Spherical AFM Probes for Adhesion Force Measurements on Metal Single Crystals

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Many technological processes demand for a detailed understanding of tribology at the nanoscale. Particularly, measurements of interfacial forces are of critical importance in the characterization of materials surfaces. The atomic force microscope (AFM) is a versatile tool for studying nanotribological properties, such as friction and adhesion forces. However, essential prerequisites to obtain reliable quantitative results from such force measurements are defined contact geometries, precise calibration of the cantilever spring constant and a controlled chemical environment. Here we introduce a simple and straightforward approach were adhesion forces are assessed directly by measuring the force interaction during approach and retraction of cantilever with a spherical probe tip from the sample surface (force distance curves). In order to reduce or even eliminate environmental influence and uncertainties due to unknown tip or sample properties, all measurements as well as AFM probe characterization and calibration are performed under ultrahigh vacuum (UHV) conditions. Using a spherical probe rather than a sharp tip allows customizing probe diameter and material. Furthermore it provides a defined contact geometry and enables quantitative comparisons with predictions from continuum scale adhesion models. The spherical probes were characterized *in situ* by reverse tip imaging. By this method, probes can also be readily re-examined to check for shape deformation or material take-up possibly occurred during curve acquisition. For non-destructive *in situ* force calibration the reference cantilever method was adopted, as it was found to deliver most reliable results. It is demonstrated that this approach enables the quantification of adhesion forces on single crystal metal surfaces and the comparison with predictions from theoretical models. Experimental aspects dealing with the preparation and characterization of suitable AFM probes are presented and complemented by results which reveal how various factors such as surface cleanliness, external load, spherical probe diameter as well as surface topography.

Keywords atomic force microscopy; force distance curves; adhesion force; ultrahigh vacuum; silver; copper; antimony

1. Introduction

The current understanding of friction is mainly phenomenological and sufficient only for the explanation of basic processes. From macroscopic data it is known that friction forces are proportional only to applied loads and do not dependent on the apparent contact area. Contrary, at the nanoscale, the friction force is clearly proportional to the contact area, i.e., the number of small asperities which make the physical contact. Detailed understanding of tribology at the nanoscopic level is required by many technological processes. For example, assembly of components and devices might depend critically on the adhesion of the materials at the nanometer scale. As the advancing miniaturization of machines and devices lead to increased surface-to-volume ratios, interfacial forces such as friction and adhesion might dominate the overall mechanical properties of the system. As a consequence, measurements of these forces are of critical importance in the characterization of materials surfaces and nanotribology emerges as a crucial field of research [1].

Today, AFM (atomic force microscopy/microscope) is a well established technique for nanotribological studies. The major advantage of the AFM is that it can be routinely used on all type of materials (such as metals, semiconductors, ceramics, minerals, polymers, and biomaterials) and in a

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variety of environments (ambient air, controlled atmosphere, liquids or under vacuum conditions). In AFM a nanoscale single asperity contact between a probing tip and rather smooth sample surface enables both imaging of the surface down to atomic resolution and the precise and accurate measurement of interfacial forces and displacements. Thus, the AFM is not only an excellent method for characterization of surface topographies but also for quantitative determination of adhesion forces at these surfaces. The focus of this contribution is on the application of the AFM technique to the determination of adhesion forces of metal surfaces. Special attention is put on a well-defined contact geometry and a controlled chemical environment.

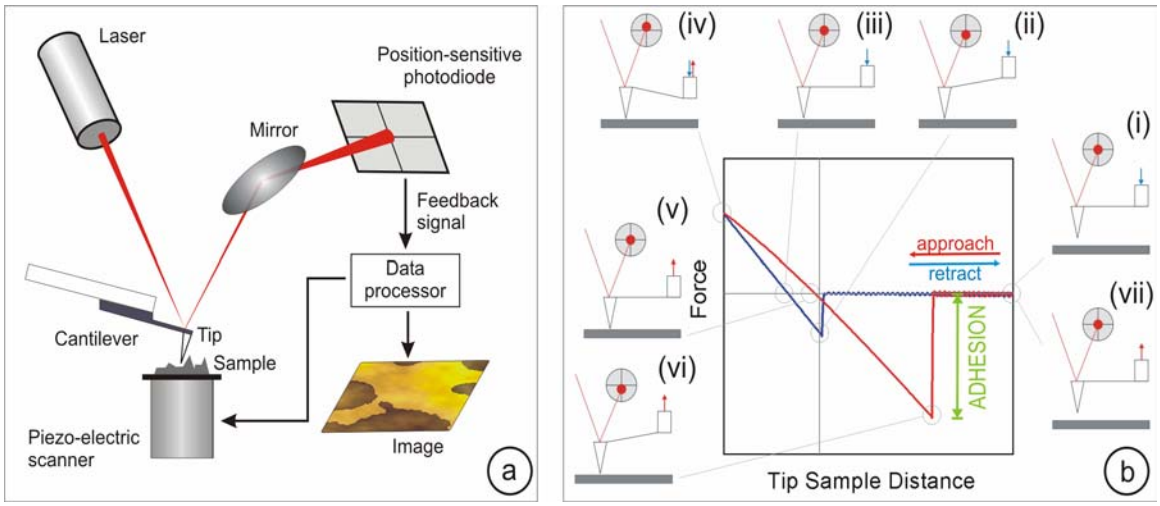

Fig. 1 a) Principle setup of the AFM for the optical beam deflection method. The cantilever deflection is detected by measuring the displacement of the laser beam with a position-sensitive photodiode while the sample is scanned in the *xy* plane. b) AFM force distance measurement. The curve plots the deflection of the force-sensing cantilever during tip approach and retraction. The labelled points show schematically the cantilever-sample interaction at several stages. The adhesion force corresponds in first approximation to the pull-off force between tip and sample.

2. Experimental Aspects

2.1 Force distance curves by atomic force microscopy

The principle of the AFM is demonstrated in Fig. 1a. Typically, an AFM consists of the following essential components:

- a cantilever with a sharp tip,
- a method to sense the cantilever deflection, e.g., a four-segment photodiode which detects the displacement of a laser beam which is reflected from the back of the cantilever,
- a feedback system which controls the vertical *z* position of the tip on the sample and keeps the cantilever deflection constant,
- a piezo-electric scanning system which moves the tip relative to the sample in *x/y* and *z* direction,
- a computer for data processing and visualization.

Forces acting between tip and sample deflect the cantilever. The sample topography can be measured when the tip is moved laterally. Adhesion forces can be measured by detecting the force interaction during approach and retraction of the tip from the sample surface. The general features of such so-called force distance curves can be summarized as follows (see Fig. 1b): The cantilever is initially far away from the sample in equilibrium position and no force is detected (i). Upon approaching the sample the cantilever jumps into contact when reaching the close proximity of the sample surface (ii). Further pushing the probe to the sample causes the cantilever to bend away (iii). In this so-called constant

compliance region the cantilever deflection corresponds to the extension of the piezo-electric scanner, as long as no sample deformation occurs (iv). During retraction the tip adheres to the sample (v) until the spring constant of the cantilever overcomes the adhesion force (vi) and the cantilever instantaneously jumps out of contact back into its equilibrium position (vii). The force necessary to pull-off the cantilever is essentially a measure for the adhesion force.

2.2 Force calibration

Reliable quantitative results on adhesion forces from the measurement of the AFM cantilever deflection require a accurate calibration of the spring constant. Unfortunately, this is a rather complicated task and no standard method has emerged yet. There are a number of methods to estimate the spring constant of a cantilever. The methods commonly used include the added mass method [2], the thermal noise method [3], theoretical methods relying on knowledge of the cantilever geometry and material properties [4,5] and the reference cantilever method [6,7]. All of these methods have their drawbacks. However, for our investigation the reference cantilever method was found to be the method of choice as it is a non-destructive *in situ* method which allows the direct measurement of the cantilever force constant under UHV conditions. This method utilizes the deflection experienced by a cantilever of unknown force constant k_{test} when it is pressed against a cantilever with precisely known spring constant k_{ref} and elastic properties (see Fig. 2a). From the deflections at the fixed end δ_{tot} and at the free end δ_{test} of the reference cantilever, respectively, k_{test} can be determined according to:

$$k_{test} = k_{ref} \frac{\delta_{tot} - \delta_{test}}{\delta_{test} \cdot \cos \vartheta}, \tag{1}$$

where ϑ is the angle between both cantilevers. In order to hit the reference cantilever really at the free end a sequence of deflections should be measured along the reference cantilever. The graph in Fig. 2b shows how the deflection of the cantilever under test decreases when it approaches the free end of the reference cantilever. In this way, reliability and accuracy of the spring constant determination is improved.

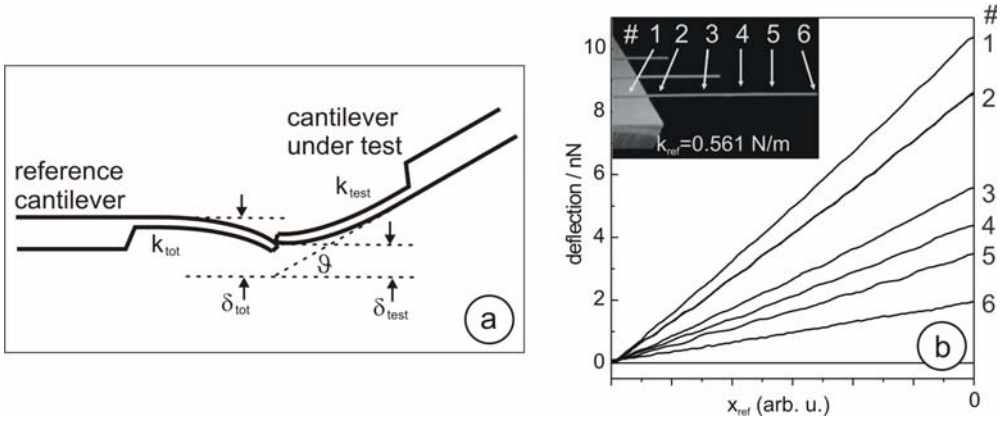

Fig. 2 a) Spring constant calibration with the reference cantilever method [7]. b) Relative deflection of the cantilever under test when approaching the free end of the reference cantilever (i.e., $x_{ref} = 0$). The insert shows a scanning electron microscopy (SEM) image of the reference cantilever. In this example, a spring constant of k_{test} = 0.116 N/m for the cantilever under test is determined according to Eq. (1) from the deflection at the fixed end (#1) and at the free end (#6).

2.3 Spherical AFM probe tips

To compare experimental results on adhesion forces with theoretical predictions several models have been developed in the past [1]. The models frequently used consider the interaction of an ideal sphere of radius R with an atomically flat surface, such as in the Derjaguin-Muller-Toporov (DMT) model [8] or the Johnson-Kendall-Roberts (JKR) model [9]. These two models improved the classical Hertz contact model by including the effect of adhesion forces. It turned out that both models present the limiting cases of more general contact theories by Maugis [10]. They differ in the prediction of the force F needed to pull-off the spherical particle. What both models have in common is that the force for pulling off the sphere from the surface is independent of the elastic material properties but is essentially a linear function of two parameters – the radius R of the sphere and the surface energy γ:

$$F \propto \gamma \times R. \tag{2}$$

Tips commonly used in AFM experiments deviate strongly from the assumed sphere/flat surface geometry as they are made as sharp as possible to achieve high lateral resolution. Accordingly, for our study the so-called colloid probe or spherical probe AFM technique was adapted, which employs a microsphere as AFM probe tip [11-13]. Besides easy comparison with theoretical models, this approach provides an improved definition of the interaction geometry and chemistry and allows the utilization of a wide range of probe sizes and materials.
For the preparation of such spherical tips microspheres of desired size and material were glued at the end of tipless AFM cantilevers using *xyz* micromanipulators and an optical microscope. To check that the microspheres were successfully attached onto the cantilevers, the probes were examined by scanning electron microscopy (SEM). Some representative SEM images of the results are given in Fig. 3.

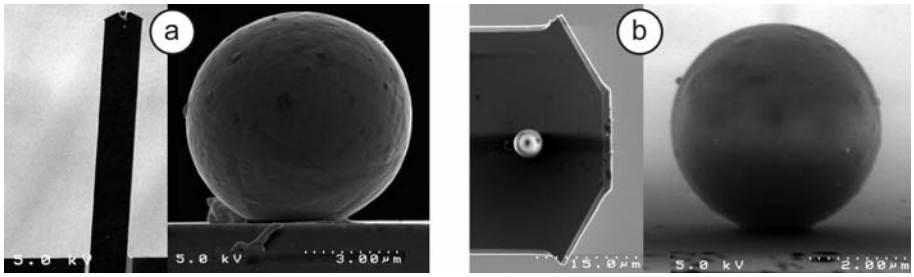

Fig. 3 SEM images of spherical AFM probes as used in the experiments: a) titanium sphere (Ø 7.4 µm) and b) silica sphere (Ø 4.4 µm) glued to single beam Si cantilevers.

The most convenient method of obtaining the effective radius of these probes is reverse AFM imaging [14]. The effect of reverse imaging is often encountered if the features on the surface are much smaller than the tip. In this case, the image reflects the shape of the tip rather than the geometry of the surface, due to the convolution of tip and sample. Though this phenomenon is normally considered as an artefact, it can be utilized for determination of the diameter of the sphere and the condition of the sphere surface from the reverse images. For this purpose a commercial calibration grating (TGT01 from NT-MDT Inc.) consisting of an array of sharp spikes with a diagonal spacing of 3.0 µm (cf. upper left inset in Fig. 4a) was employed. Scanning this grating with a spherical AFM probe creates an image consisting of an array of spherical caps, i.e., the microsphere itself is imaged repeatedly by each spike in the scanning area, as shown in Fig. 4a. This image provides three-dimensional visualizations of the microsphere confirming that the particle is rather smooth and spherical. The sphere diameter d is calculated simply from the cross-sectional data, i.e., from width and height of the microsphere images, as demonstrated in Fig. 4b.
Advantages of the method of reverse tip imaging are that it not only provides the shape and dimensions of the microsphere but also allows easy in situ re-examination to reveal shape deformation or material take-up possibly occurred during the experiment. Moreover, it does not require a conductive coating as for SEM imaging, though accuracy is comparable to size determination from SEM images.

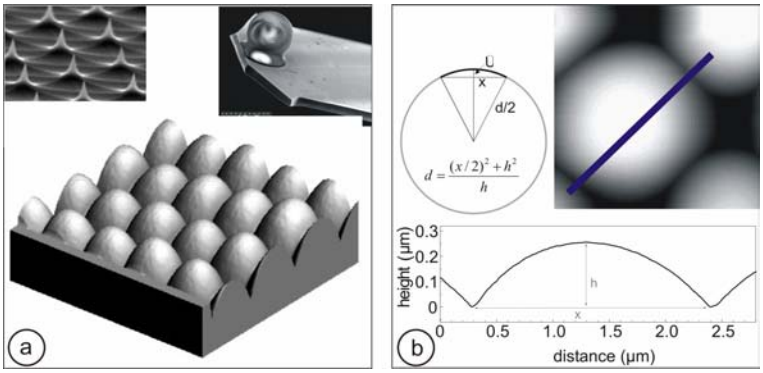

Fig. 4 Reverse tip imaging for characterization of the microspherical tip. a) Scanning the grating consisting of an array of sharp spikes (upper left SEM image) with a silica microsphere attached to an AFM cantilever (upper right SEM image) results in an image of an array of spherical caps. b) The sphere diameter is calculated from height and width of the imaged caps, as determined from cross-sectional analysis. The microsphere tested here has a diameter of 4.65 µm.

3. Adhesion Force Measurements

3.1 Adhesion force and surface cleanliness

The presence of adsorbates or oxide layers may considerably alter the adhesive behaviour of the surfaces. It is thus essential when measuring adhesion forces that the surface is chemically clean, i.e. free from contaminants and impurities, and that it has a reproducible and well-characterized surface structure. For that purpose all experiments were done within an ultrahigh vacuum apparatus (base pressure < 6×10^{-11} mbar), which provides a controlled chemical environment and enables the application of surface science techniques. Atomically clean surfaces of metal single crystals were obtained by repeated cycles of argon ion sputtering and subsequent annealing. After each cleaning cycle the samples were investigated by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) to verify the chemical and structural state of the surface, respectively. In Fig. 5a Auger electron spectra for a Cu(100) single crystal surface before and after the surface treatment are shown. Initially, the copper crystals showed considerable contamination and damage. The Auger electron spectra (cf. thin grey lines in Fig. 5a) indicate the presence of mainly carbon (KLL transition at ~271 eV). At this state it was not possible to obtain even diffuse LEED spots. The cleaning cycles were repeated until the characteristic Auger electron spectrum and a sharp LEED pattern were visible. After this treatment the intensity of the characteristic Cu transitions clearly evolved, whereas the intensity of the carbon transition vanished (cf. solid black lines in Fig. 5a). As indicated in the inset the characteristic Cu LMM AES transitions occur between 700 and 950 eV. Copper has an *fcc* crystal structure, the position of the (100) plane is indicated in Fig. 5b. Figure 5c is a LEED pattern after cleaning showing the crystalline reflexes of Cu(100).
The influence of cleaning on the adhesion force measurement is demonstrated in Fig. 5d. This graph shows force distance curves for single measurements with a silica microsphere on Cu(100) before and after the cleaning procedure. A remarkable difference in the pull-off force is evident, i.e., the adhesion force increases from about 120 nN for the contaminated surface to 250 nN for the clean surface. Accordingly, it is concluded that the adhesion force is extremely sensitive to the condition of the surface and might be considerably reduced by the presence of even marginal amounts of surface contamination.

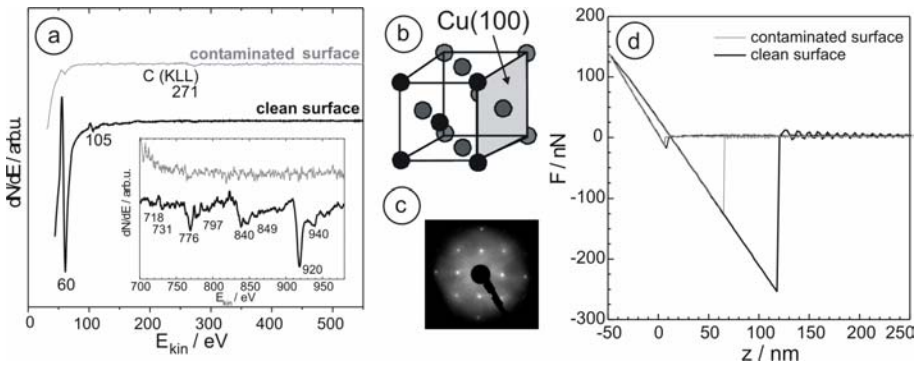

Fig. 5 a) Auger electron spectra of a single crystalline Cu(100) surface before and after surface cleaning. Primary beam energy: 3.0 keV. The inset captures the energy range of the characteristic LMM transitions. b) Crystal structure of copper. The (100) plane is shaded. c) LEED pattern of the cleaned (100) surface. d) Typical force distance curves obtained for single measurements with a spherical silica tip on the contaminated (thin grey line) and the clean (solid black line) Cu(100) surface, respectively.

3.2 Adhesion force and externally applied load

Obtaining accurate values of adhesion forces from force distance measurements by AFM requires a purely elastic contact between tip and surface. Otherwise, the simple relation between adhesion force, surface energy and sphere radius given in Eq. (2) is no longer valid. Irreversible changes like plastic deformations or material transfer between tip and surface are expected to depend on the load. To establish the absence of loading effects the adhesion forces were measured as a function of the externally applied load. As an example, results obtained with a silica sphere on a Ag(100) single crystal surface are shown in Fig. 6b. Silica particles are rigid, have a smooth surface and show normally an elastic response. In this respect they present an optimal model system for the verification of the elastic contact.
The results show, that there is no significant change in the adhesion force of about 90 nN for loads up to 200 nN. Further increase of the load up to 350 nN leads to a rise of the adhesion force. According to the model of Maugis and Pollock this effect can be attributed to the onset of plastic deformations [15]. Thus, it is concluded, that adhesion force does not depend significantly on the load as long as the load is less than the adhesion force, as it was confirmed on the surfaces of further metal single crystals as well. Consequently, adhesion force measurements were typically carried out in the low load regime, where the adhesion force does not depend on the externally applied load and plastic deformations are of minor influence.

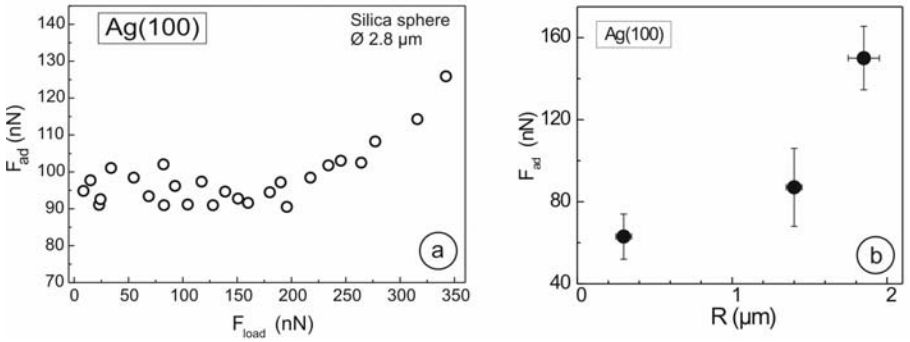

Fig. 6 a) Adhesion forces vs. applied external load measured between a silica sphere (Ø 2.8 µm) and the clean Ag(100) surface. b) Adhesion forces between Ag(100) and silica microspheres of different size.

3.3 Adhesion force and probe size

To investigate the proposed dependence of the adhesion force on the sphere radius, cantilevers with silica spheres of different size were prepared. Adhesion forces were determined from force distance measurements with these silica spheres on the same, clean Ag(100) surface. As shown in Fig. 6b, the adhesion force gets indeed larger as the sphere radius increases. This behaviour is in qualitative agreement with the models of contact mechanics. However, based on these three data points a precise verification of the linear relationship between adhesion force and sphere radius is not yet possible. Possible deviations from a linear behaviour can be explained in terms of surface roughness [13,16], which certainly varies among different microspheres.

3.4 Adhesion force and topography

Topography is of importance for the study of adhesion forces since all realistic surfaces exhibit normally some degree of roughness. Surface roughness is expected to decrease the actual area of contact, hence the measured adhesion force is lower than expected from Eq. (2) [17,18]. Layered crystals are interesting samples with respect to the measurement of adhesion forces, because they are composed of layers held together only by weak van der Waals forces. This means, that they can be cleaved easily and provide atomically flat substrates, which present ideal model systems for the study of a sphere/flat surface contact.

The most popular layered materials being applied in tribology include graphite and MoS_2, but also the structurally related group V semimetal antimony is composed of layers as well. In Fig. 7a the morphology of the (0001) cleavage plane of a Sb single crystal is characterized by AFM. This AFM image reveals two pronounced topographical features: (i) atomically flat terraces with lateral extensions of up to 10 μm, (ii) straight cleavage steps of different heights (ranging typically from a few angstroms up to a few hundreds of nanometers), which separate these terraces. In Fig. 7b an atomically resolved scanning tunnelling microscopy (STM) image of such a smooth terrace of the Sb(0001) cleavage plane is shown, which exhibits the well-ordered hexagonal arrangement of surface atoms [19].

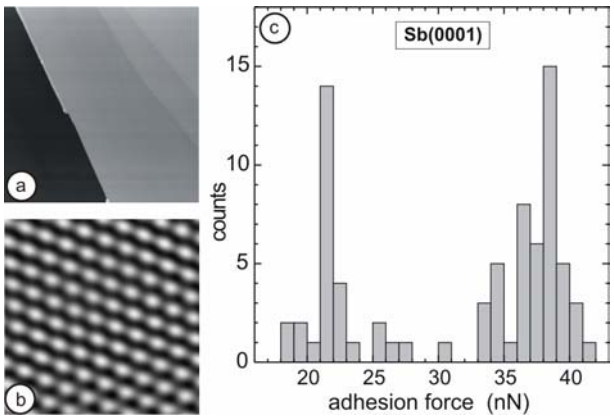

Fig. 7 a) AFM topograph (10 × 10 μm^2, height range 85 nm) exhibiting the overall morphology of the Sb(0001) cleavage plane. The heights of the three apparent steps are 47.0 nm, 4.4 nm, and 2.9 nm (from left to right). b) STM topograph (3.9 × 3.9 nm^2) resolving the hexagonal lattice structure of the Sb(0001) surface [20]. c) Distribution of adhesion forces measured with a silica sphere (Ø 5 μm) at arbitrary positions on Sb(0001).

It turned out that these two encountered cleavage plane features have a distinct influence on the adhesion force measurements. This is demonstrated in Fig. 7c, which shows the histogram of the pull-off forces acquired with a silica sphere at different positions on the (0001) cleavage plane of the Sb single crystal. Apparently, a bimodal distribution of adhesion forces is obtained. These two levels of adhesion forces can be explained in terms of topographic effects. When contacted with a silica sphere, the flat terraces and the step edges (cf. Fig. 7a) provide different actual areas of contact and yield, consequently, different adhesion forces. In this case, the reduced contact area at the step edges might account for the lower value, whereas the measurement at a flat area might yield a higher adhesion force.

4. Conclusions

Atomic force microscopy is an excellent force measurement technique for probing surface interactions. It was demonstrated, that the AFM in the spherical probe configuration, i.e. using cantilevers modified by attached microspheres, allows the quantification of adhesion forces on single crystal metal surfaces and the comparison with predictions from theoretical models. For this purpose particular emphasis was put on reliable and convenient in situ force calibration and in situ probe characterization.
Several factors having an impact on the adhesion force were elucidated. Our investigations are summarized as follows:

- Adhesion forces are extremely sensitive to the surface condition. Small amounts of contaminations lead to a distinct decrease of the adhesion force.
- Adhesion forces do not depend significantly on the load as long as the load is less than the adhesion force.
- Adhesion forces scale with the probe diameter. This behaviour is in qualitative accordance with theoretical models.
- Adhesion forces are influenced by heterogeneities at the surface, such as step edges.

It was shown, that experimental values can be related qualitatively to theoretical predictions. However, theoretical models consider ideal smooth surfaces. In contrast, all real solids exhibit a certain degree of surface roughness and surface irregularities. Thus, for precise qualitative predictions theories are needed to be developed that account for nanoscale roughness of both particle and sample surface.

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