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Friction on the Nanometer-Scale

Controlled Manipulation of Nano-Particles
by Means of a Homebuilt Scanning Force Microscope

The technique of Dynamic Surface Modification (DSM) by using a homebuilt Scanning Force Microscope (SFM) allows us to perform precise nano-manipulation experiments with adsorbed particles on surfaces and on the substrate itself. We have successfully patterned Polymethylmethacrylate (PMMA) films, Polystyrene (PS) films and manipulated miscellaneous nanoparticles on surfaces, e.g. antimony islands, gold islands, small latex spheres as well as cells. – By choosing appropriate values for the energy input into the sample surface, the presented technique allows to easily switch between the different SFM modes: imaging, »writing« on a substrate, translation or in-plane rotation of nanoparticles, marking single nanoparticles, cutting and splitting of nanoparticles and »healing« of these fragments. A direct comparison of the corresponding energy values gives evidence about motion and tribological properties of the adsorbate-substrate system. These experiments give the possibility to obtain insight into basic phenomena of motion and friction. Due to this flexibility, this manipulation technique was found to be suitable to study adhesion, cohesion, and friction of nanoparticles adsorbed on surfaces.

Tribology, the science and technology of two interacting surfaces in relative motion and of related subjects and practices, is one of the oldest research fields of natural science (the word tribology is derived from the Greek word *tribos*, meaning rubbing) [1]. These studies are needed to develop fundamental understanding of interfacial phenomena on a small scale and to study interfacial phenomena in micro- and nano-structures used in magnetic storage systems, microelectromechanical systems (MEMS) and other industrial applications. Besides direct applications, there is also a basic research interest, to understand the fundamental nature of the processes responsible for energy dissipation in friction and the modification of the rubbing interfaces by wear at the nanometer scale [2].

Struktur und Untersuchungen von Clustern

Die Arbeitsgruppe um Prof. Dr. Klaus Rademann entwickelt spektroskopische Methoden für die genaue Charakterisierung sowohl von Nanopartikeln auf Oberflächen als auch von Clustern in der Gasphase. In Zusammenarbeit mit Prof. Dr. Ludger Wöste und Dr. Knut Asmis (im Rahmen des DFG-Sonderforschungsbereiches 546: »Struktur, Dynamik und Reaktivität von Übergangsmetalloxid-Aggregaten«) wurden erstmals Infrarotspektren katalytisch relevanter Vanadiumoxidclusterkationen gemessen. Weiterhin werden Materialsysteme, wie Oxide und Halbleiter, präpariert und hinsichtlich ihrer Lumineszenzeigenschaften getestet.

Im DFG-Projekt »Nanopartikel« werden Reibungskräfte zwischen einer Oberfläche und adsorbierten Nanopartikeln quantitativ mit Hilfe eines selbst gebauten, lithographiefähigen Kraftmikroskops studiert. Dieses Projekt wird im folgenden Artikel näher vorgestellt.

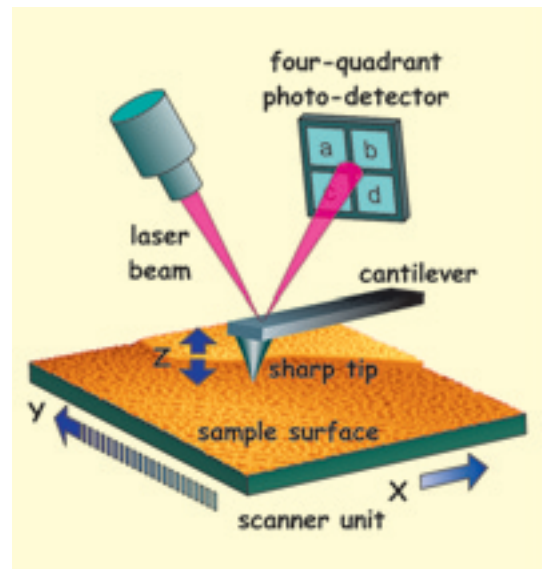


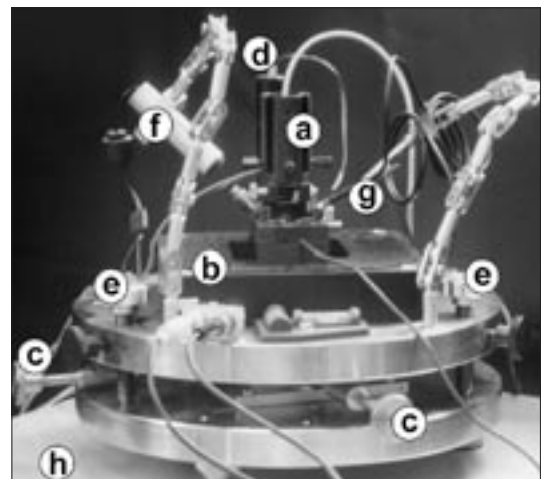
Fig. 1
Schematic drawing of a Scanning Force Microscope.

For centuries the knowledge about the friction forces between two sliding bodies were described by the phenomenological laws of friction by Amontons (I and II) and Coulomb (III):

- I) frictional forces are proportional to the loading (normal) force (The constant of proportionality, i.e. the friction coefficient, is typical for the specific combination of sliding materials.);
- II) and independent of the (apparent) area of contact between the sliding bodies;
- III) the sliding friction is independent of the sliding velocity.

These laws apply to the macroscopic scale relatively good. But there is still no theory to derive them from (microscopic) basic principles. Furthermore there is

Fig. 2
Photograph of the homebuilt SFM, the main parts are:
a – SFM head (with laser beam, cantilever, detector and sample inside),
b – scanner unit,
c – translator,
d – micrometer screw,
e – adjusting screws,
f – video camera,
g – light source,
h – vibration isolation.



no theory to predict the friction coefficient of two materials. Thus tribology was the field for engineers, because only testing of various material combinations could yield new information.

This changed dramatically with the invention of the scanning force microscope [3] and its subsequent development into a standard surface science tool, which made the field of nanotribology accessible to researchers. A schematic drawing of the SFM is illustrated in figure 1. The SFM probes the surface of a sample with a sharp tip, a couple of microns long and 10–100 nm in diameter. The tip is located at the free end of a cantilever that is 100 to 200 μm long. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. The cantilever deflection is measured as the sample is scanned (x-y direction) under the tip. This is now most commonly achieved with an optical detection scheme: A laser beam is focused onto the back of the lever and reflected onto a four-quadrant photo-detector. The difference signal between the top and bottom segments contains the topographic information, while the »left« and »right« segments allow the simultaneous recording of lateral forces twisting the tip sideways during scanning. The measured cantilever deflections allow a computer to generate a map of surface topography. SFMs can be used to study insulators and semiconductors as well as electrical conductors. They can be operated anywhere from ultra high vacuum (UHV) to ambient pressures and above, in various atmospheres, even in liquids. Through SFM measurements under perfectly clean conditions in UHV frictional properties of single asperity contacts are accessible and have already led to genuine new insights of friction at the atomic scale: At the atomic scale friction does indeed depend on the (real) contact area [4], and on the sliding velocity [5].

Normally an SFM is used to image a surface without damaging it in any way. However, the use of an SFM for surface modifications by applying an excessive force enables a large variety of new lithographic or manipulation experiments on the nanometer scale. To investigate such phenomena at the nanometer-scale distinctive experimental techniques are necessary. For example, the sample surface can be directly patterned by the tip of an SFM by scratching the surface with the small tip [6]. Alternatively, the surface can also be modified by indenting it with a vibrating tip in the dynamic mode of the SFM [7, 8]. With the same experimental set-up small particles may be manipulated on the surface of a suitable substrate [9]. In this way, nanoparticles can be translated and in-plane rotated to form two-dimensional patterns from randomly



Fig. 3

Example for the manipulation of the substrate (PMMA) by means of the DSM technique. Logo of the Humboldt-Universität zu Berlin. a) (above) overview: scan range: $3 \times 3 \mu\text{m}$, height: 5,7 nm, b) (below) detail screen: scan range: $700 \times 700 \text{ nm}$, height: 5,5 nm.

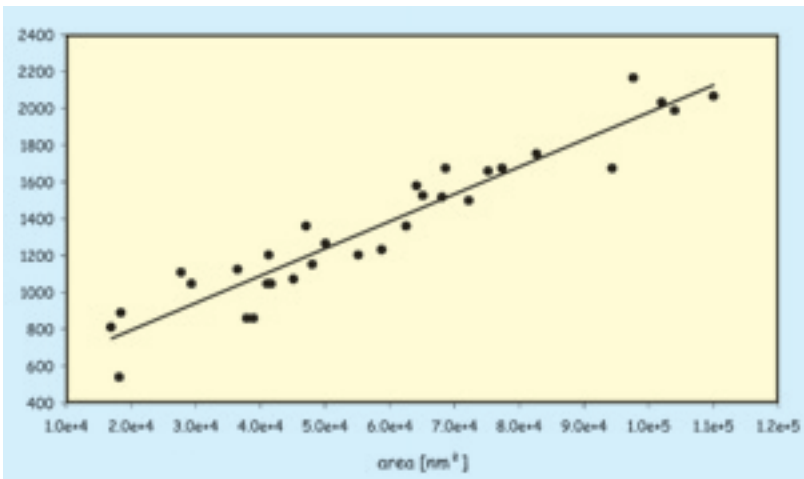
arranged arrays of deposited particles on a given substrate.

We utilise an advanced homebuilt SFM (see figure 2) in the dynamic mode, in conjunction with a special homebuilt software, for surface modifications and nanoparticle manipulation. A more detailed description can be found in reference [8]. The corresponding experimental technique should be denoted as Dynamic Surface Modification (DSM) in the following, comprising both the dynamic technique of the SFM where a local plastic deformation of the sample is induced, as



Fig. 4
 Foreground: Written poem in PMMA by the DSM technique (Hermann Hesse, *Stages*, from *The Glass Bead Game*), scan range $1.6 \times 1.6 \mu\text{m}^2$, height 26 nm. Background: SFM image of a compact disk, scan range $2.53 \times 1.95 \mu\text{m}^2$, height 243 nm. Foreground and background have the same scale. The storage capacity which can be achieved by the DSM technique is remarkably high. The dimensions of one letter are about $50 \times 100 \text{ nm}^2$.

well as the manipulation of structurally unchanged particles on a given substrate surface. As an additional benefit, a controlled sliding and dislocation of nanoparticles gives certain access to their frictional and adhesional properties that may contribute to a better understanding of the fundamental processes of friction.



Compared to the so-called contact mode, operation of an SFM in the dynamic mode (i.e., with an oscillating cantilever) allows the study of a wide range of samples, in particular of more sensitive sample surfaces and weakly adhering particles without damaging the structures or »cleaning up« the scanned area. Usually, surface modifications by means of a conventional SFM driven in dynamic mode are realised by switching off the feedback loop [10]. In this case, however, non-uniform results might occur due to sample tilt and surface roughness. To avoid such effects, we have successfully induced surface modifications by increasing the amplitude of the dither piezo that drives the cantilever oscillations, while the feedback loop has been continuously working [8, 11]. This gives us the possibility to perform very precise and controlled manipulation experiments independent of the size of the modified surface area or the specific sample corrugations.

The figures 3 and 4 illustrate examples for the application of the DSM technique to modify the substrate surface (12). The logo of the Humboldt-Universität zu Berlin and a poem (by Hermann Hesse) have been »written« with the small SFM tip in a PMMA substrate. The »storage capacity« which can be achieved by the DSM technique is remarkably high. With this technique we achieve a minimum line width of about 20 nm and a minimum line depth of about 1 nm. As an example, the amount of space needed to write one letter in a book is about 500.000.000 times higher than the space needed by means of the DSM technique.

To demonstrate the ability to design a specific pattern from randomly arranged nanoparticles using the DSM manipulation procedure, the letters »H« and »U« were formed from virtual disorder. The figures 5 (a) to (d) reflect different stages of the formation process. To study friction phenomena on the nanometer scale the controlled translation of antimony islands on graphite has been carried out by means of the DSM technique. Manipulation experiments with different amplitudes of the cantilever oscillation to translate antimony islands of different contact areas give information about a threshold amplitude, below which certain islands can not be moved. The results can be discussed in terms of the energy dissipation of a harmonic oscillator. The

Fig. 6
 Plot of the threshold value of the cantilever oscillation amplitude needed to translate an antimony island on the graphite substrate as a function of the contact area. The analysis of the experiment gives evidence that the threshold amplitude of the cantilever oscillation depends directly on the dimensions of the island. The solid line represents a linear regression for the experimental data.

threshold amplitude needed for a lateral movement can be correlated with the dissipated energy of the cantilever. The more energy the cantilever dissipates the more energy for the lateral movement should be generated. Consequently, when the dissipated energy exceeds the friction force, the particle is displaced. A manipulation experiment on up to 30 antimony islands on graphite gives evidence that the amplitude of the cantilever oscillation, needed to displace an antimony island, depends directly on the dimensions of the island (see figure 6). Another important factor that determines the threshold amplitude is the position on the graphite substrate. Antimony islands, grown on steps of the graphite surface, require a 2.5 fold factor higher amplitude than an antimony island grown on a flat area with the same dimensions. This demonstrates clearly that the steps on a graphite surface cause a higher adhesion of the antimony islands than a flat area of the graphite. Similar experiments, i.e. translation of nanometer-sized latex spheres on a graphite substrate [13] confirm that the DSM technique enables us to study adsorbate-substrate properties regarding friction, adhesion and cohesion.

Summary/conclusion

To summarise, the main advantages of the DSM technique are:

- a controlled manipulation of structurally unchanged nanometer-sized particles as well as local plastic deformations of the substrate surface can be performed reproducibly with high precision;
- the dynamic mode permits investigation of a wide range of samples, as well as of sensitive surfaces and weakly adhering particles;
- in contrast to earlier reports of surface modifications applying a similar technique, both imaging mode and manipulation mode were operated with active feedback loop to ensure uniform results of the modification steps independent of sample tilt or surface corrugation;
- the result of a manipulation experiment depends only on the effective amplitude of the oscillating cantilever and the adsorbate-substrate systems adhesion and cohesion properties;
- by choosing appropriate values for the amplitude of the cantilever oscillations, easy switching between imaging, »writing« on surfaces, translation or in-plane rotation of nanoparticles, marking single nanoparticles, cutting and »healing« of nanoparticles is possible;
- the threshold amplitude of the cantilever oscillations needed to translate a single particle can be used to calculate the force needed to overcome the static friction.

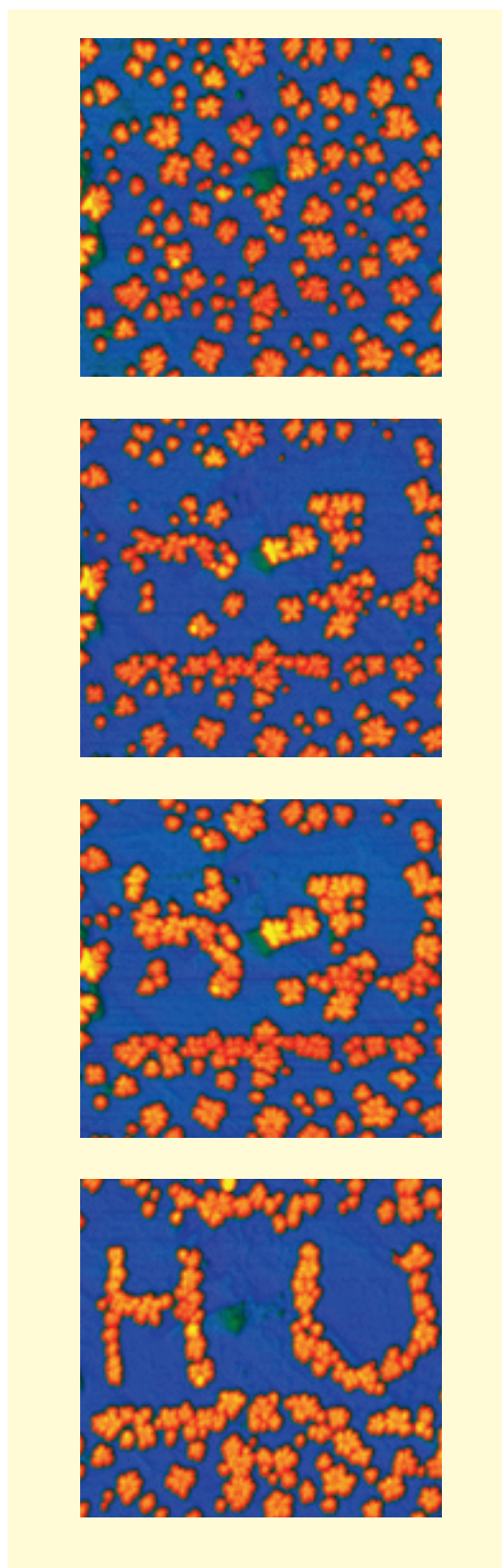


Fig. 5
Formation of the letters »H« and »U« as an example for a purposely designed two-dimensional nanostructure using the DSM technique. The figures a to d illustrate different steps of the assembly process, antimony islands on graphite, scan range $5 \times 5 \mu\text{m}^2$, height: 30 nm.



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Due to this flexibility, the manipulation technique was found to be suitable to study adhesion, cohesion, and friction of nanoparticles adsorbed on surfaces.

Co-operation partners

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