material (“ink”) with nanometre precision onto a substrate [1, 2]. Several experimental parameters have been observed to influence the ink transport in DPN. Among these, viscosity and density of the ink, relative humidity (RH), and temperature are some important parameters which play a crucial role in ink transport in DPN. It is necessary to understand and control these parameters in order to optimize DPN processes for a particular application. Though DPN has been extensively used before for patterning surfaces it is important to mention here that there is still no complete understanding of the ink transport mechanisms. In order to control the patterns one should understand the process properly. Therefore, in this work, we report on studies aimed at employing the atomic force microscope (AFM) to measure the viscosity of ink used for DPN and try to understand the ink transport in DPN using dynamic mode Atomic Force Spectroscopy.

Generally, for DPN, the inkwells are filled with ink (biological molecules in chloroform) which then gets transported to micro channels from the ink reservoir. The inkwells are dried for few hours to allow for evaporating of the chloroform before using them for coating the tip. It is difficult to measure the viscosity of this ink using standard processes of measuring viscosity. Therefore, we have used the following technique to measure the viscosity of the ink used in DPN. According to theoretical models, the resonant frequency of the cantilever is a function of the density and viscosity of the surrounding medium [3, 4]. In fluid, the oscillations of the cantilever are damped as a result of the added drag on the cantilever. The resulting increase in effective mass shifts the resonant frequency to a lower value; relative to its resonant frequency in air or vacuum and from this shift in resonance frequency we have calculated the viscosity of the ink [5]. In order to measure the amount of ink transferred to the substrate during DPN of dot patterns, we have used the harmonic vibration of a microcantilever in an AFM. The change in resonance frequency of the cantilever allowed us to calculate the mass of transferred ink with picogram mass sensitivity.

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Disentagling atomic and electronic structure
in scanning probe images of Si(100)

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Atomic resolution in non-contact atomic force microscopy (NC-AFM) of semiconductor surfaces arises fundamentally from the formation of a chemical bond – and the associated short range force - between tip and surface atoms. Scanning tunnelling microscopy (STM) images, on the other hand, effectively derive from the spatial variation in the tunnelling transmission of the tip-sample junction which depends not only on the local density of surface states but also on the contribution of bulk states, surface resonances, changes in band bending etc...

For the Si(100) surface, in particular, STM imaging is significantly complicated by the influence of bulk states (and surface resonances) and it has been recognised for a number of years that the simple picture of tunnelling into(from) dimer π^* (π) states does not adequately capture many aspects of the variation in contrast in STM images observed as a function of bias voltage.

We have used a combination of qPlus NC-AFM and dynamic STM (dSTM) at a temperature of 5K to compare the positions of Si(100) dimer atoms with the symmetry, periodicity, and separation of maxima and minima in tunnelling images. The dual regulator facility of the Omicron Matrix control system, which enables a seamless transition from tunnel current to frequency shift feedback *while scanning*, greatly facilitates the direct comparison of qPlus and D-STM images (Fig. 1).

qPlus imaging routinely gives rise to high contrast atomic resolution images of buckled dimers, whereas dSTM images generally show symmetric dimers. Dimer rows in the dSTM and qPlus images align for dSTM scans taken at low bias voltages ($\leq |1|$ V, see Fig. 1). For relatively high voltages (> 1.6 V), a shift between the dimer row position in qPlus and dSTM images is observed. We will discuss the shifts in registry of dimer row features in the qPlus and dSTM images in terms of the electronic structure of the Si(100) surface and demonstrate that the qPlus-dSTM combination is a powerful method of separating geometric and electronic effects in scanning probe images.

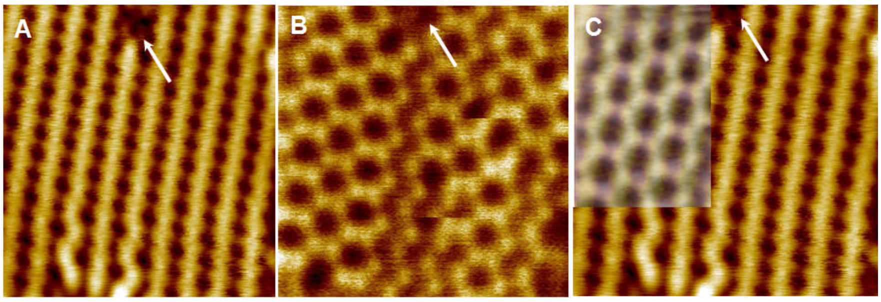

Fig. 1 Comparison of qPlus AFM (at 0 V bias) and dSTM images of the Si(100)-c(4x2) surface at 5K. **(A)** dSTM image (V= -1 V; I_t = 5 pA; A_{vib} = 250 pm); **(B)** qPlus image at 0 V bias (A_{vib}=250 pm; df_{sp} = -10.6 Hz); **(C)** Overlay of a part of image shown in (B) on image (A) showing registry of dimer atoms with features in dSTM image. Arrows highlight same defect in each image.

Nanoscopic characterisation of ion transport in solid electrolytes by time-domain electrostatic force spectroscopy (TD-EFS)

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For many technological applications, such as batteries or fuel cells, materials with good ionic transport parameters are of paramount importance. Recently, the search for improved ion conducting materials has lead to nanostructured materials, where the transport properties are often determined by interaction of different phases (e.g. crystalline and amorphous) and their interfaces.

From a theoretical point of view, the mechanisms of the ion transport in such heterogeneous materials are not well understood. One reason is that usually macroscopic experimental techniques are used for characterizing the ion transport, e.g. impedance spectroscopy or NMR relaxation. These techniques average over ionic movements in different phases and at interfaces, leading to a loss of information about the microscopic transport mechanisms.

The application of atomic force microscopy (AFM) to solid electrolytes yields information that is clearly beyond that obtainable by macroscopic techniques. We use electrostatic AFM to study the dynamics of mobile ions in nanoscopic subvolumes of solid ion conductors [1]. In this method a voltage is applied between the tip and the sample, at typical tip-sample distances of 10 nm. In this case, the voltage drop in the sample occurs mainly in a nanoscopic subvolume below the surface. Ionic movements in this subvolume influence the electrostatic forces acting between tip and sample and thus the resonant frequency of the AFM cantilever.

Using this new method we have measured the temperature dependence of the relaxation times for different glass ceramics. We find that in the probed nanoscopic subvolumes the ion dynamics follow an Arrhenius-type behavior. Depending on the temperature or time window we can identify different relaxation process and extract their activation energies.

We will demonstrate how ionic transport properties can be mapped by systematic grid spectroscopy with nanometer scale resolution and be correlated with the structure of ion conducting glass ceramics.

Special attention is focused on the influence of interfaces (e.g. grain boundaries, glass-crystal interface), Depending on the material, such interfaces can either show very high or low ion conductivity, and are therefore of crucial importance for ion transport properties.

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Electrostatic Interaction Forces in Aqueous Salt Solutions of Variable Concentration and Valency

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The electrostatic interaction forces between surfaces in aqueous electrolyte media can be explained in good approximation with the double-layer theory at the Poisson-Boltzmann (PB) level. This could be confirmed by several experimental data measured with the scanning force apparatus (SFA) or the atomic force microscope (AFM) [see e.g. 1,2]. Recently, the tip-sample interaction forces between silica surfaces in aqueous solutions of monovalent salts were studied by Dishon *et al.* [3] with the colloidal probe technique. These measurements reveal a strong dependence of the used ion species and differences in salt concentration. Up to now these effects are not well understood and a detailed description of the underlying fundamental interaction mechanisms is still missing.

In this study we utilize dynamic force spectroscopy in the frequency-modulation (FM) mode where the AFM cantilever is oscillated near the sample surface to measure the tip-sample interactions. In addition to the tip-sample force this operation mode allows for an analysis of the dissipated energy per oscillation cycle. This method gives additional information about the tip-sample interaction and the usage of sharp tips offers a better lateral resolution than the colloidal probe technique. We show a systematic analysis of numerous salt solutions with different mono- and divalent ions and different concentrations (see Fig. 1) which results in a deeper insight into the ion specific effects on the interaction mechanisms.

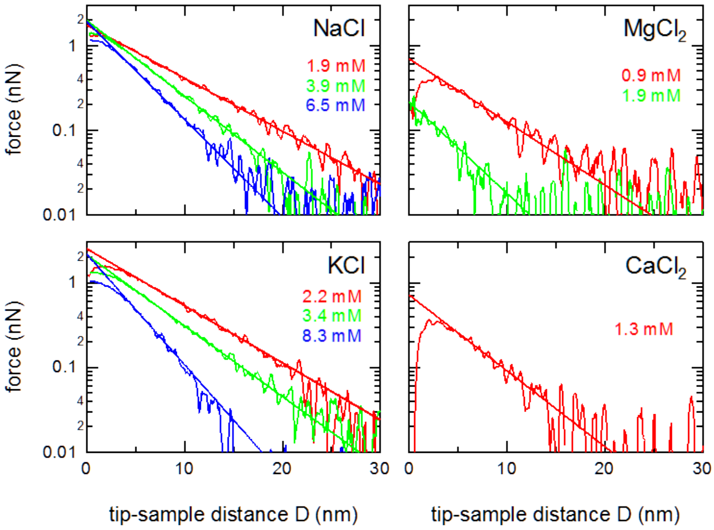

Figure 1: Tip-sample force as a function of tip-sample distance for different monovalent (left column) and divalent salts (right column).

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Towards the Ultimate Resolution of Nanoindentation: Measurement of Homogeneous Dislocation Nucleation in Three Dimensions

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Direct comparison of experimental plasticity data and atomistic computer simulation is one factor pushing forward basic research in nanomechanics. Atomic force microscopy (AFM)-based indentation on single crystals is an ideal method by which plasticity experiments can be designed to match the constraints of atomistic simulation. Furthermore, the availability of commercially available microfabricated tips with a tip radius of less than 10nm allows for the application of pressures in the range of gigapascals. This construction also approaches a continuum mechanical point-like model. Moreover, readily available diamond coated tips enhance tip durability, reducing the chance of tip damage during indentation. Finally, the high force resolution of AFM in both normal and lateral directions opens the opportunity to measure the displacement of the tip in three dimensions while performing a plasticity measurement.

A reduced geometry, in one or more dimensions, changes the mechanism by which materials can plastically deform. One deviation is the observation of discrete load-drops or displacement-bursts, often referred to as pop-ins. These pop-ins are a result of the nucleation of dislocations in defect free, crystalline materials. Glide of the nucleated dislocations results in material displacement at the surface, which in turn result in the measured pop-ins. However, in almost all materials glide of dislocations is not limited to one dimension, as is typically reported in this type of experimentation. Rather, dislocation glide can occur in several crystallographic directions within the crystal. Using AFM-based indentation to realize nanoscale geometries, the measurement of dislocation glide in three-dimensions in KBr(100) crystals has been achieved. Displacements of the tip normal to the surface and within the plane of the surface can be correlated with the preferred dislocation slip systems of the crystal. Furthermore, the convolution of tip displacements in the plane of the surface and the lateral contact stiffness has been investigated so that discontinuous displacements of the tip while indenting can be quantified.

Calibrated nanoscale capacitance and dopant profile measurements using a scanning microwave microscope

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Keywords: Atomic Force Microscopy, Scanning Microwave Microscopy, Dopant Density, Capacitance, Materials Science

A scanning microwave microscope (SMM) for spatially resolved capacitance measurements in the attoFarad-to-femtoFarad regime is presented. The system is based on the combination of an atomic force microscope (AFM) and a performance network analyzer (PNA).

For the determination of absolute capacitance values from PNA reflection amplitudes, a calibration sample of conductive gold pads of various sizes on a SiO_2 staircase structure was used (figure 1). The thickness of the dielectric SiO_2 staircase ranged from 10 nm to 200 nm. The quantitative capacitance values determined from the PNA reflection amplitude were compared to control measurements using an external capacitance bridge. Depending on the area of the gold top electrode and the SiO_2 step height, the corresponding capacitance values, as measured with the SMM, ranged from 0.1 fF to 22 fF at a noise level of ~2 aF and a relative accuracy of 20%.

For dopant profiling, n- and p-doped reference samples with densities between 10^{14} and 10^{19} atoms/cm^3 in 1.5 micron-wide regions were imaged in dC/dV modulation mode (figure 2). A calibration curve relating signal levels and dopant densities was established.

Possible applications of an SMM range from quality control of ICs, solar cells, and other semiconductor devices to materials science, (e.g. measurements of quantum dot dielectric constants), and to bioscience (e.g. the detection of viruses, and thickness measurements of protein layers).

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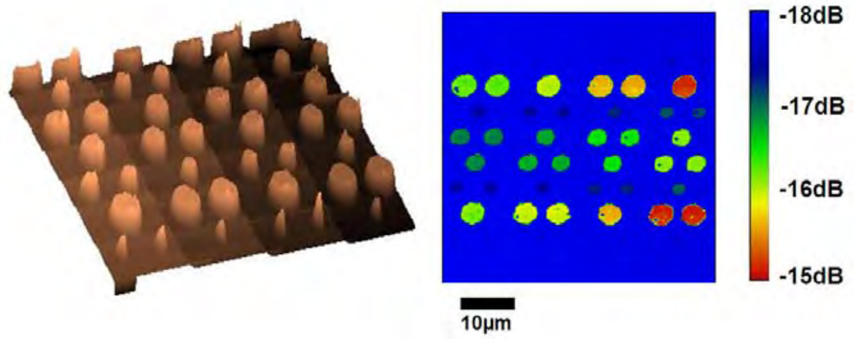

Figure 1. SiO_2 staircase in 3D-topography view (left) and corresponding PNA amplitude signal (right) used for calibrated capacitance measurements.

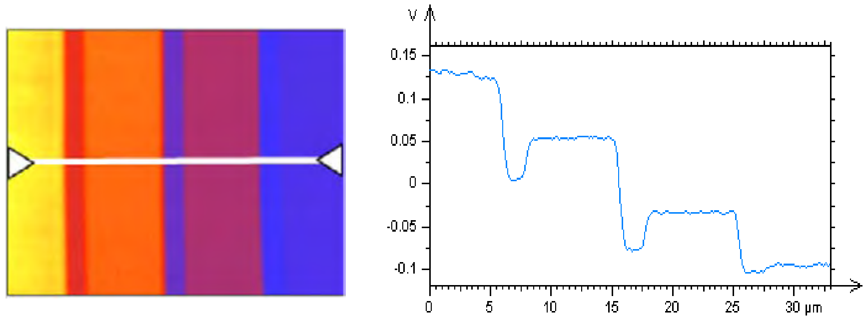

Figure 2. Dopant density calibration test sample (IMEC, Belgium) with densities ranging from 10^{14} (left) to 10^{19} atoms (right), measured in dC/dV mode.

Quantitative material properties extraction using Intermodulation AFM

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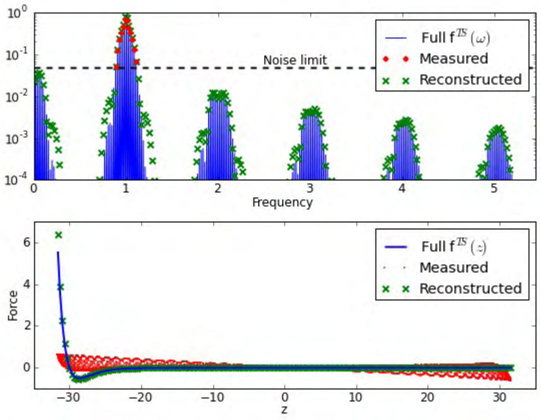
The phase image in amplitude modulation atomic force microscopy (AM-AFM) is sensitive to material properties of the surface, however phase information alone is not enough to fully quantify the tip-surface interaction. We have developed Intermodulation AFM (ImAFM) based on a spectral analysis of the cantilever's *nonlinear* dynamics. ImAFM increases the amount of information obtained without increasing scan time [1]. Previously we have shown in simulation how reconstruction of the tip-surface force can be made from the intermodulation spectrum under the assumption that the force can be described by a polynomial [2]. Here we present an alternative method in which the tip-surface force can be described by any physically well-motivated, but otherwise arbitrary model. An iterative numerical solver is used to find the parameters of the model, such that the expected intermodulation spectrum matches the spectrum measured in experiment. This approach works not only for conservative forces but also for dissipative interactions, such as velocity dependent forces or double-valued tip-surface forces. We demonstrate our method on simulated as well as measured AFM data. In the latter case we use the van-der Waals - Derjaguin-Muller-Toporov model to describe the tip-surface interaction, which allow us to extract the effective Young's modulus and the adhesion force between the tip and surface. These parameters, extracted at each pixel of the AFM image, are used to form surface property maps which can be displayed together with topography.



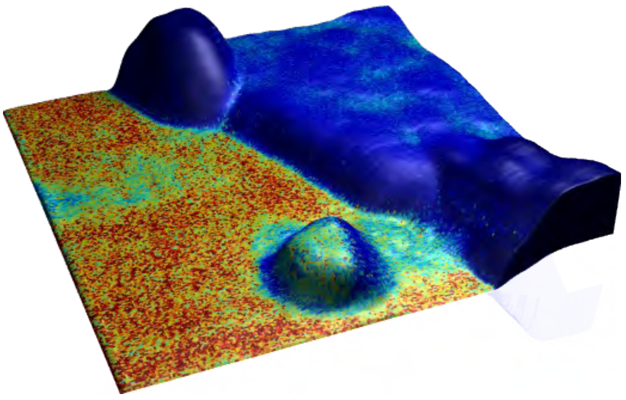


Figure 1

Figure 2

Figure 1: Top: spectrum of simulated intermodulation data. Only peaks above the noise limit (dashed line) are measured (red dots). The missing low amplitude information can be reconstructed (green crosses). Bottom: the corresponding tip surface forces, full, measured and reconstructed.

Figure 2: Stiffness parameter map in color projected on 3D height image. Sample is 10 nm thick layer of polyethylene-butylacrylate on silicon dioxide. There is a five-times reduction in modulus from polymer (blue) to substrate.

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3D dynamic force spectroscopy on KBr(001) at low temperature with a tuning fork sensor

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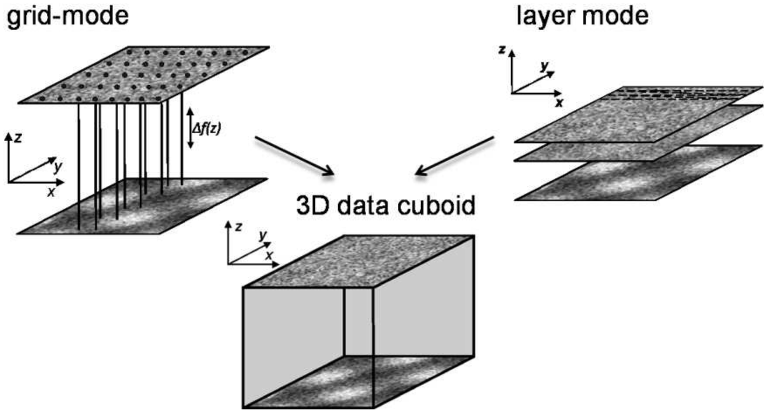
Knowledge about surface potentials at the atomic scale is of great importance to understand crystal- and thin film growth, catalysis, or nanotribology. Dynamic force spectroscopy (DFS) is a powerful tool for this topic, because the interaction potential and -force can be extracted via the measured frequency shift Δf [1]. Recently, this technique was drastically improved to collect 3D potential energy landscapes of surfaces.

So far, two different methods were demonstrated to collect 3D-Δf-landscapes; (i) taking Δf(z) curves at the different points of a x-y grid above the surface (grid mode) [2] and (ii) recording Δf(x,y) images in constant height mode varying z systematically (layer mode) [3]. Both approaches result in a 3D data cuboid [Δf(x,y,z)] used for calculations of force and potential.

We measured 3D force fields on KBr(001) at low temperature using a tuning fork force sensor [4] with amplitudes of 0.4nm and 1.1nm. The influence of tip/sample deformations on the data as well as on the extracted force and potential fields was investigated. In the grid mode, thermal drift of the relative tip-sample distance can be excluded by atom-tracked tip positioning (Nanonis AT4) on a certain maximum before each DFS measurement. Tip/sample deformations were corrected by adjusting the maxima in different layers one below the other before the force and potential extractions. We found that this correction gave a significant impact on the results. This influence prevented an accurate correction of the "*thermal drift*" in the measurement using the layer mode. Furthermore, the influence of the tip/sample deformations by the scanning tip at small tip-sample separations gave an additional impact on the force and potential extractions.



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Allophanes: Nano-Sized Particles as Basis for Nano-Structured and Functionalised Surfaces

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Allophanes are hollow spherical, nano-sized silicate particles with a narrow size distribution (diameter 5 nm) and with six pores, standing pairwise perpendicular to each other [1]. They either appear as natural material or are available by synthesis and can be seen as the inorganic equivalent to the Fullerenes. In contrast to the carbon particles allophanes carry OH-groups on the inner *and* on the outer interface which can be used for sorption processes or chemical reactions. As the pores afford chemical access to the inner part of the particles, allophanes have high potential for sophisticated application e.g. as nano-sized containers. The immobilization of nanoparticles on substrates is a very common method to prepare nanostructured surfaces for many fields of technical or medical application. Recently we showed that single natural allophane particles can be immobilized on a substrate [2]. The goal of our work is the equidistant deposition of the allophane particles on substrates to prepare well defined patterns of reactive nanospots, which can be functionalized (i) on the outer surface by recently developed chemical coupling procedures e.g. for biological application [3] and (ii) on the inner surface to tailor the allophanes for their application as nanocarrier systems. In the first part of the work presented here we show that natural and synthesized allophane particles suspended in water can be transferred to an organic toluene phase by using diblock copolymers (polystyrene-polyvinylpyridine) micells. In a second part we demonstrate the immobilization of the particle and particle aggregate containing micells on the surface of a substrate by using the organic phase for a dip coating process. The particles and particles arrays are characterized by scanning probe techniques and IR spectroscopy.

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Temperature Effects in Nanoscale Friction Revealed by Thermal AFM Probes

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Understanding the energy dissipation in frictional solid-solid contacts is essential to model and predict tribological systems as well as to develop materials with tailored frictional behavior. Recently, AFM-based nanotribological experiments have investigated single asperity friction as a function of temperature, mostly under cryogenic conditions and all involving varying the sample temperature only. In contrast, a heated tip provides an alternate means to vary the contact temperature and is potentially more representative of the localized heating that occurs in real tribological interfaces. We used custom AFM probes with integrated solid-state heaters which allowed for the cantilever temperature to be controlled between room temperature and 650 °C, with the tip temperature varied *in-situ* within milliseconds. We quantitatively investigated the nanotribological behavior of single asperity contacts between the silicon tip and a silicon sample (both with a native oxide) in an ambient environment. We observed a strong dependence whereby friction increased significantly with temperature, and decreased with sliding velocity. This is in contrast to cryogenic measurements where the opposite trends were reported. The behavior is reversible, indicating that the effects are not due to damage or modification of the tip or sample. The temperature and velocity dependences are suppressed and in some cases slightly reversed in a dry nitrogen environment, demonstrating that the effects seen in ambient arise from capillary condensation of water at the tip-substrate interface. As the formation of capillaries has been shown to be a thermally activated process, increasing the tip temperature helped to form the bridges resulting in higher friction forces. As the sliding velocity was increased it became more difficult for the capillary to follow the tip, thus friction decreased with velocity. Above a certain critical velocity, the tip broke free from the capillary bridge completely and friction plateaued or even showed a slight increase with velocity, consistent with the classical Tomlinson model. We will discuss how these results enable us to further study the kinetics of nanoscale capillary condensation and to actively control friction forces on a extremely fast timescale.

Chiral recognition and homochiral island formation on an insulating substrate

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The influence of chirality on molecular self-assembly on surfaces is of great interest within both, fundamental as well as application-oriented fields including, e.g., chiral recognition and enantioselective catalysis [1]. Ever since Luis Pasteur's famous experiment on the manual separation of a racemic mixture, the separation into homochiral structures such as two-dimensional domains, as well as chiral recognition upon dimer formation have attracted great interest [1,2].

Here, we present a study of heptahelicene-2-carboxylic acid (HHCA) on the (10-14) cleavage plane of calcite. The molecules were deposited in-situ from a heated glass crucible onto the freshly cleaved calcite surface held at room temperature. Both, deposition and NC-AFM imaging was performed under ultra-high vacuum conditions. For the racemic mixture (enantiomeric excess of 0%), uni-directional rows consisting of molecular pairs are revealed [3]. However, from the NC-AFM images alone it remained inconclusive whether these rows constitute heterochiral or homochiral structures. To address this question, we investigated homochiral HHCA molecules (M-HHCA). Upon deposition of the M enantiomer, islands are formed on the calcite surface, which is in sharp contrast to the rows observed from the racemic mixture. These results clearly indicate heterochiral recognition to be responsible for the row formation.

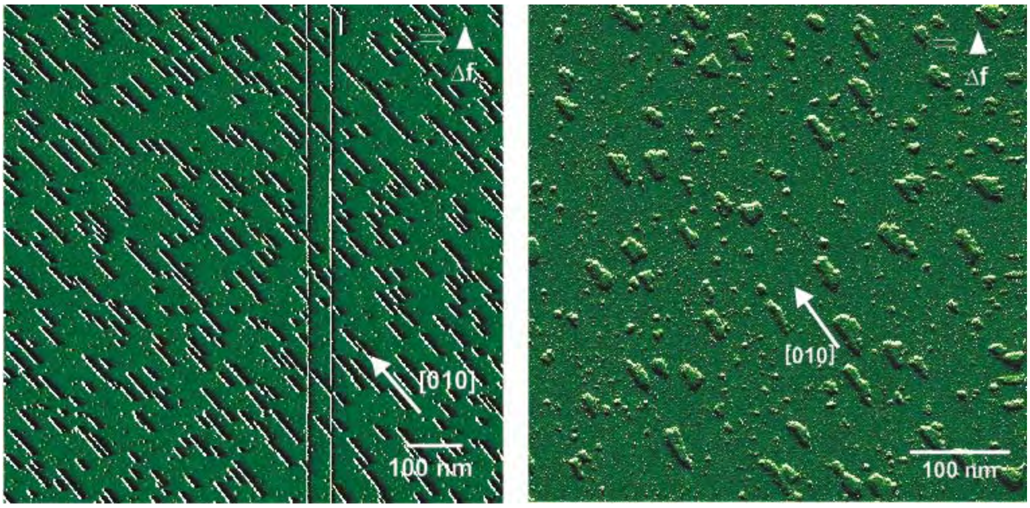

Figure 1: Frequency shift images taken at room temperature. The racemate (left) shows unidirectional rows along the [010] substrate direction [3]. The homochiral molecules (right) form larger islands, consisting of several rows oriented along the [010] substrate direction.

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Quantitative static and dynamic force spectroscopy of atomic-scale forces and energy dissipation

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Dynamic force microscopy has proven to be an invaluable technique for studying and manipulating nanoscale processes at surfaces.[1,2] In order to gain a more detailed insight into the tip-sample interaction forces and the resultant dissipation, it would be very beneficial to make observations over a single oscillation cycle. However, due to the narrow measurement bandwidth, a measurement of individual force curve upon approach-retract is impossible.

Here, we investigate the dissipative interaction in dynamic force spectroscopy as a stochastic tip and/or sample deformation process with a systematic distance dependent measurement of the quasi-static tip-sample interaction force at a certain atomic site on NaCl(001) at room temperature.[2] In order to measure the stochastic tip-sample interaction, 21 approach-retraction sweeps with different initial tip-sample distances were repeated 100 times. Infrequently observed large and wide hysteresis loops are attributed to the formation and rupture of atomic chains during tip retraction, leading to a large magnitude of energy dissipation. The “even” and “odd” dynamic force curves [3] were computed via the static force spectroscopy data. Then, frequency shift and energy dissipation for 21 different initial tip-sample distances were calculated by numerical integrations. The computed frequency shift was in good agreement to that measured by dynamic force spectroscopy at the same atomic site with the same tip. Furthermore, the dynamic force curves are extracted via the computed frequency shift. We found that the dynamic force differs significantly from the static force. The molecular dynamics simulation was in good agreement with the experiments.[3]

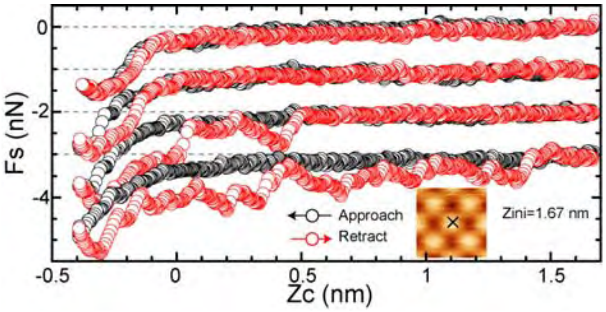

Figure: Quasi-static vertical interaction force curves upon approach and retraction, measured in static force spectroscopy with a constant initial Z position. The inset image was obtained with A2nd=1.0 nm and df2nd = -40 Hz. Fs axes of each curve is shifted by 1 nN.

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[2] U. Dürig, New J. Phys. **2** 5 (2000).
[3] S. Kawai, F. F. Canova, Th. Glatzel, A. S. Foster, and E. Meyer (submitted).

Nc-AFM Coulomb blockade observation on the few nanometer sized Au islands grown onto 4ML-NaCl/Cu(100) surface

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Abstract

Ultrasensitive cantilever suspended perpendicularly to the sample surface was used to probe energy dissipation on several nanometer sized Au islands grown onto Cu(100) surface covered previously with 4ML of NaCl. The cantilevers were operated in the non – contact regime and the sample was cooled down to 5K temperature. The experiment was done in Ultra High Vacuum (UHV).

System consisted of Cu substrate, 4ML thin insulating NaCl layer and metallic Au islands grown on top is in fact a tunnelling junction with a capacitance equal to 10^{-16}F. The small size of Au islands causes the electrons confinement in all directions. The Au islands can be treated as quantum dots, coupled to the Cu electronic reservoir underneath. Ultrasensitive cantilever positioned on top of Quantum Dot is the gate electrode capacitively coupled to the OD object and thus able to probe electronic structure of individual quantum dot.

Results show the change of the dissipated power and resonant cantilever frequency as a function of the bias voltage applied between tip and Cu sample. The observed peaks in the power dissipation signal are attributed to the single electron tunnelling events between the Cu reservoir and Au quantum dot, the so-called Coulomb blockade effect. The constant height measurements reveals how the energy is dissipated in a space around the Au quantum dot. The evolution of Coulomb blockade attributed dissipation peaks versus external magnetic field was also examined.

Nanostructuring of surfaces using AFM

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Nanostructuring of surfaces is highly desired in several disciplines and can be achieved by different methods. Especially the usage of self-assembled monolayers (SAMs) [1] has been shown to be a versatile useful approach not only to tailor surface properties but also to structure surfaces using lithographic methods or micro-contact printing. In this study an alternative nano-patterning approach is applied by using the tip of an atomic force microscope (AFM) for nano-shaving and nano-grafting a SAM on a gold surface [2]. While shaving implies only removal of molecules, the grafting is performed in an organothiol-solution containing liquid enabling re-adsorption of a different SAM. Both methods allow lateral structuring with resolutions of several nanometers and therefore offer some potential in the field of molecular electronics, where defined small regions of only few molecules of one species are desired for conductivity measurements. Furthermore, these methods enable *in situ* characterization like height or friction measurements while performing structuring and are applicable for a wide range of substrates and adsorbates. This versatile and fast approach allows even repeated usage for the selectively growth of a multilayered structure of soft organic matter like metal-organic frameworks (MOFs) which grow selectively on COOH- or OH- functionalized surfaces and can be investigated by Atomic force microscopy [3].

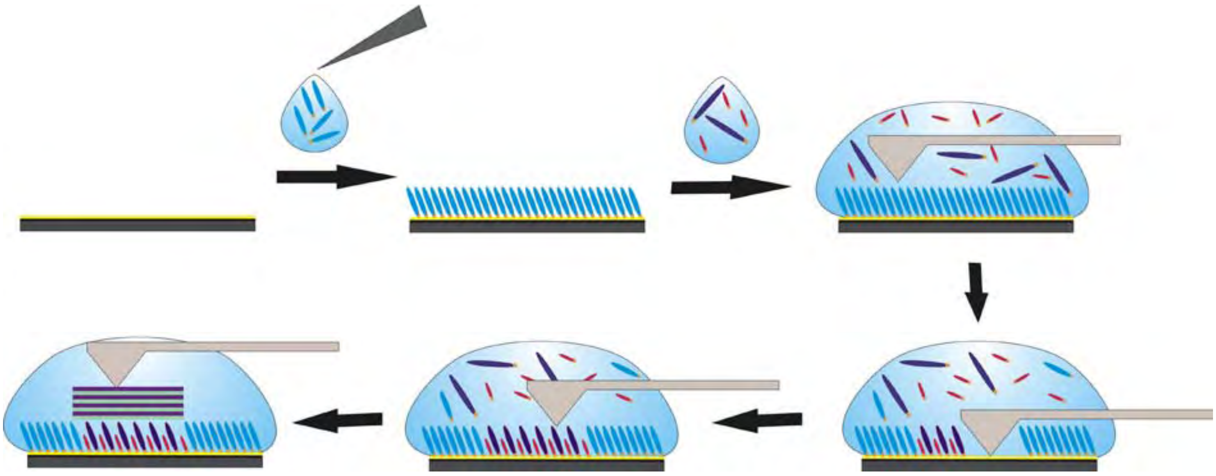

Figure 1 Graftingprocess of two different SAMs with the Atomic force microscope with a selective MOF growth on the grafted area

[1] Bain, Whitesides, *Angewandte Chemie-International Edition in English*, *28*, 506 (1989).
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Experimental and theoretical AFM/STM investigation of the adsorption of ethylene on Si(111)-(7x7) surface

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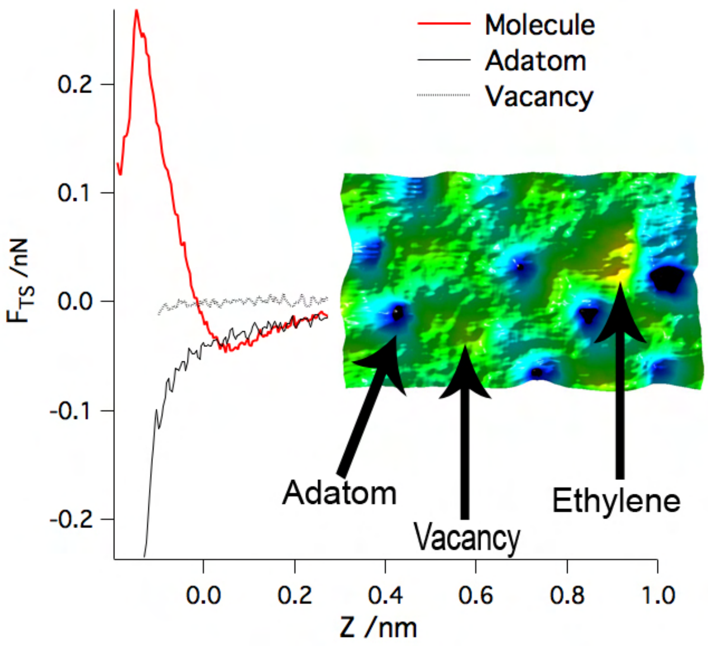
The adsorption of small molecules like ethylene, benzene on metal and semiconductor surfaces has been well studied by various techniques (such as Photoemission, STM or LEED). For the adsorption of these species on the Si(111)-(7x7) surface a quite general adsorption mechanism, the adatom-restatom model was proposed [1]. Providing direct evidence for this mechanism is not a simple task. Even with high resolution STM one cannot directly image molecules on surface due to wide molecular band gap and its alignment to surface electronic states. Usually only missing adatoms can be observed by STM, which makes difficult to distinguish between vacancies and molecular adsorption places.
The capability of the Atomic Force Microscope for high resolution of molecules in real space has been already shown [2]. This capability turned AFM into a very promising surface chemistry tool [3].

Here we present a combined experimental and theoretical study of the adsorption of ethylene (C_2H_4) on the Si(111)-(7x7) using AFM. Based on force site spectroscopy and DFT simulations we were able clearly discriminate between absorbed molecules and vacancies on surface. We have found that over the molecule only a very weak attractive force appear and mainly the repulsive interaction contribute along tip approach, while there is no repulsive interaction over vacancy sites at the same tip-sample distance (see Fig).



Force spectroscopy measured over the molecule (red), over a free adatom of the 7x7 unit cell (black) and over a vacancy (gray). (a_{OSC} = 0.13 nm, k = 4354 N/m, f_0 = 71096 Hz)

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AFM Characterization of Graphene

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Graphene is a two dimensional highly crystalline material and can be described as a single layer of all-sp2 carbon atoms packed into a benzenoid ring structure [1]. It is widely used to describe the structural and electronic properties of many carbon-based materials, including graphite, fullerenes and nanotubes. For example, carbon nanotubes are usually thought of as graphene sheets rolled up into nanometre-sized cylinders. In 1859, Brodie discovered that pure graphite, when treated with potassium chlorate and nitric acid, formed crystalline graphitic acid (also known as graphitic oxide or graphene oxide). It is likely that he also made small amounts of graphene and in any case he speculated a new form of carbon was present and proposed the name Graphon (Gr)[2]. However, graphene was not shown to be stable until 2004 when Geim and Novoselov [3] described the “Scotch tape” method to peel graphene from samples of crystalline graphite. This mechanical exfoliation method is slow and labour-intensive as an optical microscope is required to hunt for single and few-layer graphene (FLG) amongst the material peeled-off.

Currently, the interest of physicists in graphene is enormous, but the interest of chemists has so far not been as great, probably resulting from the absence of well-established large scale methods to produce graphene. Therefore, the most important role chemists can play is the establishment of an inexpensive and simple wet-chemical method for making graphene. For example, intercalation compounds of graphite have been of interest for many years [4]. More than 100 reagents can be intercalated into graphite [5]. In this talk, we describe an intercalation method to make clean graphene that has good electrical properties [6]. The graphene material was characterized by AFM, Raman and HRTEM.

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Measuring Wear by Combining Friction Force and Dynamic Force Microscopy

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One can observe wear on every moving part during its lifecycle. The economic costs of wear are billions of dollars every year. Therefore, reducing the wear is the goal in every device and production process even thou the microscopic origins of wear process have not been completely understood. With the invention of the *friction force microscope* (FFM) 1987, one get a tool to examine friction and wear on the nano-scale [1]. While the wear of the sample surface can easily be measured via the change of the samples topography [2], it is not possible to measure the tip's wear simultaneously in a direct way.

From an experimentalist's point of view, tip wear is a well-known effect from everyday experience as for example a blunted tip reduces the resolution of the microscope. To quantify the tip's wear, it is possible to image the cantilevers tip in a *scanning electron microscope* (SEM) [3], but this is a very time consuming procedure. For many experiments it is also not practicable, because the tip has to be transferred from the FFM to the SEM, which rules out the continuance of the wear experiment.

For measuring nano-scale wear of the tip, we introduce a new technique combining friction force and dynamic force microscopy. We are using the FFM for "weighing" the cantilevers tip mass. As the cantilever resonance frequency depends on mass of the tip, we can measure the increase (the tip picks up some material from the sample) or decrease (wear of the tip) of the tip's worn mass down to some picograms due to the resonance frequency shift of the cantilever [4]. By attaching a small sphere to the upper end of the cantilever's tip we can detect the nano-wear of several material combinations with this approach [5].

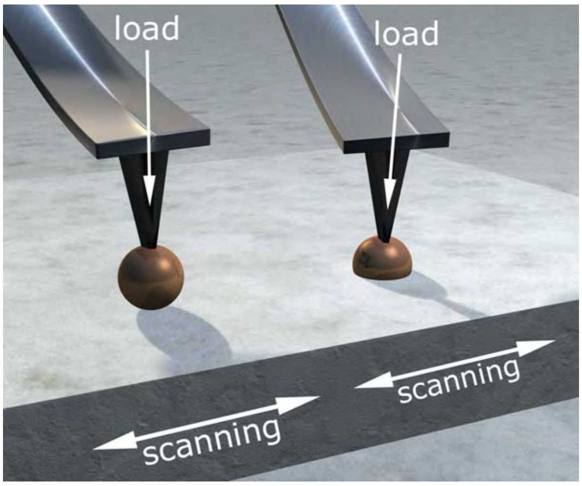

Fig 1: Experimental setup

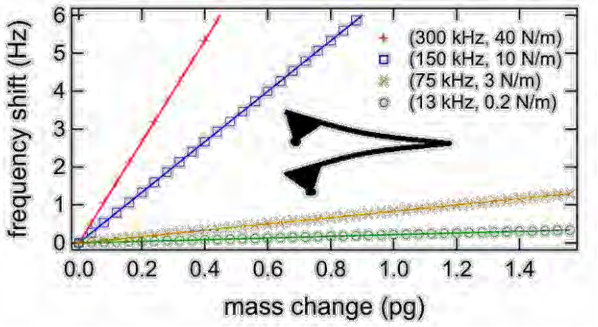

Fig 2: Frequency shift depending on the mass change

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High-resolution imaging of bare and hydrogen-saturated diamond C(100) using NC-AFM

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[1]Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Germany
[2]Institut des Sciences Moléculaires d'Orsay, Université Paris-Sud, France
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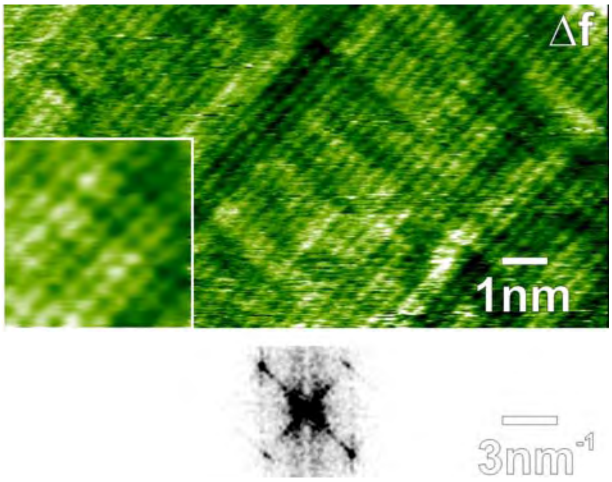
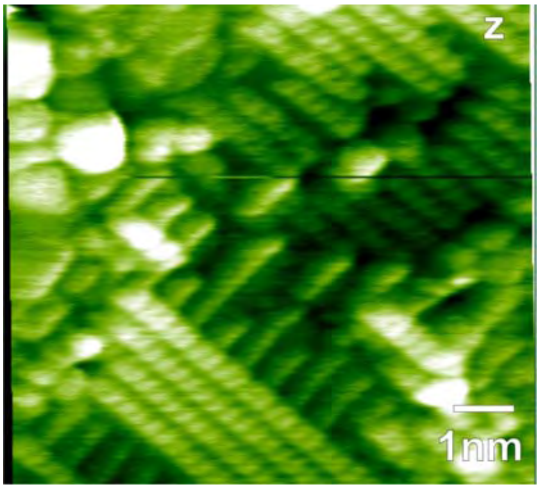
[1]Institut für Experimentalphysik, Freie Universität Berlin, Germany

Hydrogenated and bare diamond surfaces have attracted considerable interest in recent years, motivated by the unique electronic, thermal and mechanical properties of diamond [1]. Diamond shows large electron and hole mobilities [2], but in spite of this, the lack of charge carriers turns high-purity diamond into a perfect insulator. However, the surface electronic structure can be modified by chemisorption of hydrogen, resulting in p-type conductivity [3]. Therefore, diamond is in general regarded a promising material for high-performance electronic applications such as metal semiconductor field effect transistors (MESFETs) or high voltage switches, especially since the synthesis of high quality diamonds by means of chemical vapour deposition (CVD) has made significant progress in recent years.

However, a thorough scientific understanding of diamond, including a detailed characterisation of its surface structure, is necessary for further progress in this field. In this contribution, we present results of our NC-AFM study of both, the bare and the hydrogen-terminated diamond C(100) of high-purity, type IIa CVD-diamond [4]. In contrast to previous scanning tunnelling microscopy experiments, NC-AFM imaging allows both hydrogen atoms within the unit cell of the hydrogenated surface to be resolved individually, indicating a symmetric dimer alignment. In case of the bare diamond C(100) surface, we present atomic-resolution images providing real-space evidence for a (2×1) dimer reconstruction. We also observed a number of surface features such as dimer vacancies, different types of step-edge formations and dimer row dislocations, allowing for a better surface characterisation.



Hydrogen-terminated diamond C(100)



Bare diamond C(100)

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Vizualisation of “pore-like” structures of **t**win **a**rginine **t**ranslocation (Tat) system in supported lipid bilayers by AFM.

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Karlsruhe Institute of Technology (KIT), Germany

The twin arginine translocation (Tat) system can transport fully folded proteinsacross bacterial or thylakoid membranes. The Tat system of *Bacillus subtilis*, which serves to export the phosphodiesterase (PhoD) consists of only two membrane proteins, TatA$_d$ and TatC$_d$. The larger component TatC$_d$ has a molecular weight of 28 kDa and several membrane-spanning segments. The TatA$_d$, with molecular weight of 7.3 kDa, consists of an N-terminal transmembrane segment, followed by an amphipathic helix and a highly charged, possibly unstructured C-terminus. Multiple copies of TatA$_d$ are supposed to form the transmembrane channel.

The aim of our study was to visualize in the supported lipid bilayers the protein structures responsible for the Tat membrane transport.

The recombinant TatA$_d$, TatA$_d$ without unstructured C-terminus, and TatC$_d$ proteins were expressed in *E.coli*, purified and reconstituted into the lipid vesicles. The samples for the AFM investigations were established by the fusion of the vesicles on the surface of mica according to the standard procedure.

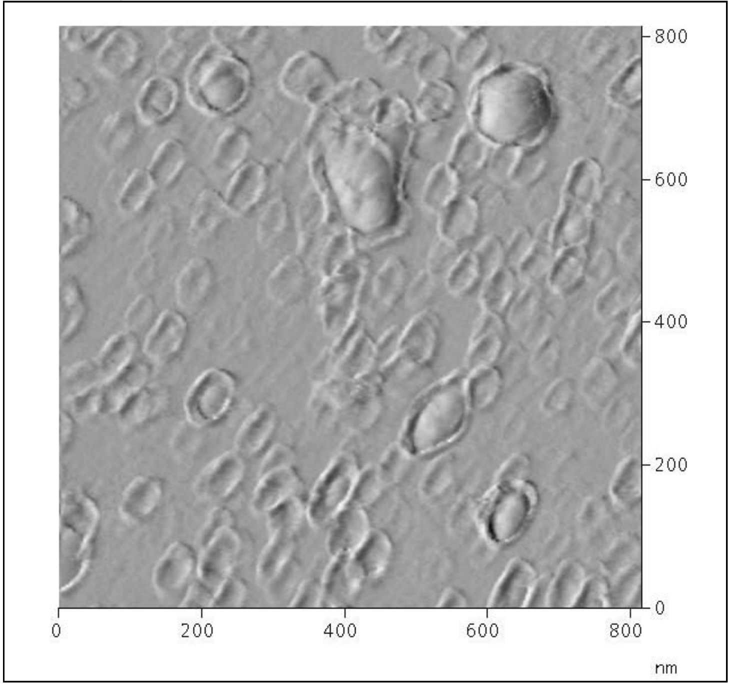

Figure 1. AFM (Tapping Mode) Amplitude Image (800 nm × 800 nm) DMPC lipid bilayer with reconstituted TatA$_d$ (1:1000 mol/mol protein to lipid ratio) on mica.

Some samples demonstrate the “pore-like” structures with diameter of 20-60 nm. (See for instance Fig.1). The dynamic of the “pore” formation is under investigation.

We expect that this approach will provide more detailed information about the structure and functionality of the Tat translocase.

Low temperature STM/ncAFM studies of adsorbed organic molecules : high resolution imaging and manipulation

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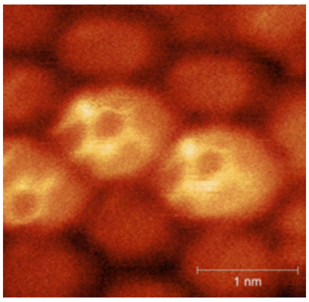
Last past years, impressive improvement has been made in the field of non contact atomic force microscopy (nc-AFM), allowing for example atomic resolution of a single-walled nanotube [1]. Recently, Gross and co-workers have reported unprecedent resolutions of the chemical structure of different molecules adsorbed on a NaCl thin film growth Cu(111) [2-4] with a tuning fork sensor [5] at low temperature.

In this contribution, we will show a combined scanning tunnelling microscopy (STM) and nc-AFM study of the buckyball C_{60} adsorbed on Cu(111). Whereas many STM studies supported by DFT calculations gained insights into their orientations [6], no direct observation at the atomic scale were obtained so far. With ncAFM, previous experiments were principally focused on the C_{60} self-assembly properties on insulators [7]. Our results first demonstrate unambiguous observations of orientated C_{60} by resolving their inner chemical structure by ncAFM (*cf.* Fig. a). In addition, three-dimensional spectroscopic measurements of force and current obtained above single molecules will be presented bringing detailed informations about the tip-molecule interactions allowing such sub-molecular resolutions.
We will also discuss the controlled manipulation of porphyrins functionalized with carbonitrile groups (CN) and adsorbed on Cu(111). The process consists of linking the tip to the one of these CN groups of the molecule *via* single *z* spectroscopic curves. Thereafter, spontaneous rotations as well as controlled vertical and lateral manipulations can be achieved in a reproducible way (*cf.* Fig. b). All presented experiments were performed with a tuning fork based LT-STM/ncAFM (Omicron) operating at 5K in ultra high vacuum conditions.

a



b

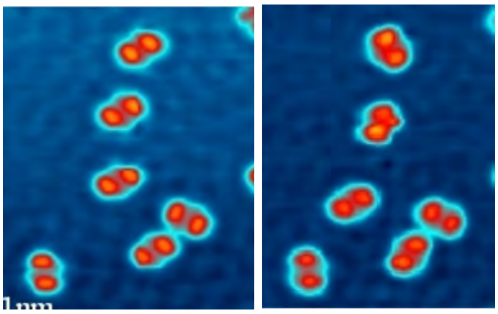


Fig. a) High resolution frequency shift image of adsorbed C_{60} on Cu(111) performed with a tuning fork based LT STM/nc-AFM .

Fig. b) STM images showing porphyrins before and after manipulation.

[1] M. Ashino, D. Obergfell, M. Haluska, S. Yang, A.N. Khlobystov, S. Roth and R. Wiesendanger, *Nature Nanotechnology*, **vol 3**, 338, (2008).
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Reconstructing conservative and non-conservative interactions with intermodulation atomic force microscopy

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Methods based on dynamic atomic force microscopy (dynamic AFM) are important for surface characterization on the nanoscale. Operation at frequencies close to a cantilever resonance increases sensitivity and dynamic methods allow for the measurement of the phase of the cantilever response. This phase is traditionally interpreted as a measure of the energy dissipation due to the tip-sample interaction. However, a quantitative understanding of conservative and dissipative interaction forces remains a challenge in conventional dynamic AFM. To address this problems we have developed Intermodulation AFM[1]. With this multi-frequency technique we can tremendously increase the number of information carrying signals close to resonance. Using Fourier analysis and linear algebra we combine the amplitudes and phases of these signals to reconstruct the tip-sample forces[2]. We have further developed this technique to separately reconstruct the conservative and non-conservative tip-sample interactions. The reconstruction algorithm was tested on both simulated and experimental data. The method works at one probe height, providing quantitative high resolution maps of surface properties while imaging at normal rates.

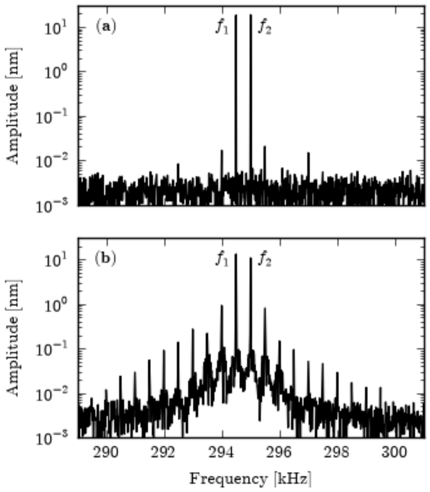

Figure 1

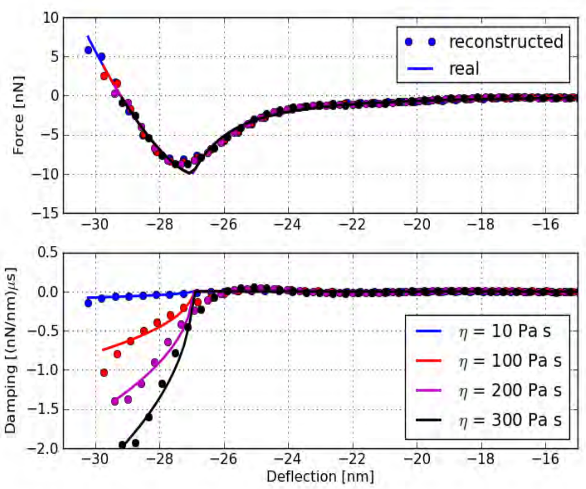

Figure 2

Figure 1: The measured spectrum of the tip motion when driven with two frequencies on resonance far away from a surface (a) and close to a surface (b).
Figure 2: Reconstruction of conservative tip-sample force and distant-dependent damping from simulated data.

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[2] C. Hutter et al. Phys. Rev. Lett. 104, 050801 (2010)

Atom-tracking system for reproducible 3D NC-AFM data acquisition under large-drift conditions

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[2] Fachbereich Physik, Universität Osnabrück, Barbarastraße 7, 49069 Osnabrück, Germany
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In numerous fields including surface chemistry, thin-film growth, molecular electronics and nanotribology, it is of utmost interest to measure AFM data in three-dimensional (3D) space [1]. From these data, forces along any direction and the energy landscape can be derived, leading to a most detailed understanding of the investigated sample system.

Acquiring a large and dense 3D data set is usually hindered by distortions originating from thermal drift. In low-temperature studies using a bath cryostat, these artifacts are comparable small and can be compensated for easily [2]. However, when performing experiments in ultra-high vacuum at room temperature, thermal drift is large and often highly non-linear and, therefore, only small 3D data spaces were presented so far [3]. An elegant method to compensate for thermal drift at room temperature is the atom-tracking technique [4].

In this contribution, we present a newly developed, flexible atom-tracking system. Due to its design, the system can be adapted to various AFM systems. Besides the most useful drift measurement and compensation procedure, we realized a new data acquisition protocol for an automatic and reproducible 3D data collection. The protocol relies on alternating steps of drift measurement and data acquisition and is, therefore, able to easily handle large and non-linear drift. By employing this protocol, we are able to measure complete 3D data spaces at room temperature. Moreover, the data acquired with this protocol do not require a subsequent drift correction.

As an application example, atomic-resolution 3D NC-AFM data measured on a $CaCO_3(104)$ surface at room temperature will be presented. The total data space consists of 85×85×500 pixel ($1.74\times1.74\times2.18\ nm^3$), while the acquisition took 3 h in total.

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[2] L. Gross *et al.* Science **325**, 1110 (2009), B. Albers *et al.* Nature Nanotech. **4**, 307 (2009)

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A. Schirmeisen *et al.* Phys. Rev. Lett **97**, 136101 (2006)
D.-A. Braun *et al.* J. Vac. Sci. Technol. B **28**, C4B6 (2010)

[4] M. Abe *et al.* Nanotechnology **16**, 3029 (2005),
Y. Sugimoto *et al.* Nature **446**, 64 (2007)

AFM Analysis of Gecko-mimicking Polymer Structures

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Geckos have an impressive attachment system that makes them able to climb on nearly every surface. Like various other mechanisms developed by nature, the gecko effect is strongly connected to the structuring of surfaces. The toes of the Tokay Gecko for example are divided into several lamellae which are covered with millions of setae, delicate hairs which are about 100 µm in height and 4 µm in diameter. The setae branch into hundreds of tiny endings, the so called spatulae. Thus the gecko is capable of achieving intimate contact with smooth and rough surfaces which leads to a strong adhesion due to intermolecular forces, in particular van der Waals forces.

Mimicking these micro- and nano-structures leads to artificial dry attachment systems. Here we introduce two methods, suitable for the cost-effective development and manufacturing of hierarchical gecko-type structures.

The technique of 3D laser lithography allows for the fabrication of arbitrary 3D nanostructures in suitable photoresists and is based on multiphoton polymerization. The center wavelength of the laser is chosen so that the photoresist is perfectly transparent, as the one-photon energy lies well below the absorption edge of the material. By tightly focusing the light of an ultrashort pulsed laser, the intensity is sufficiently high to expose the photoresist by multiphoton absorption within the focal volume. This absorption causes a chemical and/or physical change of the photoresist within a small volumetric pixel (a ‘voxel’) that can be scaled by the laser power. Using a developer bath, unexposed or exposed regions are removed, depending on the used photoresist [1].

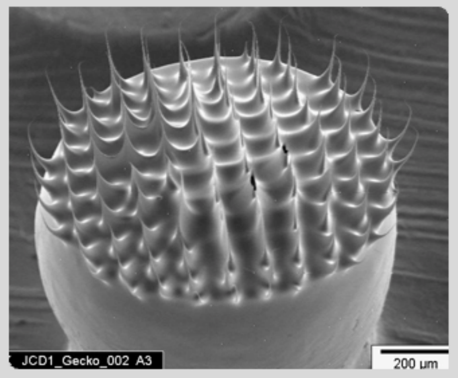

Figure 1-1: Hierarchical polycarbonate structures fabricated by hot embossing and hot pulling

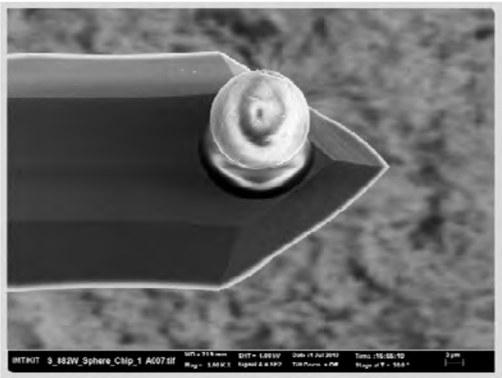

Figure 1-2: Cantilever with manually mounted silica sphere (Ø 10 µm)

Hot pulling is a recently introduced hot embossing process, enabling the fabrication of delicate polymer fibrils with highest aspect ratios and diameters in the nanometer range. The hot pulling process comprises the polymer’s softening via a heated mould insert. Once the cavities of the mould insert are completely filled with the softened polymer, the mould insert is pulled out of the polymer layer. Provided that the polymer’s rheological properties are in the correct range, the polymer inside the mould’s cavities is elongated and forms high aspect-ratio fibrils with tiny diameters. The combination of hot pulling and classical hot embossing [2] leads to hierarchical attachment devices.

The adhesion of the bio-mimicking polymer sheets is analysed via AFM by using spherical tips. Spherical tips are required because the radii of commercial available cantilever tips are smaller then the most tiny structure details and hence the advantage of hierarchy could not be detected.

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Development of a diamond-based scanning-probe magnetometer with single spin sensitivity

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The detection of weak magnetic fields at small length scales is a long-standing challenge in physics. We report on our work constructing a scanning-probe magnetometer capable to measure small magnetic fields and single spins with sub-nanometer spatial resolution.

This experiment employs a nitrogen-vacancy (NV) center in diamond as an ultrasensitive magnetic field sensor. Its spin state can be monitored using optically detected magnetic resonance [1]. Attaching a nanodiamond containing this “probe spin” to the tip of an atomic force microscope (AFM) working in ultra-high vacuum at low temperature allows studies of magnetic fields at the atomic scale [2,3]. The details of the experimental setup are presented along with experimental data characterizing the individual components.

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NC-AFM Studies of Oxide Surfaces, Defects and Adsorbates - Atomic Scale Structure and Electronic Properties

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Noncontact atomic force microscopy (NC-AFM) has been used to study the surface termination of an ultrathin alumina film on NiAl(110), its line defects and adsorption sites of single gold ad-atoms. Atomic resolution images of the unit cell confirm in great detail the corrugation of an earlier scanning tunneling microscopy based density functional theory model [1-3]. This favorable contrast mechanism between our metal probe and the oxide surface has been subsequently used to study the rich domain boundary network of the alumina film, i.e. antiphase-, translation- and reflection domain boundaries as well as their junctions. Details of their geometric surface structures obtained from atomic resolution images have been merged into a comprehensive picture. Kelvin probe measurements complement this by giving insight into electronic properties of the defects. Local band bending has been confirmed at the type I antiphase domain boundaries of the film. This corroborates transfer of individual charges from F^{2+}-like centers into the substrate [4,5].

In connection with the observed contrast, NC-AFM has been demonstrated to be capable of adsorption site determination for rather easily movable gold ad-atoms on this complex oxidic surface [6].

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Abstract for "2nd International Workshop on Advanced Atomic Force Microscopy Techniques 2011", Karlsruhe

Atomic Force Microscopy for Electrical Characterization of Silicon Quantum Dots for High-Efficiency Solar Cells

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Atomic force microscopy based techniques are applied to probe the electrical properties of ultrathin layers of Si quantum dots (QDs) embedded in a SiO_2. Such structures are considered as viable building blocks in future all-Si tandem solar cells with highest efficiencies, since they provide band gap tunability and thus adaptation to the solar spectra via utilization of quantum size effects.

QD preparation was done under ultrahigh vacuum conditions by self-organized growth from thermally deposited silicon-rich silicon oxide (SiO_x, $x < 2$) layers, which are thermodynamically unstable and therefore undergo phase separation upon appropriate *in situ* post-annealing. By controlling layer thickness and stoichiometry, QD density and size were adjusted, allowing for a tuning of the quantization energies and of the interlayer transport properties.

Local conductivities and surface potentials across individual QDs are detected in the current-sensing AFM (CS-AFM) regime and by Kelvin force microscopy (KFM), respectively. KFM images visualize dot-like structures due to material contrast and confirm QD formation. CS-AFM data prove the electrical conductivity of the QDs which increases with increasing annealing temperature and reaches its maximum when phase separation is completed. By X-ray photoelectron spectroscopy (XPS) a direct correlation to the electronic properties of the QDs is established. Moreover, photoelectrical measurements reveal a lateral photocurrent indicating a charge transfer from QD to QD via ultrathin SiO_2 barriers and hence imply photovoltaic applicability of such structures.

The role of the tip apex in non-contact atomic force microscopy imaging of the Si(100) surface: Probing the tip

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Scanning probe microscopy now regularly demonstrates atomically precise imaging and control on a wide range of surfaces [e.g. 1, 2]. Despite these advances, the tip apex, often a critical experimental unknown, plays a central role in defining both the qualitative and quantitative nature of the interaction [3, 4]. In this work we present data taken on the Si(100) surface at 5K using small amplitude qPlus NC-AFM which demonstrates that although we regularly acquire excellent 'conventional' images of the surface, we also see a wide range of different topologies that nonetheless demonstrate atomic resolution. Critically, we present measurements of the force and dissipation variation with tip height that provide an insight into the *quantitative* differences between tip apices and their interactions with the surface.

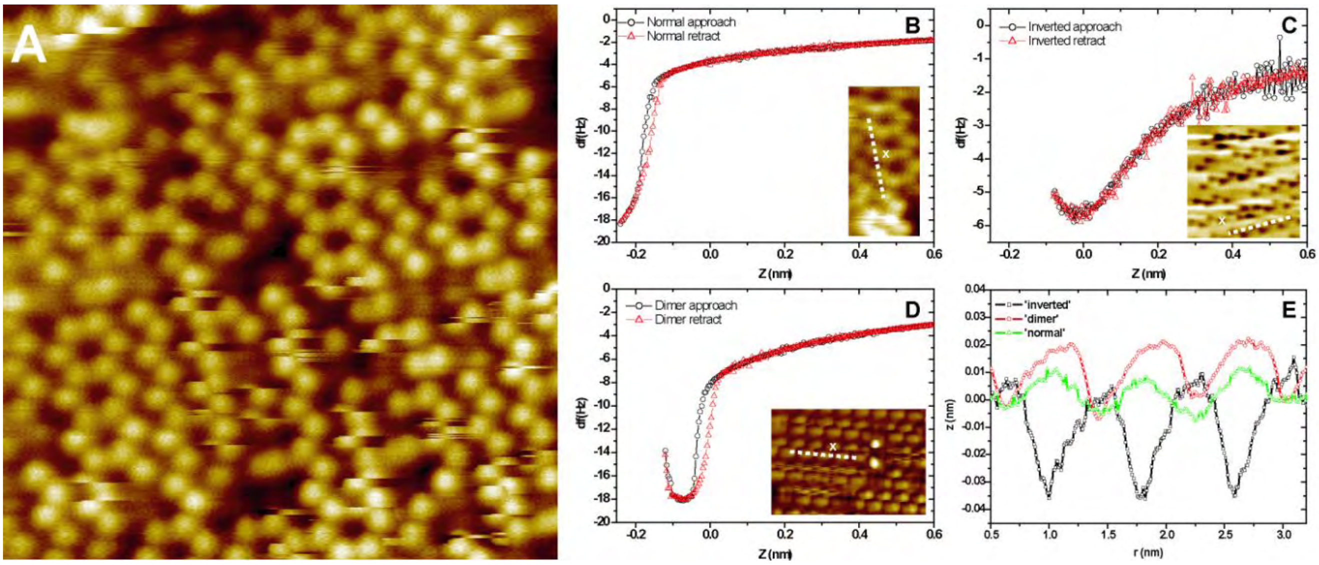

Figure 1: Imaging with different tip apices. **(A)** High quality qPlus NC-AFM image of the Si(100) surface at 5K showing 'conventional' imaging. A_0: 250 pm; Δf setpoint = -6.1 Hz **(B)** frequency shift (Δf)-vs-z spectrum acquired during 'conventional' imaging. A_0: 250 pm; Δf setpoint = -4.2Hz **(C)** Δf-vs-z spectrum acquired with a tip demonstrating 'inverted' imaging. A_0: 100 pm; Δf setpoint = -5.1Hz **(D)** Δf-vs-z spectrum acquired with a 'dimer terminated' tip [4]. A_0: 250 pm; Δf setpoint = -8.4 Hz **(E)** Topographic line profiles along dimer rows from images (**B – D**) showing differences in apparent corrugation. [**Insets:** Constant Δf images corresponding to each spectrum, a white cross indicates the location of each spectrum, and a dotted line indicates the location of the line profiles in **(E)**. All images acquired at 5K with zero applied bias.]

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DFT analysis of contrast modes obtained in combined 3D NC AFM and STM measurements of Cu(100)-O surface reactivity

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Investigation of novel catalytically active surfaces requires an understanding and quantification of interactions between nanoscale probes and different surface features. Additionally, a comprehensive experimental method is valuable for the identification and rapid characterisation of prospective catalytically active sites. The new method of three-dimensional atomic force miscroscopy (3D-AFM) in non-contact mode [1] has been combined with scanning tunnelling microscopy (STM) to characterise the oxygen-terminated copper (100) surface. This surface oxide layer features domain boundaries and a distinct structure of the Cu and O sublattices which is ideally suited for model investigations that consider the role and effectiveness of various surface defects such as vacancies, impurities, steps, kinks, and domain boundaries as active sites. Complex 3D data sets obtained by simultaneously recording the tunnelling current and the AFM frequency shift allow for site specific quantification of forces and tunnelling currents and additionally, different tips give rise to different chemical contrasts.

We combine DFT total-energy calculations with Non-equilibrium Green's Function (NEGF) methods for electronic transport to determine the tip-surface interaction and tunnelling current [2,3,4] for a large set of tip models in order to clarify the different contrast modes obtained in the experiments. At the outset, we obtained a stable Cu(100)($2\sqrt{2}$x$\sqrt{2}$)R45°-O surface reconstruction model. Surface features were found to be in good agreement with experimental data, and the analysis of surface electronic properties enabled us to identify prospective reactive sites. The effect of tip changes on contrast modes was explored by considering tips of different reactivity. Our simulations, in comparison with AFM experimental images, identified a contaminated tip with a Cu-terminated experimental configuration. Charge density and current calculations further helped to investigate the STM imaging mode and explain the lateral shift between surface features identified separately in AFM and STM images. The combination of conductance calculations with total energy methods provides insight into (1) the fundamentals of contrast formation in this novel experimental technique and (2) into the correlation between tip sample forces and local chemical reactivity, factors that are essential for the further development and application of this novel approach to characterise catalytic activity.

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What could atomic force microscopy tell us about solid-liquid interfaces: atomistic simulations.

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High-resolution imaging and force spectroscopy using AFM in solution opens wide areas of possible application as it allows real-time and real-space imaging of surfaces in solution [1]. To obtain full benefit, and provide a significant new analytical ability, it is vital to understand the underlying imaging mechanism(s) that can lead to high (possibly atomic or molecular) resolution. However, fully interpreting the experimental data presents significant challenges and both experiment and theory/simulation will be needed. Our simulations of solvated nanoparticles near surfaces show several possible mechanisms that lead to measurable force differences and image contrast over surface sites [2].

A solution environment presents challenges to simulation compared to vacuum. It becomes vital to include temperature into the calculations to understand the role of solvent movement, and to carry out long simulations where the solvent and the rest of the system come into equilibrium. We have conducted large scale molecular dynamics simulations using the GROMACS package [3] and use free-energy perturbation theory to calculate the free energies of nanoparticle-surface interaction.

We apply our methodology to fully solvated inorganic surfaces and particles {MgO (001), CaF_2 (111)} to calculate the forces experienced by nanoparticles nearing crystal surfaces. By contrasting our data to previous studies of similar systems in vacuum [4], we can show that significant differences between the vacuum and solvated systems exist. In particular, with “blunter” nanoparticles direct tip-surface interactions become relatively insignificant. However, water mediated interactions can cause significant force differences above different surface sites, and are in most cases larger, and longer ranged, than the direct vacuum-like interactions. We will also show that the dynamics of water confined between tip and surface can become orders of magnitude slower than in bulk solution. This slowing down could lead to hysteresis between tip approach and retraction curves, and may provide a channel for dissipation at small tip-surface distances.

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Magnetic Resonance Force Microscopy

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Magnetic Resonance Force Microscopy (MRFM) combines the nondestructiveness, subsurface sensitivity, and elemental specificity of Magnetic Resonance Imaging with the high spatial resolution of Atomic Force Microscopy. In MRFM, spins in the sample exert a force on a cantilever with a magnetic tip. The spins, in turn, feel a magnetic field gradient from the cantilever tip and can be manipulated by applying radiofrequency electromagnetic pulses. By monitoring the cantilever vibrations while varying the pulse frequency as well as scanning the sample, the density of spins can be mapped in three dimensions. In order to reduce the force noise it is essential to use ultrasoft cantilevers with a low intrinsic damping and to perform the measurement at cryogenic temperatures. We present an MRFM detection scheme in which the cantilever motion is detected by monitoring the flux change through a sensor coil in the proximity of the magnetic tip. This sensor coil is inductively coupled to a Superconducting Quantum Interference Device (SQUID), which is a low noise flux-to-voltage amplifier. With this setup, we have already been able observe the thermal motion of cantilever at an effective temperature of 25 mK, thus achieving a force noise of 0.5 aN/SqrtHz. We also present our first measurements of electron spins on the sensor coil chip surface. Future work includes implementing a 3-D coarse approach and scanning mechanism that will enable us to image spin densities.

Nano-scale magnetic resonance force microscopy without magnetic dissipation

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Cantilever thermal noise and dissipation set the sensitivity of magnetic resonance force microscopy (MRFM). In this letter we report a MRFM where magnetic dissipation in an ultrasensitive cantilever is eliminated by arranging the long axis of the cantilever normal to both the external magnetic field and the RF microwire source. By measurements of the statistical polarization of 1H in polystyrene, we demonstrated gradients greater than 10^6 T/m within 50 nm of the magnetic tip and rotating RF magnetic fields over 12 mT at 115 MHz. These parameters are crucial for applying nanometer-scale MRFM to nuclear species with low gyro-magnetic ratios and broadened resonances, such as In spins in quantum dots.

Analysis of untreated cross sections of $CuIn_{1-x}Ga_xSe_2$ thin-film solar cells applying Kelvin Probe Force Microscopy

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We present Kelvin probe force microscopy experiments on untreated cross sections of $CuIn_{1-x}Ga_xSe_2$ (CIGS) thin-film solar cells. With our experimental setup we can analyze the potential distribution of the CIGS/CdS/ZnO layer structure, which forms the pn-junction in the CIGS solar cells, with nanometer resolution. The potential differences between the CIGS absorber and the ZnO window layer in solar cells with different Ga-content (x=0, 0.32, 0.63 and 1) are systematically investigated and allow the analysis of the work function variation of the CIGS absorber. The result provides a direct evidence of the Fermi-level shifting in the CIGS absorber depending on the Ga-content.

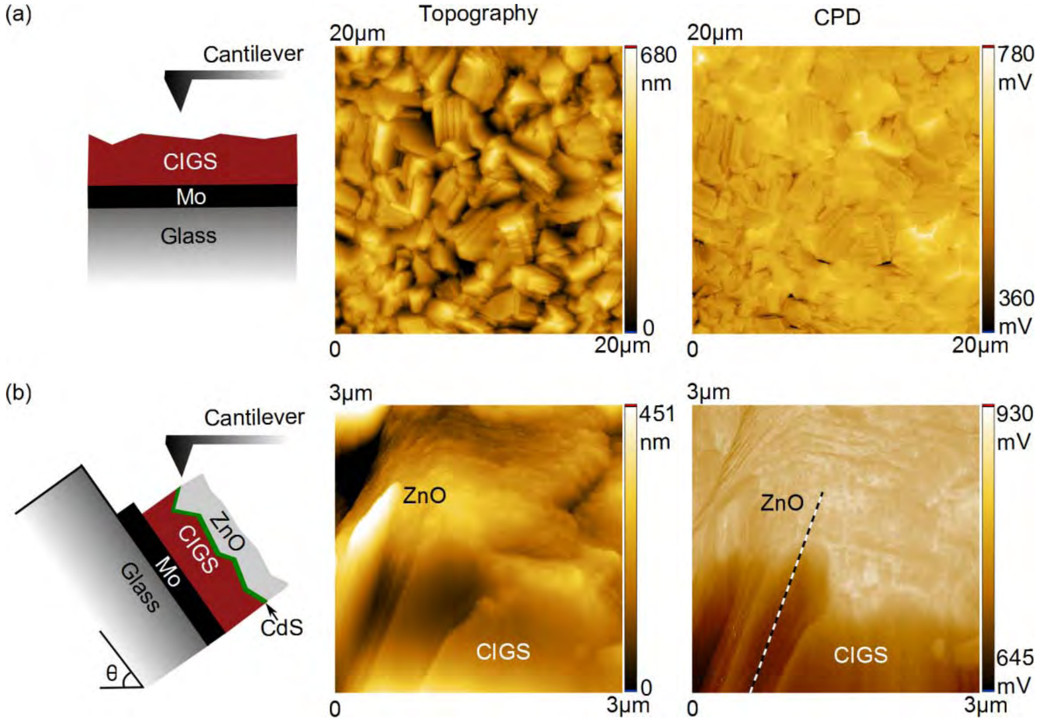

FIG 1: Columns from left to right are the sample alignments, the topography images and the contact potential difference (CPD) images of Kelvin probe force microscopy **(a)** on the surface of CIGS absorber and **(b)** on an untreated cross section of the solar cell. The dashed line in the CPD image in (b) indicates the pn-junction of the solar cell formed by the CIGS/CdS/ZnO layer structure.