MEMS GENERATED AND AFM-BASED SURFACE MODIFICATION

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MEMS GENERATED AND AFM-BASED SURFACE MODIFICATION

DISSERTATION

to obtain
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on the authority of the rector magnificus,
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on account of the decision of the graduation committee,
to be publicly defended
on Friday 4 March 2005 at 15.00

by

Szabolcs Deladi
born on 24 June 1973
in Gheorgheni (Gyergyószentmiklós), Romania
This doctoral dissertation is approved by

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To my wife and my parents
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Chapter 1

Introduction

Abstract

The motivation of the project, which generated the subjects discussed in this dissertation, is introduced. Decisions concerning the approach taken to meet the aim of the project are explained. Finally the structure of the thesis is presented.

1.1. Motivation of the work

The work presented in this dissertation is generated in the frame of the project “Contactless detection and monitoring of micro- and macro-wear using imaging methods”, financially supported by the Dutch Technology Foundation (STW). Three research groups worked together on the project, namely the Surface Technology & Tribology (STT), Measurement and Instrumentation (MI) and Transducers Science and Technology (TST), all from the University of Twente. The work was divided in a complementary way between the groups with different scientific and technological backgrounds.

The goal of the research was the development of measurement tools (hardware and software) for detection of micro- and macro-wear of materials, using imaging methods. The driving force of the project was the ever-increasing demand for better performance of tools and products. Knowledge about the nature and extent of wear is important for prediction of the lifetime of products which consist of contacting components.

Traditional methods to detect or quantify wear tend to lose applicability as the amount of wear to be detected becomes smaller and smaller with the increasing wear resistance of many materials and the reduced size of the components (micro-mechanisms). In these conditions measuring wear during or after an experiment with available techniques such as interference microscopy might be insufficient.

Most wear measurements are carried out offline, e.g. the samples have to be taken out of the test rig or tribometer to measure the microgeometry of the surfaces by various instruments such as interference or atomic force microscopes. This reduces the accuracy of wear measurement because subsequent removal and repositioning in the tribometer changes the contact and loading conditions, which generally influence the wear behavior when the experiments are resumed after alternatively performed wear generation and characterization. Furthermore, the method is not suitable for tribological measurements in the field of micro-electro-mechanics (MEMS devices) due to small dimensions of the structures and limited
access to the contacting surfaces. As the choice of materials used in MEMS devices is
influenced by the fabrication technology at least at the same extent as their tribological
performance, it is important to have appropriate adhesion, friction and wear data on eligible
materials.

1.2. General approach of the project

In order to meet the proposed aim of the project, two possible approaches were considered:

(i) development of an online wear measurement methodology, based on imaging
methods. Such a technique should allow faster characterization of wear, and essentially is not
based on mechanical contact during measurements. Although several physical effects limit
the resolution, it might enable dynamic measurement of wear.

(ii) development or improvement of measurement techniques which would push the
resolution limit to subnanometer level. High-resolution topography data can be obtained
offline using methods such as interference microscopy and atomic force microscopy. In
order to enable measurement of local height changes below 1 nm, efficient and accurate
processing and analysis of the acquired data is needed.

The first approach was chosen by the MI group since their expertise is much closer to
developing new measurement methodologies. STT and TST chose the second approach, but
the research was carried out on different scales in the two groups, and by using different
instruments for surface modification and characterization. For generation of wear the SST
group used a pin-on-disk rig and the modified surface was inspected by white-light
interferometry. The research of the TST group was directed towards the design and
fabrication of special MicroElectroMechanical Systems (MEMS) in order to evoke wear in a
reproducible way at micro- and nano-scale, and then to characterize the generated surface
modification with Atomic Force Microscope (AFM). Tribological problems encountered by
micro-scale structures and devices are not restricted only to wear, because the importance of
adhesion and friction significantly increases compared to macro-scale. Because the adhesion,
friction and wear are strongly dependent on each other at micro-scale, the subject of the
research was defined in a broader term: microtribology.

The dissertation is based on the work carried out in the TST group. Surface
modification was generated by MEMS devices and by atomic force microscope. The
development of a particular microtribological test instrument (microtribosensor) was the first
approach to the project subject. After preliminary tests it has been observed that for
comprehensive tribological characterization of the contacting MEMS surfaces a
complementary technique such as atomic force microscopy is needed. By studying the AFM-
based tribological characterizations, possible ways of improving available surface
modification and characterization techniques were identified. In consequence, a new in-situ
technique was developed, which uses a special AFM-probe mounted into standard AFM
equipment. The AFM-probe was further developed for fluid enabled surface modification.
Besides the tribological investigations it is also possible to carry out other applications (e.g.
nanolithography, electrochemical deposition etc.) by using the novel AFM-probes.
1.3. Outline of the dissertation

The work, which consists of two major parts, was structured in ten chapters. Excepting chapter one, two, and seven, presenting the motivation of the work, the background of microtribology (state-of-the-art), and an introduction to atomic force microscopy, the dissertation is based on reviewed and published work during the Ph.D. studentship.

In chapter three the requirements and the design of a microtribotester are presented. The requirements are based on adhesion [8] and friction considerations for microstructures. The part describing the design and numerical simulations of different actuators, components of the microtribosensor, is assembled from work reported in [2, 9].

Chapter four comprises the work carried out on technological developments for fabrication of complex MEMS devices like the microtribosensor. It is composed of a part describing investigations on the change of residual stress of undoped sacrificial silicon-oxide at high temperature processing, a part consisting of studies carried out on optimizing reactive ion etching processes for thick silicon-oxide layers and Si₃N₄/poly-crystalline-Si/silicon-oxide stacks [1], and a third part about the development of a new release technique which enables freeing complex MEMS structures consisting of multiple structural layers built up on multiple sacrificial layers, but which do not contain enclosed cavities [4].

Chapter five is based on characterization of electrothermal actuators and describes an empirical method of discriminating reversible and irreversible actuation regimes of electrothermal actuators [2, 3], since their main disadvantage is the plastic deformation at high temperatures, which modifies their geometry and hence their initial neutral position.

In chapter six the fabrication process of the microtribotester is presented [1, 4], and its successful operation is shown. The reason of continuing the work in the direction of atomic force microscope-based surface modification and characterization is also discussed in this chapter.

Chapter seven is a prologue to the second major part of the dissertation. The basics of the atomic force microscopy are introduced in order to help in the interpretation of data presented in chapters 8-10.

In chapter eight a new in-situ AFM-based surface modification and characterization technique is described. The technique developed enlarges the possibilities of micro- and nano-tribological investigations using atomic force microscopy, since it enables in-situ wear, friction and adhesion studies for various material-couples and loading conditions. This chapter is assembled from work reported in [6, 10].

In chapter nine further development of the AFM-probes is presented. In order to allow AFM-based fluid enabled surface modification, new probes were designed and fabricated, comprising reservoir(s) and fluidic channels in their structure [5, 7]. The proof of principle of the devices, based on experimental evidence, is also shown in this chapter.

Chapter ten focuses exclusively on new applications which can only be carried out by using the AFM-probes with fluidic capabilities. In-situ AFM-based surface modification and characterization technique can be used in combination with the new probes, hence tribological investigations can be carried out with local lubrication. The chapter is assembled
Chapter 1

from work presented in [5, 7, 11], and provides evidence that the new probes considerably enlarge the field of AFM-based applications. Further opportunities have also been identified and presented.

1.4. References


Chapter 2

Background of microtribology

Abstract

State-of-the-art theoretical modeling and experimental microtribological investigations are presented in this chapter. The difference between tribology at micro and macro-scale is emphasized and adhesion, friction and wear mechanism are described.

2.1. Introduction in tribology

The term tribology originates from the Greek word tribos, meaning rubbing. Despite this, the contemporary significance of tribology as science comprises studies of two interacting surfaces in relative motion, and of related subjects. The concern about reducing friction during transport of different materials in order to spare effort has always existed, first records are dated 3500 BC [1]. However, the conception of tribology as science can be attributed to Leonardo da Vinci (1452-1519), who postulated the first time a scientific approach of friction. He introduced the coefficient of friction as the ratio of the friction force to normal load. Amontons found that the friction force is independent of the apparent contact area. Coulomb made a clear distinction between static and kinetic friction (1781). The industrial development, starting at the end of the 19th century, expanded tremendously the interest in studying tribology for minimization and possible elimination of losses resulting from friction and wear due to rubbing of surfaces. Prediction of tribological phenomena such as adhesion, friction and wear became important for the design of machinery and estimation of its lifetime. Various theoretical models, supported by experimental investigations, were developed. The tests were conducted on components with relatively large mass under heavy loading conditions. The wear in this situation is inevitable and the bulk properties of contacting components dominate the tribological performance. The technological explosion in the second half of the 20th century enabled the miniaturization of devices and components, a tendency which was mainly driven by economical and ergonomical reasons. However, new problems emerged due to small dimensions. The light components, small applied loads and relatively smooth surfaces made predictions of the tribological effects using theoretical models developed for large systems impossible. As the size of the components approached the micrometer scale, it was observed that the surface properties dominate the tribological performance. In these conditions the contact between surfaces became important and investigations were initiated on how the scale influences the contact parameters. In fact this
represented the formation of a new branch: microtribology.

2.2. Microtribology

Friction and wear of microcomponents are highly dependent on the surface interactions. Friction is critically influenced by adhesion, because the apparent load due to adhesion is supplementary to the normal load externally applied on contacting surfaces. Wear is dependent at this scale on both, adhesion and friction, to which the effect of stiction can be added (Figure 2.1.). The wear expected in microsystems is usually low, limited to few atomic layers.

Adhesion between surfaces plays a significant role at microscale due to extremely smooth surfaces. Adhesion works via four main mechanisms: van der Waals forces, hydrogen bridging, electrostatic forces and asperity deformation forces. Van der Waals forces are called dispersion forces and arise from the interaction between the instantaneous dipole moments of the atoms. The attraction between two flat surfaces separated by a distance \( \varepsilon < \lambda \) (\( \lambda \) is the retardation length) is proportional to \( \varepsilon^{-3} \) and it is affected by the material properties. At larger separation the nonretarded van der Waals forces are replaced by retarded Casimir forces, which influence the attraction force between two parallel plates proportional to \( \varepsilon^{-4} \), and are not affected by the material properties [13].

Hydrogen bridges are a special case of polar molecule bonds between hydrogen atoms and occur when hydrophilic surfaces contain adsorbed water layers, which is almost imminent under atmospheric conditions. The hydrogen electrons in the water molecule are strongly attracted to the oxygen and leave partially exposed protons to attract lone pairs of electrons on adjacent oxygen atoms, thus the proton forms a bridge between two negatively charged atoms.

Figure 2.1. Relation between factors which contribute to the extent of the microwear.
Electrostatic forces can arise due to externally applied voltages across the interface, differences in material work functions of the surfaces, electrostatic charging resulting from release-etch, rinsing, drying [14].

The asperity deformation forces are repulsive due to the tendency of recovery subsequent to deformation of interacting asperities in case of (partly) elastic deformations.

The capillary forces are caused by liquid trapped between surfaces which exerts a force due to the Laplace pressure difference between inside and outside of the liquid junctions. The behavior of the surfaces, hydrophilic or hydrophobic, determines the wetting contact angle of the surfaces and the extent of adhesion. Adhesion due to capillary forces is often called stiction in micromechanics, where structures adhere to each other due to condensation of liquid on surfaces or due to inappropriate release of the structures.

2.2.1. Contact modeling

From the schematic in Figure 2.1. it is obvious that the study of contact mechanics at microscale is crucial in determination of the tribological performance. In the late 19th century Hertz developed a contact model [2], which is still the basis of the largest majority of theories. He constructed the model on the following assumptions: (1) each body can be considered an elastic half space loaded over a plane, (2) the surfaces are continuous, smooth and nonconforming, (3) elliptical contact area, (4) the dimensions of the contact area are small compared to each body and to the radii of curvature of the surfaces, (5) small strains so that the linear elasticity is valid, (6) frictionless contact, in this way only the normal pressure is transmitted. The Hertizian theory was developed for macroscale, but it can be used for contact of single asperities also at microscale with certain modifications [3]. As machined surfaces became smoother and smoother, research was directed towards multiasperity contact. The models approach the effects of individual asperities in two different ways: (i) by considering separately each individual asperity and the final effect is the summation of the individual action of the asperities, and (ii) by solving the equations of elasticity for the entire body simultaneously. The parent of the multiasperity theories is the Greenwood-Williamson model [4], which assumes that a surface composed by hemispherical asperities (with the same curvature) is in contact with a smooth surface. A plasticity index depending on the surface topography, elastic modulus and hardness of the contacting materials, is introduced for the transition from elastic to plastic deformation. This parameter is used to delimit elastic and plastic deformations of asperities in the contact model of rough surfaces [20]. Multiasperity contact models have also been developed for fractal surfaces with certain height distribution functions [5, 6].

Studies on the influence of adhesion in the contact between two rigid bodies have already been reported in the first half of the 20th century by Bradley [7]. In the 1970’s two contact models taking into account adhesion have been proposed, one by Johnson et al. (JKR theory) [8] and the other one by Derjaguin et al. (DMT theory) [9]. The JKR theory assumes that adhesive forces act inside the contact area, while the DMT theory considers that adhesive forces act outside of the contact area. These two models appeared to be
contradictory until Tabor [10] pointed out that the two models are appropriate to opposite extremes of a certain parameter depending on the surface topography, elastic properties of the materials and the work of adhesion. A model that can be considered the transition between JKR and DMT theories has been developed by Maugis (M-D theory) [11], which takes into account the adhesion forces acting outside the contact area too, in an annular region.

The validity of all above mentioned contact models has been confined by Johnson and Williamson [3] in a so called adhesion map (Figure 2.2.) defined by two parameters: the elasticity parameter $\lambda$ and the ratio between the total load and the adhesion part of load $\overline{P}$.

$$\lambda = \left( \frac{9R\sigma_0}{2\pi W^* z_0^2} \right)^{1/3}, \quad \sigma_0 = \frac{16W}{9\sqrt{3} z_0}, \quad \overline{P} = \frac{P}{\pi WR} \quad (2.1)$$

where $P$ is the total load, $W$ is the work of adhesion, $R$ is the equivalent radius, $E^*$ is the equivalent Young’s modulus, and $z_0$ is the interatomic spacing [13].

In the area where the Hertzian theory is valid, the contribution of the adhesive force is less than 5%. Johnson showed that most practical applications in the area of nano-tribology fall in the JKR zone of the adhesion map [12], but the small radius of an AFM probe-tip leads to contact parameters which correspond to the M-D theory.

Fuller and Tabor [18] introduced an adhesion parameter $\theta$, in order to relate the effect of the surface roughness to the adhesion of elastic solids. This parameter allows the comparison of different theories developed on the adhesion of contacting rough surfaces [17, 19].

2.2.2. Adhesion and stiction studies on microstructures

The surfaces of microstructures can be very smooth (standard deviation ~1 nm) due
Background of microtribology

to the evolution of the micromachining techniques. Since the contact in microsystems is usually between flat-flat surfaces, experimental investigations on adhesion and stiction have to be based on contacting microstructures rather than AFM-based studies [32, 33].

Mastrangelo and Hsu [15] presented a simple but still very much used method to measure the work of adhesion between micromachined surfaces, defined as the energy needed to separate unit areas of two adhering surfaces. The technique is based on the detection of free and pinned beams with a Michelson interferometer attached to a microscope. The beams with different length are pulled into contact with the substrate by the capillary force during microstructure drying. The beams longer than a certain detachment length remain adhered while the stiffness of the shorter beams will overcome the adhesion forces. The beams at the transition region are adhered to the substrate only at their tips and the work of adhesion can be calculated from the balance between the elastic energy stored within the beam and the beam-substrate interfacial energy. De Boer and Michalske [16] extended the model further to S-shaped adhesion mode of the beams.

Tests on double-clamped polycrystalline-Si beams were carried out by Legtenberg et al. [24]. After drying in the release process of the structures, some of the beams remained permanently attached to the substrate. The detachment length was measured for hydrophilic and hydrophobic samples. In the model the work of adhesion takes into account that the stored elastic energy contains a stretching term in addition to the bending term. It was observed that the van der Waals forces are responsible for the stiction of hydrophobic surfaces and hydrogen bridging is the dominant mechanism in the case of hydrophilic surfaces.

Although adhesion and stiction are undesired for most of the microstructures which during operation have to execute a motion, these phenomena can be used effectively when structures or larger systems have to be bonded together. Such examples are the fabrication of microchannels by bonding a wafer in which the profiles are patterned to another one for sealing purpose, and the fabrication of contact mode AFM-probes where the cantilevers are patterned on a wafer that has to be bonded to another one, from which the support of the cantilevers is machined. Wafer bonding has extensively been studied by Gui et al. [17]. A statistical model was developed for elastic contact between a flat and a rough surface. The surface roughness was represented by asperities, modeled as spherical caps with equal radii, and the heights of the asperities obey a Gaussian distribution.

Diminution of the adhesion requires first of all reduction of the real contact area, which is possible by replacing contacting surfaces with contact bumps, by depositing sidewall spacers (fluorocarbon spacers [21]), and by roughening the surfaces. Water adsorption on micro-machined surfaces must be prevented because it represents the main cause of stiction due to capillary forces. The techniques of stiction diminution are mainly based on the replacement of the polar groups on the surfaces with nonpolar ones. The problem can be divided into release-related stiction and in-use stiction.

The release-related stiction due to evaporation drying was extensively studied by Abe et al. [22, 23]. For short rigid structures the water dried from the tip towards the clamping, these being completely released, while for longer compliant structures the water dried towards the tip and the cantilevers were stuck to the substrate as they rolled down from the
tip to the base. Release techniques have been developed based on other principles than using water as last processing fluid, in order to increase the yield of successfully fabricated microstructures. Freeze-drying based on sublimation of cyclohexane [24], supercritical CO₂ drying based on bringing the liquid CO₂ to supercritical phase [25], and vapor HF (hydrofluoric acid) releasing based on removing the sacrificial layer in vapor HF [26, 27] improved the yield to some extent.

In-use stiction can be reduced by chemical surface modification techniques, which are based on hydrogen passivation, hydrogen-bonded fluorinated monolayers, plasma-deposited fluorocarbon thin films, diamond-like carbon coating [29] and different monolayer coatings [30, 31]. Self Assembled Monolayers (SAM) possess low surface energy, large wetting contact angle, and because they form ultra-thin layers of densely packed organic molecules, they are also used as lubricants for MEMS [28]. SAM films appear to eliminate capillary condensation, and they have good long-term stability in various conditions, which recommend them for antistiction coatings.

2.2.3. Friction studies at microscale

Tabor suggested that three basic elements are involved in the friction of unlubricated solids [34]: (i) the real contact area between sliding solids, (ii) the strength of the bond formed at the interface where contact occurs, and (iii) the way in which the material in and around the contacting regions is sheared and ruptured during sliding. These elements differentiate the modern vision on friction from classical theories (Amontons [35], Coulomb [36]). A static friction model taking into account these elements and based on the assumptions of the G-W model [4] was developed by Chang et al. [37] for metallic rough surfaces. The model showed that for a given external force the static friction coefficient decreases as the plasticity index increases and as the surface energy decreases. For a given plasticity index the static friction coefficient decreases as the external force increases. It turned out that the classical friction model overestimates the static friction coefficient at high external force and underestimates it at low external load.

The friction investigations at microscale are dominated by experiments carried out by using atomic force microscopes or friction force microscopes [38-42]. Only few works have been reported on using other microtriboapparatus [43, 44] or microelectromechanical systems [45-47] for friction studies. The aim of the first two categories of experiments is to investigate the friction of materials by using probe-tips or micro-balls, or to simulate the friction for contact between similar material-couples than those encountered in microsystems, by using appropriate substrate and coated probe-tips or micro-balls. Measurement of friction with AFM is possible due to monitoring the torsional behavior of the cantilever when the probe-tip is in contact with a substrate and the direction of relative motion is orthogonal to the longitudinal axis of the cantilever (chapter 7). Friction studies using MEMS devices are advantageous because investigations are carried out under exactly the same operating conditions. Friction in flat-flat contact systems can be tested with MEMS devices [46], which is difficult if not impossible with other instrumentation at microscale. The
MEMS devices and the results obtained for friction measurements are discussed in section 3.3.

2.2.4. Wear at microscale

Adhesive wear is predominant in micromechanisms, debris or dust particles only rarely have contribution to abrasive wear. This type of wear mainly results in material transfer. Rabinowicz [48] showed that the tendency of the sliding metals to adhere strongly to each other is indicated by their metallurgical compatibility, which is the degree of solid solubility when the two metals are melted together. As the metallurgical compatibility decreases the amount of wear reduces, but the lubrication plays the most important role in diminution of the wear. The amount of wear is generally proportional to the normal load and sliding distance and inversely proportional to the hardness of the softer contacting material [49]. The amount of wear to be detected becomes smaller and smaller with the reduced size of the components and by using wear-resistant coatings. Therefore, techniques like optical interferometry, conventionally used for determination of the amount of wear generated due to relative motion between contacting structures, loose applicability for wear detection in MEMS devices where the wear can be just few atomic layers. Wear of materials at micro and nanoscale is usually studied with atomic force microscopy, although the wear generated by an AFM probe-tip is mostly caused by ploughing, which can significantly differ from the adhesive wear in microsystems. State-of-the-art wear studies at nanoscale [40-42, 50] use the same tip for wearing and measuring. Wearing is done at a high load, while subsequent imaging is done with the same probe on a larger area applying a smaller load. Generally, the AFM probe-tip used for wear experiments is made of a wear resistant material like silicon-nitride or diamond. These types of investigations give information about the wear of the tested material in certain conditions rather than on what happens if contacting components of MEMS devices are in relative motion. A solution is to measure the wear directly on components of the MEMS device, subsequently to its operation for a certain period [51]. The drawback is that operation of the same device could not be resumed after wear characterization in the case of inspection of a critical part. An alternative is to construct a scaled-up test-rig such as pin- or surface-on-disk, made by the same fabrication technique and from similar materials as the MEMS device [52].

Lubrication can reduce wear in MEMS devices, although the so called lubricant has to be chosen carefully because it can also enhance wear, or can cause stiction. Self-assembled monolayers [28, 53] or fluorocarbon-based organic monolayers [47] can also reduce friction besides wear.

2.3. References

Chapter 2

[23] T. Abe, W.C. Messner, M.L. Reed, “Effects of elevated temperature treatments in
Background of microtribology


[42] V.N. Koinkhar, B. Bhushan, “Microtribological studies of unlubricated and lubricated


Chapter 3

Requirements and design of a microscale tribosensor

Abstract

In this chapter the design and simulation of electrothermal actuators are presented, which combined form a complex MEMS device that can be used for microscale tribological investigations. An adhesion model, developed for 3-D arbitrary rough surfaces, and considerations of friction studies carried out with various MEMS devices constitute the requirements for the design of a tribotester, which should enable microscale adhesion, friction and wear studies of contacting surfaces under different loading conditions.

3.1. Introduction

The study of interaction between surfaces is phenomenologically different at micro and macro-scales. Effects such as adhesion, friction and wear of microstructures critically influence the reliability of MEMS devices. Small structural parts often contact each other during operation, hence the investigation of the effect of friction and wear, caused by deliberate or accidental contact, on reliability is very important. Once two very smooth surfaces (e.g. standard deviation $\sigma$ few nanometers) contact each other, it is extremely difficult to separate them with forces that can be generated by microstructures. Tangential forces that have to be provided by a microtribosensor are augmented by the adhesion between smooth surfaces. This has to be taken into account when the required force which can initiate tangential motion between surfaces is estimated.

3.2. Adhesion model for arbitrary rough surfaces

A model for estimation of adhesion between two arbitrary rough surfaces is presented. The numerical computation is based on the incremental decrease of the separation between the surfaces, and the subsequent change of the free total energy of the system. The 3-D adhesion model developed is based on the JKR theory [1], applied locally for each contacting asperity couple. The choice for this particular theory was determined by the consideration of adhesion inside the real contact area. Additionally to this model, the van der
Waals interaction between surfaces in the calculation of the total normal load applied on the contacting surfaces is considered, in the regions where there is no contact.

The model is applicable for both, computed or measured surfaces. The limitation of the measured surfaces is the convolution effect due to probing, while for computed surfaces the very spiky asperities must be eliminated because of the finite atom radius. Computational surfaces can be generated either by using fractal approach or by using certain distribution functions if the surface topography parameters are known from available measurements. The surfaces separated by a certain distance can be described then by the functions $z_1(x,y)$ and $z_2(x,y)$, as shown in Figure 3.1.

The surfaces are divided in finite areas (discretized) similarly to the meshing for finite element analysis. An incremental approach of the upper surface to the lower one is used in the computation. Equation (3.1) describes the position change of the surfaces within an iteration step

$$
\mathcal{f}^{(k)} \rightarrow \begin{cases} 
    z_1(x, y)^{(k)} = z_1(x, y) \\
    z_2(x, y)^{(k)} = z_2(x, y) - \delta \cdot k
\end{cases}
$$

where $k = 0..s$ is the iteration step and $\delta$ is the incremental distance. For convenience the indices of the iteration steps are further on neglected in the equations.

An immediate consequence of decreasing the separation between the surfaces is that after the first asperity couples are brought into contact, the real contact area increases for each iteration step (Figure 3.2.).

3.2.1. Forces

The weight of the microstructures is very small due to relatively thin surface-micromachined layers, therefore it can be neglected comparatively to other forces.
encountered.

When contact occurs between two surfaces, the adhesion is determined by four main mechanisms: van der Waals interaction, electrostatic forces, hydrogen bridging and the forces due to asperity deformation. The model accounts for these mechanisms by considering the interfacial energy within the contact regions according to [1].

Figure 3.2. Contact interfaces for (a) separation $d_1$; (b) separation $d_2 < d_1$.

An attractive force will be created outside the contact regions, which can be regarded as an additional term to the externally applied load. Two mechanisms can contribute to this force: the van der Waals interaction and electrostatic forces due to charging. In the regions where there is no contact but the surfaces are in close proximity, the van der Waals interaction plays an important role. When the radii of the asperities are much larger than the size of the incremental surfaces, it can be assumed that the force due to van der Waals interaction is proportional to $d^{-3}$ (parallel-plate approximation of the incremental surfaces)

$$F_{w} = \begin{cases} \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \frac{H A_{i,j}}{6 \pi d_{i,j}^3} & \text{if } \xi(\mathbf{x}, \mathbf{y}) > \xi(\mathbf{x}, \mathbf{y}) \\ 0 & \text{otherwise} \end{cases}$$  \hspace{1cm} (3.2)

where $H$ is the Hamaker constant and $d$ is the distance between the middle points of the finite area pairs of size $A$, located outside the real contact area. For very rough surfaces the van der Waals interaction is weak due to large separation distances between the finite areas.

Charging can occur accidentally or it can be generated on purpose between surfaces as
the MEMS devices are operated. The force generated by electrostatic attraction between two finite areas is

\[
F_e = \begin{cases} 
\sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \frac{\varepsilon A_{i,j} V^2}{2 (d_{i,j} + t_{i,j})^2} & \text{if } z_2(x_i, y_j) > \zeta I(x, y) \\
\sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \frac{\varepsilon A_{i,j} V^2}{2 t_{i,j}^2} & \text{otherwise}
\end{cases}
\]

(3.3)

where \( t \) is the thickness of the dielectric layer (typically < 1 \( \mu \)m) and \( V \) is the applied voltage.

The model can account for mechanically applied loads \( F_m \) by simply adding it to the normal force. Thus, the total normal load \( F \) that must be distributed on the contacting asperities is obtained by summation of \( F_w, F_e \) and \( F_m \).

3.2.2. Computational background

By analyzing the sign function defined by Eq. (3.4) the contact areas and the non-contact regions can be separated like in Figure 3.3(a).

\[ S = \text{sign}[z_2(x_i, y_j) - \zeta I(x_i, y_j)] \]

(3.4)

The computations showed that it is important to take into account the three-dimensional shapes and positions of the asperities because the tilt angle \( \beta \) between the planes defined by the perimeters of the theoretical interferences of contacting asperities and the horizontal plane can vary up to 10-11 degrees (Figure 3.3.(b)).

In the regions where the surface profiles would theoretically interfere, the dimensions of the areas determined by the perimeters of the interferences are computed in \( x \) and \( y \) directions and then used for substituting the asperities with spherical cap shaped ones. The radii of the
base planes of the spherical caps \( r \) are assumed equal to the half of the mean value of the dimensions in \( x \) and \( y \) directions. The distance between the centre point of the base plane and the value of the profile function for \( x \) and \( y \) coordinates of the centre point determines the height \( \delta_c \) of each spherical cap. The radius of the spherical cap can be determined by forcing a circle to pass through three points designated to be on the spherical cap.

With the computed radii of the contacting asperities for both surfaces we have the possibility to apply the JKR adhesive contact model for all contacting asperity couples. In order to simplify the algorithm and to gain computation speed, the contacting asperities have been renumbered and thus vectors have been used in further calculations instead of matrixes. The composite radius \( R \) of the asperity couple \( i \) will be

\[
R_i = \frac{R(z1_i \cdot R(z2)_i)}{R(z1)_i + R(z2)_i} \quad i = 1..p
\]  

(3.5)

Due to the finite compliance of the matter and random distribution of the asperities the total normal load is assumed to be distributed according to their geometrical characteristics

\[
F_i = F \frac{(3\sigma_i^2 + \delta_i^2)\delta_i^2}{\sum_{i=1}^p (3\sigma_i^2 + \delta_i^2)\delta_i^2}
\]  

(3.6)

The apparent contact load due to the interfacial energy \( \Gamma \) can be obtained by modifying the JKR formula [1] for the contacting asperities

\[
F_{a_i} = F_i \cos \beta_i + 3\pi R_i \Gamma + \sqrt{6\pi R_i \Gamma F_i \cos \beta_i + (3\pi R_i \Gamma)^2}
\]  

(3.7)

The equilibrium position of the surfaces can be determined with the free total energy \( E_t \) of the system Eq. (3.8), which consists of the mechanical energy \( E_m \) of the normal loads, the surface energy \( E_s \), and the stored elastic energy \( E_e \).

\[
E_t = E_m + E_s - E_e
\]  

(3.8)

Previously reported multi-contact models [2-4] considered elastic deformation of the asperities and defined the limitation of the models using the plasticity index. From the assumption that the surfaces consist of asperities with equal composite radii \( R_i \) (e.g. for \( i=1 \) the radii of all asperities are \( R_1 \)) and by calculating the plasticity index accordingly, the behavior of the asperity couple \( i \) can be estimated.

\[
\varphi_i = \frac{E}{Ha} \left( \frac{\sigma}{R_i} \right) \quad i = 1..p
\]  

(3.9)
\[
\frac{1}{E} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}; \quad \sigma = \left(\sigma_1^2 + \sigma_2^2\right)^{1/2}
\]

where \(\sigma\) is the composite standard deviation, \(E\) is the composite elasticity modulus and \(Ha\) is the hardness of the softer material. By taking separately the cases of \(i\) ranging from 1 to \(p\), an indication about the plasticity index of all contacting asperity couples can be found.

This model proposes a way to include all three deformation regimes, namely the elastic deformation for \(\phi \leq 0.6\), the fully plastic deformation for \(\phi > 1.1\), and the intermediate (elasto-plastic) regime. The free total energy of the system has to be modified accordingly, thus the stored elastic energy due to deformation of contacting asperities has to account for all three deformation regimes, Eq. (3.10.3). The oblique contact of asperities is taken into account in the equations by considering the influence of the tilt angles \(\beta\) (between the horizontal and the contact planes) on the normal force.

\[
\begin{align*}
E_m &= \sum_{i=1}^{p} \frac{F_i \cos \beta_i}{R_i^{3/2}} \left[ \frac{1}{3} \left( F_i \cos \beta_i \right)^2 + \frac{2}{3} \left( F_i \cos \beta_i \right)^2 \left( F_i \cos \beta_i \right)^{-1} \right] ; \quad K = \frac{4}{3} E \\
E_s &= \pi \Gamma \sum_{i=1}^{p} r_{ci}^2 \\
E_e &= \sum_{i=1}^{p} \frac{1}{K^{2/3} R_i^{1/3}} \left[ \frac{1}{15} \left( F_i \cos \beta_i \right)^5 + \frac{1}{3} \left( F_i \cos \beta_i \right)^2 \left( F_i \cos \beta_i \right)^{-1} \right].
\end{align*}
\]

\[
\begin{align*}
1 & \quad \text{if} \quad \phi_i < 0.6 \\
1 - 2(\phi_i - 0.6) & \quad \text{if} \quad 0.6 \leq \phi_i \leq 1.1 \\
0 & \quad \text{if} \quad \phi_i > 1.1
\end{align*}
\]

The iteration stops at a certain separation between the surfaces for which the incremental free total energy becomes zero. Subsequently, the parameters of the adhesive contact can be calculated, such as the real contact area and the pull-off force. Generalizing the pull-off force of the single asperity-couple adhesive contact and adding the term due to van der Waals interaction, which also must be overcome, the force needed to pull two surfaces off will be

\[
F_p = -\frac{3}{2} \Gamma \pi \sum_{i=1}^{p} R_i - F_w
\]

A larger interfacial energy will reduce the separation between two surfaces for which the equilibrium position is reached, thus the number of iterations increases.
A large fraction of the MEMS structures are made of polycrystalline-Si and single-crystal Si. Therefore, contact between two silicon plates was simulated and the results were compared with a previously reported model and with experiments carried out on wafer bonding [3]. A mean value of the adhesion parameter $\theta$ has been considered in order to allow comparison of the computed results with other models and experimental measurements.

$$\theta = \frac{1}{\rho} \sum_{i=1}^{p} \frac{E_i \Gamma}{R_i} \sqrt{\frac{E_i}{\sigma}}$$  \hspace{1cm} (3.12)

Three regimes are defined depending on the values of the adhesion parameter [3]: the bonding regime for $\theta < 1$, the adherence regime $1 < \theta < 12$, and the nonbonding regime $\theta > 12$. The results presented in Figure 3.4 illustrate that even outside the bonding regime the specific bonding energy is still high enough to cause adhesion related problems for microstructures. If some asperities deform plastically or elasto-plastically, then the iteration stops few steps later relative to the case when only elastic deformation occurs due to diminution of the stored elastic energy. The real contact area as well as the pull-off force will increase in this case, as one can see in Figure 3.4 and 3.5.

![Figure 3.4. Normalized bonding energy variation with the adhesion parameter.](image)

![Figure 3.5. Normalized contact area variation with the adhesion parameter.](image)
The results are used in section 3.5.1. for the estimation of the normal force of an out-of-plane actuator, required to pull two micromachined surfaces off.

3.2.3. Conclusions

A numerical model has been presented which is capable of estimating adhesive forces between two arbitrary rough surfaces. The model takes into account the van der Waals interaction, interfacial energy, externally applied loads, and different deformation regimes of the contacting asperities (elastic, elasto-plastic and plastic).

If there are asperities which deform plastically and/or elasto-plastically, then the real contact area and the pull-off force will increase compared to the case when all asperities deform elastically. The van der Waals interaction is strong also in the regions where the asperities are not contacting each other but they are in close proximity. Subsequently, some asperities on two arbitrary rough surfaces deform plastically after being brought into contact, even without applying any external load.

Outside the bonding regime the adhesion is still high enough to cause problems for microstructures. The model can also serve as a ground for static friction study at micro/nanoscale between surfaces.

Further improvement of the model is possible by substitution of some assumptions used in the computation with more complex numerical modeling: e.g. redistribution of the total normal force on the contacting asperities; calculation of the plasticity index of contacting asperities by using the load applied on them individually, the elastic properties and the hardness of the materials.

3.3. Friction studies using MEMS devices

Although extensive work has been carried out on friction at microscale using different instruments specific to tribological investigations such as atomic force microscope, pin-on-disk etc., only a few works have been reported on friction between two micromachined surfaces [18-20]. The friction study at this level is important for the design of MEMS devices, since their working principle can be based on moderate and predictable friction and adhesion between contacting surfaces [19, 20, 22]. Another target area is the reliability of MEMS devices which have components moving tangentially relative to each other when mechanical contact exists between them during operation.

The work on the aspects of friction using micromachined structures was started up by Lim et al. [18]. They tried to characterize static friction for polycrystalline-Si/polycrystalline-Si and polycrystalline-Si/LPCVD Si3N4 interfaces by using phosphorous-doped polycrystalline-Si structures. The device consists of a parallel-plate and a comb-drive electrostatic actuator, suspended by a spring system (Figure 3.6.). Dimples micromachined on the backside of the shuttle (top electrode of the parallel-plate actuator) contact the substrate, which is either
made of polycrystalline-Si or LPCVD Si$_3$N$_4$.

Initially the suspended polycrystalline-Si structure is displaced from the neutral position by the comb-drive actuator, and then the normal force is applied on the dimples by operating the parallel-plate electrostatic actuator. The tangential force to measure the friction is produced by the restoring force of the suspension with known spring constant. The static friction coefficient of course-grained polycrystalline-Si/polycrystalline-Si interface was found larger than that of the polycrystalline-Si/LPCVD Si$_3$N$_4$ interface. The result is consistent with the theory of interfacial surface energy [21], which states that “the use of similar materials for both sliding surfaces is bad, the use of dissimilar but compatible materials is questionable, whereas the use of incompatible materials for sliding is the best”. The very high friction coefficients of 2.5±0.5 for polycrystalline-Si/LPCVD Si$_3$N$_4$ and 4.9±1.0 for polycrystalline-Si/polycrystalline-Si interface, and the large error limit indicate that the externally applied load is not the total normal load.

The importance of taking into account the apparent normal load due to adhesion between micromachined surfaces has been reported by Tas et al. [19]. The MEMS device used for this purpose was a surface micromachined linear electrostatic stepper motor, consisting of two drive units that alternatively generate step-like motion to move a shuttle. The design is symmetrical to the longitudinal axis of the shuttle (Figure 3.7.), therefore one side was neglected in the sketch. Friction force is measured by recording the pull voltage at the onset of the slip when the clamping shoe is pushed against the wall of the shuttle with a normal force, defined by the clamp actuator. The actuators used for clamping and pulling are both gap-closing electrostatic actuators, which enable easy actuation voltage to force conversion. The contacting vertical surfaces are both made of Boron-doped LPCVD polycrystalline-Si, on which native oxide is present due to storing in ambient conditions. In the calculation of the static friction coefficient the total normal load is taken as the sum of the
externally applied normal load by the clamp actuator and the apparent normal load due to adhesion between the clamping shoe and the wall of the shuttle. The actuation voltage of the pull actuator at the onset of the slip is converted to friction force, and then the static friction coefficient is determined. Friction coefficients were found in the range of 0.8±0.3, which strikingly differ from results calculated in [18] for almost the same contact interface. Although different grain size and dopant concentration can result in change of friction coefficient for the same interface of materials, the discrepancy between the results of the two works, [18] and [19] respectively, can be attributed to the contribution of adhesion to the total normal load.

Recent investigation on static and dynamic friction in MEMS systems [20] demonstrated that even without externally applied load there is always an apparent normal load due to adhesion when two surfaces contact each other. The device used for this purpose was a surface-micromachined MEMS inch-worm actuator, which is a modified version of the shuffle motor [22]. The working principle is presented in Figure 3.8. The actuator consists of two frictional clamps connected by an actuation plate, which through an appropriately phased sequence of clamping provide large displacements in step-like motion. The material used for fabrication was polycrystalline-Si, then the whole device was coated by a fluorocarbon-based organic monolayer for reducing surface energy, preventing condensation and for diminishing the shear stresses between contacting asperities.

Static friction was studied by displacing the actuator against a suspension system with known spring constant, then holding the system in place by a large clamping force. By ramping down the clamping force, at a critical value the spring force equals the static friction force and sliding initiates. Subsequently, the static friction coefficient is calculated by taking into account the out-of-plane restoring force of the suspension, the mass of the system, and the adhesion between surfaces. Static friction coefficient of 0.33±0.02 was found for the contact of two fluorocarbon coated polycrystalline-Si surfaces.

The dynamics of the inchworm actuator were also investigated, by considering it as a mass and spring system riding atop a planar surface. The actuator is displaced against the suspension system, it is held in position, and then released. The motion is subjected to air and dynamic friction damping. Dynamic friction coefficient of 0.24±0.02 was calculated by including the effect of adhesion between contacting surfaces in the model based on the

![Figure 3.7. Sketch of the surface micromachined linear electrostatic stepper motor used for static friction investigations. Only the topside driving unit is illustrated for symmetry reason.](image)
behavior of the system.

![Diagram of a microtribosensor](image)

Figure 3.8. The working principle of the shuffle motor consisting of two frictional clamps and an actuation plate. An appropriately phased sequence of clamping provides step-like motion.

3.4. Design of a microtribosensor

An ideal MEMS device that would enable all kinds of tribological tests should allow coupled and decoupled in- and out-of-plane motions. The simultaneous control of these motions is important for different kinds of test set-ups (e.g. friction and wear investigations under various normal loading require both in- and out-of-plane motions).

The tribotester which satisfies these conditions must at least consist of an in-plane actuator, an out-of-plane actuator to bring test surfaces into contact, another out-of-plane actuator to pull contacting surfaces off, and suspensions which assure that the test surfaces are not in contact with the substrate for the neutral position of the device. The sketch of such a device is presented in Figure 3.9.

Two out-of-plane actuators were considered and two test surfaces for symmetry consideration. The axis of the plate (shuttle) carrying the test surfaces is regarded as symmetry axis. When both actuators are operated, the test surfaces are pulled off simultaneously, without lateral tilting. The in-plane actuator is connected to the shuttle and provides reciprocatory motion during testing. In order to decouple in- and out-of-plane motions, the shuttle and the out-of-plane actuators are separated by a certain gap when the device is in neutral position. Coupling of the vertical and horizontal motions during operation must be executed by mechanical connection of the structures. Normal load is applied on the contacting surfaces (test surface and substrate) by electrostatic attraction between two electrodes, such as in [18]. The shuttle can be used as top electrode, while the bottom
electrode can be created in the substrate (section A-A in Figure 3.9.). Short-circuiting
between electrodes is avoided by electrical isolation with Si₃N₄. Operation of different
actuators is done individually, because they are electrically isolated from each other. Electrical
domains are defined either by local doping of the polycrystalline-Si structures or confined by
using dielectric materials. Inspection windows on the shuttle are designed on both sides of
the test surfaces in order to allow observation of surface topography modification on the
substrate. When test surfaces are loaded against the substrate and the in-plane actuator is
operated, then it is expected that wear will be generated.

Figure 3.9. Sketch of a microtribosensor.

3.5. Design of in- and out-of-plane actuators

The demand for powerful actuators, which can be embedded in complex MEMS
devices, draws attention to electrothermal actuators, although there can be drawbacks due to
heat management problems during operation. Appropriate design allows good temperature
control over the entire device, and thus the main advantage of using much lower actuation
voltage in comparison with electrostatic actuators [5-7] for generating much larger forces can
effectively be exploited.

3.5.1. Requirements of in- and out-of-plane actuators

In order to make an appropriate design of a microtribosensor, the requirements of the in-
Design of a microtribosensor

and out-of-plane actuators have to be set. From the adhesion model of arbitrary rough surfaces the maximum force can be predicted, which is needed to separate two surfaces. The estimated force to pull off two 5x5 µm² surfaces with standard deviation σ of 0.6 nm can be as large as 500 µN if the adhesion parameter is below 1. However, θ is usually larger than 9 for micromachined surfaces and only by special processes like chemical-mechanical polishing [3] the adhesion parameter can be reduced to values in the bonding regime. In these conditions the pull-off force is decreasing to 100-150 µN for 5x5 µm² micromachined Si or polycrystalline-Si surfaces exhibiting large interfacial energy.

External normal force can be applied mechanically or electrostatically on the contacting surfaces. Previously reported tribological studies with MEMS devices used electrostatic attraction to generate normal force, an approach which will also be adopted in the design of the microtribosensor. The normal force that can be generated with a 100x100 µm² parallel-plate electrostatic actuator is 100 µN for an actuation voltage of 50 V and a 1 µm gap between the electrodes. The gap is defined partially by the thickness of the dielectric material required for electrical isolation of the electrodes, and partially by the height difference between the test surface and the top electrode, needed to avoid contact between large surfaces (Figure 3.10.), which can result in very strong adhesion. The test surfaces have to be placed symmetrically to the center of the top electrode, thus in the case of two test surfaces the normal force exerted to one of them will be 50 µN. Adding this force to the estimated pull-off force of the surfaces, the total force that has to be counteracted by the electrothermal out-of-plane actuator is in the range of 150-200 µN. The range of vertical displacements that has to be covered by the actuator is small (few micrometers) because only the separation of the surfaces is intended.

![Figure 3.10. Schematic of applying a normal force on the test surfaces electrostatically, when they are in contact with the dielectric material.](image)

The requirements of the in-plane actuators depend on the expected static friction coefficient and on the range of distances that the test surface has to slide on the substrate. The maximum displacement has to be at least equal to the side of the test surface, in order to allow inspection of the surface modification (wear generated during sliding) with different instruments (e.g. optical microscope, interferometer, etc.) through the inspection windows on the shuttle (Figure 3.9.). The expected static friction coefficients for polycrystalline-Si/polycrystalline-Si, polycrystalline-Si/Si-rich Si-nitride (Si₅N₃) and Si₅N₃/Si₅N₃ interfaces are in the range of 0.2-1. This is based on the tribological investigations carried out by Tas et al. [19] and Corwin et al. [20], which took into account the effect of adhesion between...
contacting surfaces. The force of the in-plane actuator has to be in the range of 40-200 µN.

### 3.5.2. Materials considered for fabrication

Surface-micromachining is chosen for the fabrication of the actuators, since the geometrical precision of the structures can be controlled better than with bulk micromachining processes. The control of the heat transfer during operation of the device is also enhanced due to conduction to a relatively large substrate in which the heat can easily dissipate.

Polycrystalline-Si is chosen as material for the electrical circuits of the actuators, since the electrical properties can be controlled by the amount of Boron diffused into it. It is also a good structural material, which makes it suitable for all types of electrothermal actuators no matter which is the working principle: (i) the mismatch between thermal expansion of unlike materials (bimorph effect) [8-10]; (ii) based on the differential expansion of various geometries micromachined from the same material [11-13]; (iii) thermal expansion of constrained structures [14-17].

The material for electrical isolation of the electrodes is chosen Si₃N₄. An important advantage to Si₃N₄ is that the residual stress in LPCVD Si₃N₄ is much lower. Silicon-oxide is considered for sacrificial material, therefore it is not appropriate for electrical isolation. Polycrystalline-Si, Si₃N₄ and silicon-oxide can all be used as structural materials. However, when silicon-oxide is used as structural layer, then it has to be encapsulated by other materials in order to protect it during releasing.

Properties of the materials depend on the parameters of the deposition processes, therefore assumptions based on the extensive literature [23-34] are difficult to make. However, materials properties such as temperature dependence of the linear thermal expansion coefficients \( \alpha(T) \) [26, 27, 30], temperature dependence of the thermal conductivity \( K(T) \) [28], and electrical properties [29] have been adopted from the literature. The Young’s moduli of the materials have been measured using the technique presented in [35].

Measurement of the resonance frequencies of AFM-probe cantilevers were carried out before and after being coated with the investigated materials. Conformal deposition (uniform coating all over the cantilever) is needed to avoid bending of the cantilever due to residual stress in the deposited layers. Low pressure chemical vapor deposition fulfills this requirement, therefore LPCVD polycrystalline-Si deposited at 590 °C, LPCVD Si₃N₄ deposited at 850 °C, and LPCVD TEOS-based silicon-oxide deposited at 700 °C were the tested materials. The cantilevers were excited by the piezo-stack of an atomic force microscope in tapping mode operation. For a beam with rectangular cross section the resonance frequency ratio of coated and uncoated cantilevers is

\[
\frac{f_2^2}{f_1^2} = 12 \rho_l \frac{E_l}{E_t} \frac{\frac{t}{12} + \frac{E_2}{E_1} \delta \left( \frac{w}{2} + \frac{t}{6} \right)}{\rho_1 t w + 2 \rho_2 \delta (w + t)}
\]  

\[ (3.13) \]
Design of a microtribosensor

where the indices 1 and 2 correspond to uncoated and coated cantilevers respectively (material 1 and 2), $E$ is the Young’s modulus, $\rho$ is the density, $w$ and $t$ are the width and the thickness of the cantilever beam, and $\delta$ is the thickness of the coating.

Single-crystal Si cantilevers have been used for the experiments, with geometrical specifications given by the provider (Nanosensors). The resonance frequencies of the cantilevers have been measured and the Young’s modulus of single-crystal Si has been calculated with

$$E = f_1^2 \cdot \frac{(2\pi)^2}{l_0} \cdot \frac{\delta^3}{t^2}$$

(3.14)

where $l$ is the length of the cantilever. The resulted Young’s modulus of 169 GPa is in good agreement with the data presented in [36]. Subsequently, the single-crystal Si cantilevers were coated with approximately 100 nm thick polycrystalline-Si, $\text{Si}_x\text{N}_y$, and silicon-oxide respectively. The thicknesses of the layers were determined by using wafers on which materials were deposited during the same processes. Ellipsometry was used for $\text{Si}_x\text{N}_y$ and silicon-oxide, while the thickness of the polycrystalline-Si was calculated from the difference of weight before and after deposition. Young’s moduli of the materials were determined from the resonance frequency shift (Eq. 3.13), caused by additional mass. The Young’s moduli determined using this simple technique are in good agreement with data from selected literature (polycrystalline-Si [24], $\text{Si}_x\text{N}_y$ [32, 33], silicon-oxide [34]).

Table 3.1. Determination of Young’s moduli of the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$f_1$ (uncoated) [kHz]</th>
<th>$f_2$ (coated) [kHz]</th>
<th>$\delta$ [nm]</th>
<th>$E_2$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>polycrystalline-Si</td>
<td>282.84</td>
<td>298.23</td>
<td>97</td>
<td>161.0</td>
</tr>
<tr>
<td>$\text{Si}_x\text{N}_y$</td>
<td>277.35</td>
<td>310.44</td>
<td>101</td>
<td>298.1</td>
</tr>
<tr>
<td>silicon-oxide</td>
<td>279.24</td>
<td>280.70</td>
<td>99</td>
<td>69.3</td>
</tr>
</tbody>
</table>

3.5.3. Design and simulation of electrothermal actuators

The design of the electrothermal actuators was directioned so that each of the operating principles is represented: (i) the mismatch between thermal expansion of unlike materials (bimorph and trimorph actuators), (ii) based on the differential expansion of various geometries micromachined from the same material (hot-leg/cold-leg actuator), (iii) thermal expansion of constrained structures (double-clamped beam). Experimental characterization of the actuators is presented in chapter 5.

Finite Element Modeling (FEM) was used for the performance simulation of the actuators (Ansys 6.0). The preprocessing consists of creating the geometry of the device, assigning materials and the type of elements for the structures (brick, tetrahedral, etc.), defining properties of the materials (mechanical, thermal and electrical), discretizing the structures, and finally, applying constraints and eventually loads on the device. The
constraints are structural for clamping, thermal for heat sinks and electrical for actuation through the contact pads. For this type of analysis the loads are also structural (force, pressure, etc.), thermal (convection, heat flux, etc.) and electrical (current, charge, etc.). Coupled-field analysis was used since the simulations are based on the combination of electrical, thermal, and mechanical effects. Simulation results were used as feedback to change the design of the actuators, in consequence to change the performance.

Initially, constant materials properties were considered (at room temperature), in order to simplify the computations. Nevertheless, for the simulation of the fabricated actuators the temperature dependence of the thermal conductivity $K(T)$ and the linear thermal expansion coefficient $\alpha(T)$ of the materials have been used. The clamping of the actuators are considered heat sinks in the simulations, because the surface-micromachined structures are very small compared to the size of the substrate, and the generated heat can easily diffuse.

a) Coupled hot-leg/cold-leg in-plane actuator

The design is based on hot-leg/cold-leg actuators [13, 37] coupled together in order to increase the force that can be provided. Motion is generated due to differential expansion of a hot (2 µm wide) and a cold (14 µm wide) leg, micromachined from the same material. The tips of six actuators are connected to a beam (Figure 3.11.), so that the force of the device is the sum of the individual contribution of each hot-leg/cold-leg actuator. The calculated in-plane force of the device is 81 µN in neutral position, if the length of the hot and cold-legs is 250 µm and the thickness of the polycrystalline-Si is 2 µm. The maximum deflection of the shuttle that can be achieved (Figure 3.12.) is limited in simulations by reaching the melting temperature of the polycrystalline-Si. In experiments there is an additional effect that reduces the actuation power at which reproducible performance of the actuator can be obtained. This will be discussed in chapter 5, and it will be shown that this is a common feature of all types of electrothermal actuators.

![Figure 3.11. Finite element simulation of coupled hot-leg/cold-leg actuator: temperature distribution at 23 V DC operation.](image)
b) Multimorph actuator

The actuator consists of three layers of dissimilar materials, which upon Joule heating expand differentially, and the linear thermal expansion mismatch produces a deflection of the free end of the structure. Two symmetric legs of 1.5 µm thick B-doped polycrystalline-Si (length - 250 µm; width - 14 µm; gap between legs - 2 µm) form the electrical circuit (Figure 3.13). A 0.8 µm thick silicon-oxide is encapsulated (length - 244 µm; width - 8 µm) between the polycrystalline-Si and a 0.25 µm thick Si₃N₄ layer. The silicon-oxide is used as structural material because it has the lowest linear thermal expansion coefficient from known materials. The capping Si₃N₄ layer is needed to protect the silicon-oxide during sacrificial releasing.

Figure 3.14. shows the temperature distribution along the actuator at operation near to the melting point of the polycrystalline-Si. The temperature profile along the actuator (Figure 3.15.(a)) shows that the maximum temperature is obtained at the tip of the actuator, where the symmetric legs are connected by a 4 µm wide polycrystalline-Si beam. The graph also shows the efficiency of the contact pads as heat sinks. Simulated and measured tip-deflection of the actuator are compared in Figure 3.15.(b).

The structural force vs. actuation voltage dependence can also be estimated for the neutral position of the actuator (Figure 3.16.). The force that the actuator generates upon heating when held in its neutral position is equal to the force necessary to deflect the structure without heating to the same deflection as it would deflect when heated and not obstructed [38].

Figure 3.12. Displacement of the shuttle vs. actuation voltage.

Figure 3.13. Sketch of the trimorph actuator: top-view (upper graph) and cross-section (lower graph).
Chapter 3

Figure 3.14. FEM simulation of the trimorph actuator – temperature distribution at 15 V DC operation.

Figure 3.15. (a) temperature distribution along the actuator leg for 15 V and 12 V DC operation in ambient conditions, (b) simulated and measured tip deflection vs. actuation voltage.

Figure 3.16. (a) - structural force vs. actuation voltage and (b) - maximum temperature vs. actuation voltage.
c) Double-clamped parallel-beams

The working principle of this device is based on buckling of a constraint beam upon Joule heating. The preferential buckling direction is defined in the design by the stress gradient across a bimorph structure of a 1.5 µm thick Boron-doped polycrystalline-Si and a 0.25 µm thick Si₃N₄ layer (Figure 3.17.(a)). If the bimorph structure is clamped only at one end and is free at the other (Figure 3.17.(b)), then the neutral position of the tip of the structure is above the horizontal plane after fabrication (chapter 5).

The simulated temperature distribution at the limit of operation (melting temperature of the polycrystalline-Si) is presented in Figure 3.18. The calculated maximum deflection of the middle of a 300 µm long double-clamped beam is 11.7 µm, which is in good agreement with the deflection of 13 µm measured in ambient conditions using a micrometer mounted on an optical microscope. The difference can be caused by the limited accuracy of the measurement, fabrication imperfections of the structures, or discrepancy between the adopted and real temperature dependence of the materials properties.

![Figure 3.17. Design of the bimorph structures: (a) double-clamped parallel-beams, (b) bimorph structure with one clamped and one free end.](image)

![Figure 3.18. Temperature distribution along the double-clamped beam at the limit of operation.](image)

The estimated maximum force that can be generated with one 300 µm long double-clamped beam is 90 µN at neutral position. Multiple beams operated together can produce larger force, a solution which can be realized by mechanical connection and electrical isolation of several beams. The design of such a device is shown in Figure 3.19.

The out-of-plane actuator consists of two pairs of double-clamped parallel-beams connected by a lever. The geometrical characteristics of the device used for simulation are
given in Table 3.2.

Table 3.2. Geometrical characteristics of the actuator.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>[µm]</td>
<td>300</td>
<td>4</td>
<td>14</td>
<td>4</td>
<td>230</td>
<td>14</td>
</tr>
</tbody>
</table>

The actuator can provide upward or downward motion if only one pair of parallel-beams is actuated, the motion being defined by the relative position of the actuated pair of beams (Figure 3.20). It can also work as a crane if both pairs of parallel-beams are actuated simultaneously at the same electrical power. In this case the force contributions of both pairs of parallel-beams to the total force of the actuator are the same. The crane-like actuation can provide a deflection equal to the deflection of the individual beams. Downward actuation of the lever-tip is limited by the fabrication, the magnitude of the motion is determined by the gap between the substrate and the lever. The calculated upward lever-tip deflection of the device with characteristics listed in Table 3.2, was 25 µm. The provided force and deflection ranges can be changed by varying the ratio between the lengths of the lever-arms.

Figure 3.19. Design of a powerful out-of-plane electrothermal actuator based on double-clamped parallel-beams mechanically connected by a lever.

Figure 3.20. Finite element simulation of upward and downward actuation of the lever-tip.
3.6. Simulation of the microtribosensor

The operation of the microtribosensor presented in Figure 3.9. was simulated by finite element modeling for adhesion and friction mode, in order to test the viability of the idea from mechanical and electrical points of view. Figure 3.21. shows the microtribosensor in neutral position. In the simulation of the friction mode only the in-plane actuator is operated and the device performs a reciprocatory motion (Figure 3.22.).

When the trimorph actuators are operated, the shuttle carrying the test surfaces is pulled off the substrate (Figure 3.23.). The conclusion of numerical simulations is that unless fabrication problems are encountered, the microtribosensor should enable adhesion, friction and wear testing.

![Figure 3.21. Neutral position of the microtribosensor.](image)

3.7. Conclusions

The requirements of a microtribosensor have been estimated by using a contact model which takes into account adhesion, and by using data from literature on friction encountered in microsystems.

A microtribosensor has been designed which provides coupled and decoupled in- and out-of-plane motions for adhesion, friction and wear investigations. The microtribosensor consists of different in- and out-of-plane actuators, which performances were simulated by finite element method. The operation principle of the microtribosensor was simulated for friction and adhesion testing modes. It was shown that unless fabrication problems are encountered, the microtribosensor should enable the tribological tests it was designed for.
3.8. References

Design of a microtribosensor


Chapter 4

Technological development for fabrication of complex MEMS devices

Abstract

A study on thick Si₃Nₓ/polycrystalline-Si/silicon-oxide multilayer-stacks obtained by LPCVD and PECVD techniques is presented. The pattern transfer into the multilayer-stacks is achieved by an optimized reactive ion etching process. The steep profiles and good selectivity obtained allow the fabrication of complex MEMS devices consisting of multiple Si or polycrystalline-Si layers built up on multiple sacrificial layers. A new etch-stop technique has been developed, which enables accurate stopping on any particular layer with an SF₆-based ICP plasma etch process. In order to obtain freestanding structures for tribotesting purposes, the residual stress variation of thick undoped silicon-oxide layers (obtained by various methods) has been studied for high temperature processing.

In the second part, a novel timesaving and cost-effective release technique is described which allows successful releasing of MEMS devices built up on multiple sacrificial layers, but which do not consist of (almost) sealed cavities. The physical nature of the process is explained in combination with experimental observations. Results of the flash release process are compared with those of freeze-drying and supercritical CO₂ releasing. It is demonstrated that the new technique is not only simpler but it also gives higher yield for long cantilevers.

4.1. Introduction

New micromachining challenges arise as MEMS devices become more and more complex from structural and operating points of view. A device that can be operated as shown in Figure 4.1. demands new technological solutions. The properties of materials [1-3] and micro-machining techniques [4-7] available in the literature were considered as starting point for the fabrication of such a device.

If simultaneous motions in different directions are needed, then the electrical circuits must be separated by dielectric materials or gaps. In order to allow this, the change of properties during processing of available sacrificial materials has been investigated. The thickness of these layers is determined by the thickness of the structural layers, as well as by the vertical gap between different structures which are mechanically contacting each other.
only during operation (tribological tests).

![Figure 4.1. Motions that must be provided by an ideal microtribotester.](image)

Another challenge during surface-micromachining of complex devices was the elimination of misalignment between structures, needed to protect various materials during fabrication (e.g. releasing) and operation. As an example, Figure 4.2. shows the trimorph out-of-plane actuator, which can deliver a few hundred of µN at a few µm displacement [8, 9]. The silicon-oxide layer, used for structural purpose, is encapsulated between a polycrystalline-Si and a capping Si₃N₅ layer for protection during sacrificial releasing.

![Figure 4.2. Out-of-plane multimorph actuator: front view and cross section.](image)

4.2. Undoped silicon-oxides as sacrificial material for multilayer-stack structures

Complex MEMS devices often need multiple electrical circuits for simultaneous operation of different actuators. In order to avoid short-circuiting, the electrical circuits can be isolated from each other either by inserting dielectric materials or by using local doping techniques. The first solution [26, 27] would further complicate an already complex fabrication process by depositing and etching additional materials, while the second method requires appropriate choice of materials for high temperature processing. Phosphorous Silicate Glass (PSG) as a sacrificial layer is not suitable for local doping of multiple Si or
Fabrication of complex MEMS

polycrystalline-Si layers because it provides global (wafer-wide) doping. Therefore, Solid Source Dotation (SSD) of Boron was chosen as technological solution to locally dope polycrystalline-Si layers. The residual stress change of undoped silicon-oxides was investigated for processing up to 1100 °C. This temperature is required for diffusion of B into Si and polycrystalline-Si in order to obtain a uniform distribution through a 2 µm thick layer in reasonably short processing time.

Problems related to residual stress and fracture have already been reported for thick (>10 µm) Plasma-Enhanced Chemical Vapor Deposited (PECVD) tetraethylorthosilicate-based (TEOS) and SiH4-based silicon-oxide layers \[2, 25\]. The focus point of this work is to create and optimize thinner (~2.5-3 µm) undoped sacrificial silicon-oxide layers, which allow crack-free fabrication of complex MEMS devices and avoid other stress related problems, such as bent structures which after releasing touch the substrate or modify the designated neutral position of the device.

There are certain drawbacks of using a particular silicon-oxide, no matter how it is obtained. The deposition parameters of the investigated materials are listed in Table 4.1. Low Pressure Chemical Vapor Deposited (LPCVD) TEOS-based silicon-oxide cracks if a thickness of 1.8 µm is exceeded, but it was observed that deposition of layers thicker than 1.4 µm is critical if a process step follows which requires temperatures above 800 °C. Big wafer bow results from the deposition of PECVD SiH4-based silicon-oxide. As a consequence, no accurate pattern transfer can be applied without additional treatments. Silicon-oxide obtained by wet oxidation at 1150 °C (WOX) of a polycrystalline-Si layer deposited at 590 °C comprises very high compressive residual stress. The WOX silicon-oxide exhibits rather rough surfaces (R\text{a}~ 4.5-6.5 nm for a 2.5 µm thick layer), which act as mould for the next structural layer. Nevertheless, all of these silicon-oxide layers have several interesting features. First of all they are no doping sources for Si or polycrystalline-Si. The PECVD silicon-oxide does not crack during annealing. Moreover, the compressive stress is released to a certain fraction due to processing at high temperatures (Table 4.2.). The WOX silicon-oxide is very stable during processing, once it has been obtained, the stress variation is within narrow limits and the layer does not crack. It has good step coverage, similar to LPCVD silicon-oxide. The stress in LPCVD silicon-oxide is tensile but small, and the effect of residual stress on the wafer bow is minimal due to double-sided deposition.

<table>
<thead>
<tr>
<th>Mat.</th>
<th>TEOS [sccm]</th>
<th>SiH4 [sccm]</th>
<th>N2O [sccm]</th>
<th>p [mTorr]</th>
<th>T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPCVD</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td>700</td>
</tr>
<tr>
<td>PECVD*</td>
<td>-</td>
<td>200</td>
<td>710</td>
<td>650</td>
<td>300</td>
</tr>
<tr>
<td>WOX</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>250</td>
<td>590</td>
</tr>
</tbody>
</table>

* 13.56 MHz plasma frequency, 2% SiH4 in N2

Experiments demonstrated that the combination of PECVD and LPCVD silicon-oxide layers have ideal properties for use as sacrificial layer. The PECVD silicon-oxide looses its high compressive stress due to the temperature at which the LPCVD silicon-oxide is...
Chapter 4

deposited (acts as annealing step). Additionally, the LPCVD silicon-oxide layer confers good step coverage. The residual compressive stress still left in the PECVD silicon-oxide compensates the tensile stress of the LPCVD silicon-oxide layer and prevents crack formation. It was observed that 1.6-1.7 µm thick LPCVD silicon-oxide layers deposited on top of 1 µm thick PECVD silicon-oxide did not crack even after 3 hours annealing at 1100 ºC. When sacrificial layers thicker than 2.5 µm are required, then a PECVD silicon-oxide layer can be deposited on top of the PECVD+LPCVD silicon-oxide stack, or the thickness of the first PECVD silicon-oxide can be increased. Both cases have been explored up to a thickness limit of 3.0 µm. The properties can easily be estimated because the PECVD silicon-oxide gives the dominant properties for processing up to 850 ºC. A comparison of the wafer bows due to PECVD silicon-oxide and silicon-oxide stacks (backside LPCVD silicon-oxide removed) with the same thickness and annealed at 1100 ºC showed no important difference. The explanation is that the compressive stress is built up when the silicon-oxide is cooled down from temperatures that exceed its softening point, after which the different silicon-oxide layers will have similar morphology.

<table>
<thead>
<tr>
<th>status</th>
<th>parameters</th>
<th>LPCVD</th>
<th>PECVD</th>
<th>WOX</th>
<th>PECVD + LPCVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>as deposited</td>
<td>thickness [µm]</td>
<td>2.55</td>
<td>2.54</td>
<td>2.80</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>stress [MPa]</td>
<td>-21.5</td>
<td>+362</td>
<td>+289</td>
<td>+42.5</td>
</tr>
<tr>
<td></td>
<td>roughness Rₐ [nm]</td>
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<td>0.5</td>
<td>6.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>wafer bow [µm]</td>
<td>-7</td>
<td>+110</td>
<td>+84</td>
<td>+12</td>
</tr>
<tr>
<td></td>
<td>cracking</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>annealed at 800 ºC</td>
<td>stress [MPa]</td>
<td>-79</td>
<td>+143</td>
<td>+285</td>
<td>+53</td>
</tr>
<tr>
<td></td>
<td>wafer bow [µm]</td>
<td>-25</td>
<td>+44</td>
<td>+82</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>cracking</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>annealed at 1100 ºC</td>
<td>stress [MPa]</td>
<td>+184</td>
<td>+173</td>
<td>+306</td>
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<td>wafer bow [µm]</td>
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<td>+56</td>
<td>+90</td>
<td>+53</td>
</tr>
<tr>
<td></td>
<td>cracking</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 4.2. shows the influence of high temperature processing on the residual stress and wafer bow of various silicon-oxide layers. The + and - signs indicate compressive and tensile behaviors, respectively. The spread in results is smaller than ±7% of the average values presented in the table.

An interesting effect was observed after annealing the LPCVD silicon-oxide at high temperatures. The tensile stress increased after annealing at 800 ºC, while after annealing at 1100 ºC it turned to compressive one. This can be a reasonable explanation why cracking enhances significantly for the latter case. In contrast, the high compressive stress of the PECVD silicon-oxide releases to one-half after annealing at 1100 ºC and to about one-third at 800 ºC. The WOX silicon-oxide seems to be the most stable during temperature changes.

Investigations showed that the most advantageous undoped sacrificial silicon-oxide can be obtained by a combination of PECVD and LPCVD techniques. The sacrificial layer does not crack up to a (tested) thickness of 2.5 µm, it has a relatively low residual stress
during high temperature processing, and it confers good step coverage.

4.3. Directional etching

MEMS structures (e.g. sealed cavities, bi- or multi-morph elements) often require straight walls and very good alignment due to narrow structures (couple of µm) and small gaps between them (down to 1 µm). Therefore, investigations were carried out on recipes for directional etching of Si<sub>x</sub>N<sub>y</sub>/polycrystalline-Si/silicon-oxide multilayer-stacks with the so-called Bosch process, and on recipes for etching thick silicon-oxide layers with SF<sub>6</sub>-based inductive-coupled plasma (ICP) etch process. Etch-stop techniques have also been studied in order to allow accurate stopping on any particular layer.

4.3.1. Directional etching of thick multilayer-stacks

Si<sub>x</sub>N<sub>y</sub>/polycrystalline-Si/silicon-oxide thick multilayers can be etched in one run or in different steps specific to each of the materials. Experiments were carried out to optimize various processes for one run etching of multilayer-stacks, because the fabrication sequence in the second case often gives misalignment problems, which are critical for further processing. Another problem may arise during operation of the device, when the gaps between structures deviate from the designed ones.

The samples used in the experiments consisted of three layers deposited on a 100 mm p-type <100> single-crystal Si wafer, specifically a 2 µm thick PECVD or LPCVD silicon-oxide, a 1.8 µm thick LPCVD polycrystalline-Si and finally a 0.5 µm thick LPCVD Si<sub>x</sub>N<sub>y</sub> layer.

Various etching masks have been tested such as chromium (Cr), chromium-oxide, and positive photoresists. On top of the Si<sub>x</sub>N<sub>y</sub>/polycrystalline-Si/silicon-oxide stack a Cr layer was sputtered and patterned by wet etching. The quality of the edge of the Cr mask determined the topography of the vertical walls (Figure 4.3.), therefore the optimum thickness of the mask has been determined empirically, which was ~30 nm in this case. Directional etching of Si<sub>x</sub>N<sub>y</sub>/polycrystalline-Si/silicon-oxide multilayer-stacks has been investigated with the Bosch process [7] using the PlasmaTherm SLR Series shuttle-lock system. Perfect directional profiles have been obtained with the process parameters listed in Table 4.3. Etch-stop accuracy of 4-5 nm can be achieved on silicon-oxide if the non-uniformity of the layers is below 5%. This stopping precision is high due to the very low etch-rate of the silicon-oxide and good selectivity between silicon-oxide and polycrystalline-Si. In Figure 4.3. the comparison of the depth of two trenches with different widths denotes good etch uniformity. Furthermore, no notching is observed at the polycrystalline-Si/silicon-oxide interface [10]. The etch-rates of the materials and the input parameters of the optimized Bosch process for multilayer-stack directional etching are listed in Table 4.3.

The directional etching of Si<sub>x</sub>N<sub>y</sub>/polycrystalline-Si/silicon-oxide multilayer-stacks with SF<sub>6</sub>-based ICP plasma (continuous) etch process is difficult to control due to the high ion
energy which creates high etch-rates and poor selectivity. Stopping with high accuracy on a particular layer is not possible, unless additional etch-stop methods are used, which will be discussed in the next section.

Table 4.3. Etch-rates (ER) and input parameters of the Bosch process optimized for multilayer-stack etching.

<table>
<thead>
<tr>
<th>Material</th>
<th>Si₃N₄</th>
<th>poly-Si</th>
<th>silicon-oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER [nm/cycle]</td>
<td>4.6-5.2</td>
<td>150</td>
<td>2.3-2.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>deposition of FC</th>
<th>removal of FC</th>
<th>directional etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄F₈ [sccm]</td>
<td>70</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>SF₆ [sccm]</td>
<td>2</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Ar [sccm]</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>t [s]</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>ICP [W]</td>
<td>950</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>CCP [W]</td>
<td>1.0</td>
<td>14.0</td>
<td>1.5</td>
</tr>
<tr>
<td>VDC [V]</td>
<td>16</td>
<td>70</td>
<td>21</td>
</tr>
</tbody>
</table>

4.3.2. Directional etching with continuous etch process

When thick layers have to be patterned, it is convenient to use processes with high etch-rates. Development of a recipe that allows etching up to 3 µm silicon-oxide with thick photoresist (Olin 908-35) was the target.

The tests have been performed at low pressure in order to increase the mean free path of the ions for a more directional high energetic ion bombardment [6]. Figure 4.4. reveals that the tapered profile of the post-baked photoresist is copied into the material due to poor
selectivity, which excludes the possibility to etch narrow, deep trenches.

Experiments showed that the best silicon-oxide/photoresist selectivity was found for low substrate temperature and low capacitive-coupled plasma (CCP) (Table 4.4. – recipe 3 and 4). Nevertheless, there are limitations given by the low ion energy, thus a decrease of the CCP will reduce the etch-rate of the silicon-oxide drastically.

Table 4.4. Directional etching of silicon-oxide with the continuous etch process using photoresist (PR) as mask – recipes and etch-rates.

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<tbody>
<tr>
<td>5</td>
<td>1200</td>
<td>30</td>
<td>60</td>
<td>9</td>
<td>6</td>
</tr>
</tbody>
</table>

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<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>160</td>
<td>10</td>
<td>&gt;350</td>
<td>&lt;230</td>
<td>&lt;0.65</td>
</tr>
<tr>
<td>2</td>
<td>-40</td>
<td>18</td>
<td>68</td>
<td>5</td>
<td>201</td>
<td>170</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>-40</td>
<td>15</td>
<td>61</td>
<td>2</td>
<td>75</td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>-40</td>
<td>5</td>
<td>34</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

The Cr etch mask allows etching trenches with rectangular shaped cross-section as shown in Figure 4.5. There were no significant differences in etching silicon-oxides obtained by LPCVD, PECVD or WOX techniques using the recipe listed in Table 4.5.

Due to the high etch-rates of the examined materials additional etch-stop methods and endpoint detections have been investigated in order to improve the accuracy of stopping on a particular material. It has been observed that the self-bias voltage VDC changed when one particular layer had been etched through. The change is in the order of 1-2 V and it depends on the material. This method can be used efficiently as endpoint detection.
By using the etch process with the recipe listed in Table 4.5, a new etch-stop technique has been developed, which allows stopping accurately on polycrystalline-Si layer after the silicon-oxide is selectively removed (Figure 4.6). This method can also be used for stopping on other materials such as silicon-oxide, Si$_x$N$_y$, and Si, despite the poor selectivity between them.

Table 4.5. Etch-rates and input parameters of the continuous process using Cr mask.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>pressure [mTorr]</td>
<td>5</td>
</tr>
<tr>
<td>ICP [W]</td>
<td>1200</td>
</tr>
<tr>
<td>SF6 [sccm]</td>
<td>30</td>
</tr>
<tr>
<td>Ar [sccm]</td>
<td>60</td>
</tr>
<tr>
<td>He [sccm]</td>
<td>9</td>
</tr>
<tr>
<td>He [Torr]</td>
<td>6</td>
</tr>
<tr>
<td>Temp [°C]</td>
<td>20</td>
</tr>
<tr>
<td>CCP [W]</td>
<td>18</td>
</tr>
<tr>
<td>VDC [V]</td>
<td>114</td>
</tr>
<tr>
<td>etch-rate silicon-oxide [nm/min]</td>
<td>201-210</td>
</tr>
<tr>
<td>etch-rate Si$_x$N$_y$ [nm/min]</td>
<td>246</td>
</tr>
<tr>
<td>etch-rate poly-Si [nm/min]</td>
<td>&gt;750</td>
</tr>
</tbody>
</table>

The technique consists of sputtering a thin (~30 nm) Cr layer onto the layer on which etch-stopping is required. This Cr layer efficiently stops etching, but we observed that chromium-oxide layer is formed during silicon-oxide deposition or annealing step when one or both sides of the Cr layer are in contact with silicon-oxide. Chromium-oxide also proved to be a good etch-stop layer, but it can cause limitations (design or in further processing) if it is not removed.

Figure 4.6.(b) shows that the Cr or chromium-oxide can be removed before deposition of the layer that needs to be patterned, from areas where it is not needed as an etch-stop. After using the etch-stop layer for directional etching, it can be removed from the
surfaces by wet etching.

![Figure 4.6. Chromium-oxide etch-stop layer: (a) left on the whole wafer and buried by a top layer; (b) removed from where it is not needed as etch-stop before deposition of a top layer.](image)

4.3.3. Conclusions

Etching of directional profiles in multilayer-stacks can be carried out with the optimized Bosch process, without notching.

Thick silicon-oxide layers can be etched with the SF₆-based ICP plasma etch process with relatively high etch-rate. The directional profile depends on the mask layer used in the process.

Using Cr or chromium-oxide as etch-stop layer allows stopping on polycrystalline-Si, single-crystal Si, Si₃N₄, and silicon-oxide, with both reactive ion etching processes.

4.4. Flash release – an alternative for releasing complex MEMS devices

The release process plays a crucial role for MEMS devices fabricated by surface-micromachining. Special precautions need to be taken to prevent stiction of structures, which is easily induced by the relative large surface tension and capillary forces encountered by the micro-sized structures.

Although there are well known techniques such as evaporation drying [11, 12], freeze-drying (sublimation) [13], supercritical CO₂ drying [14], wet releasing [15], vapor HF releasing [16, 17], the concern generally remains on how to simplify release processes without diminishing the yield. Techniques based on processing with two or more liquids (e.g. freeze-drying [13]: hydrofluoric acid (HF) or buffered HF (BHF) for sacrificial etching, deionized water, isopropyl alcohol (IPA), cyclohexane) require good handling skills. Nevertheless, liquids used in subsequent steps of the process can get trapped between structures and can obstruct the release of complex MEMS devices.

The fabrication of the MEMS device shown in Figure 3.19 needed special requirements, thus various micromachining techniques have been developed or adapted [18]. However, the bottleneck proved to be the releasing of the device, since relatively long and narrow (down to 1.5 µm) structures are used, and the gaps between structures of 1.5-2 µm
turned out to hamper substitution of different processing liquids during releasing. The device could not be released successfully using freeze-drying, apparently due to incomplete substitution of the IPA by cyclohexane in the critical parts (Figure 4.7.), hindering full-scale sublimation of the cyclohexane in a subsequent process step.

An alternative release technique has been investigated in order to obtain good yield without using too many intermediate steps and processing liquids. The technique developed was tested on cantilevers, membrane-like structures (etched cavities) and the results were compared with those obtained with freeze-drying and supercritical CO2 releasing.

4.4.1. General considerations

The mechanism of releasing microstructures by evaporation of different liquids has been studied on cantilevers with different geometrical characteristics [11, 12]. For short rigid structures the water dried from the tip towards the clamping, these being completely released, while for longer compliant structures the water dried towards the tip and the cantilevers were stuck to the substrate. Theoretical models for both stiction modes of the cantilevers (s-shaped and tipping) have been developed by de Boer et al. [19].

The alternative release technique, called flash release due to extremely fast dynamics, is inspired from the supercritical CO2 releasing. The principle of the supercritical CO2 releasing is that liquid CO2 is brought to supercritical state in a closed chamber. Nevertheless, the pressure and temperature of the critical point of CO2 are far below that of the water (CO2: 73 bar, 31.1 °C; water: 218 bar, 374 °C). The conditions of the supercritical zone of the water are difficult to reach without special equipment, hence supercritical water releasing has not been explored extensively.

The flash release is the result of investigations to reach the conditions nearby the critical point just locally, in close proximity to the wafer. This can be achieved by heating the wafer (including the water that covers the microstructures) very fast to temperatures above that of the critical point. The fast temperature rise of the water by using open systems such as multifunctional oven is only possible if the temperature of the oven is well above the targeted one. This is equivalent to a thermal shock with subsequent drastic increase of pressure.

Figure 4.7. Cross-section of the critical part of the microtribosensor (gaps 1.5-2 µm). Structure 1 is electrically and mechanically decoupled from 2 but during operation it generates out-of-plane motion transmitted to structure 2.

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4.4.2. Physical nature of the process

The release process consists of three major steps: (i) removal of the sacrificial material, (ii) substitution of the etching fluid by deionized (DI) water, and (iii) removal of the DI water from the wafer. The last step is in fact the key issue of the process. In this section we will try to elucidate its physical origin. Assumptions, calculations and experimental observations are presented in order to understand the release process.

Subsequent to the second step (ii) the Si wafer, on which the microstructures are micromachined, is covered with about 1 mm thick DI water layer. It is placed horizontally on a rack and shifted very fast (\(\tau_i \sim 0.5\) s) into an oven at a temperature of 600 °C. The time \(\tau_h\) needed to heat the wafer up to the critical temperature of the water can be estimated from the energy balance of the lumped capacitance method [20]

\[
- h A (T - T_{in}) = \rho_s V \frac{dT}{d\tau_b}
\]  

(4.1)

\(\tau_i\) is in the range of 4-5 seconds for a 4 inch Si wafer (for symbols see the nomenclature at the end of the chapter). This time almost coincides with the time required for heating the water layer, calculated by taking into account the thermal diffusivity of water.

It is important to calculate whether the water has time to evaporate before the wafer reaches its place in the oven or before the temperature of the water, covering the microstructures, reaches temperatures near \(T_c\). The speed of normal vaporization without boiling [21] can be estimated with

\[
v_r = \alpha p(T) \cdot \left( \frac{2 \pi m k T}{\rho} \right)^{1/2} \frac{m}{\rho}
\]  

(4.2)

If we assume that the water is heated very fast, then the recession velocity in one-dimensional situation is

\[
v_r = \alpha \cdot \rho_d(T) \cdot \left( \frac{1000}{T} \times \frac{100}{M} \right)^{1/2} \times 5.28 \times 10^7 \text{ [monolayers /s]}
\]  

(4.3)

From Eq. (4.3) results that about 20 seconds would be needed for recession of 1 mm thick water layer at critical temperature. It means that there is still thick enough water layer on the wafer to cover the microstructures when the wafer reaches its position in the oven and by the time the temperature of the water increases to near critical value \(T_c\). This fact was also confirmed by visual observations.

The key phenomenon in the release process is the boiling. Since the wafer is almost atomically smooth, there are little defects where bubbles can be generated. Also by using DI water the number of seeds where bubbles can form is very small. All of these will delay the heterogeneous (ordinary) boiling. The temperature in the oven was chosen to be about 600
°C in order to avoid ordinary boiling by speeding up the heating process. It was observed that during heterogeneous boiling all the microstructures were broken due to formation of large vapor bubbles.

When the conditions to avoid ordinary boiling are fulfilled (τ_\text{i} \ll τ_\text{h} and τ_\text{h} small, T_{\text{ov}} \sim 600 ^\circ \text{C}), then homogeneous (explosive) boiling occurs. Although it is a fast dynamic process, it is helpful to use a schematic phase diagram (Figure 4.8.) to discuss the process cycle.

The initial and the final points of the process are designated \( i \) and \( f \) respectively, these are the two equilibrium points of the process, while \( c \) corresponds to the transitional critical point.

![Figure 4.8. Schematic phase diagram of the water (spinodal and binodal not to scale). i – initial point of the process (ambient conditions); f – final point of the process; c – critical point.](image)

Besides the binodal line describing the normal phase transition, the p-T diagram contains a spinodal line [21], which describes the boundary of thermodynamic stability. Between the spinodal and binodal curves there is a metastable region where liquid can be superheated. As the wafer is shifted into the oven, the process will follow the curve \( i-b \), which means that the water is superheated without major pressure change in the very first instance. When the temperature of the water approaches the critical value \( T_c \), significant volume fluctuations appear [21]. These fluctuations support spontaneous bubble formation. Small nuclei of vapor in liquid must have a critical size to start to evolve, otherwise they will shrink and disappear.

The pressure inside the bubbles is balanced by the pressure in the liquid and by the surface tension

\[ p_x - p_\text{l} = \frac{2\gamma}{r_c} \]  \hspace{1cm} (4.4)

from which the estimated critical size of the bubbles is several micrometers for near room temperature and few nanometers in the vicinity of the critical conditions. The minimal nucleation energy for the critical bubble [22] is
The probability of homogeneous nucleation at a given temperature $T$ is proportional to $exp(-W_{\text{min}}/kT)$. For room temperature the nucleation energy is several orders of magnitude larger than $kT$, hence the probability of homogeneous nucleation is negligible. However, in the vicinity of $T_c$ the magnitude of this energy becomes comparable with that of $kT$, and the probability of nucleation increases considerably.

The rate of homogeneous nucleation [22], specifically the number of nuclei in 1 cm$^3$ in one second, can be estimated with

$$I_n = \lambda \cdot N_0 \cdot \exp\left(-\frac{W_{\text{min}}}{kT}\right)$$

where $\lambda = kT / b_p$

(4.6)

Calculations show that $I_n$ is zero for near room temperature, while at near critical temperature the number of nuclei is extremely large, e.g. for $T = 0.93 \cdot T_c$ the order is $10^{28}$ nuclei/cm$^3$·s [21]. At temperatures in the vicinity of the critical point the water suddenly transforms to bubbles with high pressure inside. The coalescence of this large number of small bubbles instantly produces high pressure inside the volume and the system gets in point $b$ on the binodal line, near the critical state. The experimental evidence that such a high pressure develops during the release process will be shown and discussed in the following section.

It is impossible to pass the boundary of thermodynamic stability during the release process in an open system, thus it is interesting to investigate possible scenarios for the rest of the process. The simplest is that the high-pressure vapor diffuses into the air and subsequently the pressure in the vicinity of the wafer drops to 1 atmosphere, while the environment around the wafer is heated to 600 °C. However, the phase explosion (explosive boiling) takes place within 30 nanoseconds [21], during which large volume fluctuations occur. The diffusion process is much slower, 1 mm thick water layer needs about 0.04 second to diffuse into the air. The limitation due to diffusion combined with the large volume fluctuation during extremely short time can cause slight pressure rise, which could be enough to reach the critical conditions locally, in close proximity of the microstructures. Very fast pressure relaxation follows and the temperature stabilizes at 600 °C (Figure 4.8, curve $c$).

4.4.3. Experimental investigations

Although the process has first been tested on complex structures like the microtribotester, the unexpectedly high yield using the flash release prompted detailed investigations.

The best results have been obtained in the oven heated to 600 °C, when cantilevers with various widths were released up to a length of 1 mm with good uniformity on the wafer. It was observed that for lower temperatures (in the range of 500-550 °C) the yield is decreasing as well as the uniformity. For even lower temperatures of the oven (about 450 °C)
ordinary boiling occurred. The same phenomenon took place when the shifting speed of the wafer into the oven was low. In both cases the microstructures (cantilevers, bridges, membranes) were almost 100 percent destroyed. This can be explained with the heat exchange between the wafer and its environment, causing alteration of the appropriate conditions for homogeneous boiling.

Simple microstructures such as cantilevers, bridges and etched cavities (membranes) were fabricated in order to compare the yield of the flash release to that of other release techniques. The fabrication layout was almost identical to the first part of the processing of the microtribosensor [18]. A <100> single-crystal Si wafer was first thermally oxidized to obtain a 2 µm thick sacrificial silicon-oxide layer, then a 2 µm thick small-grained polycrystalline-Si was deposited at 590 °C with LPCVD technique, and later doped with Boron at 1050 °C for 1 hour long. Subsequently the wafer was annealed at 1100 °C for 3 hours. The doped polycrystalline-Si was patterned using a Bosch RIE process [18]. The releasing of microstructures was carried out with three different techniques: freeze-drying, supercritical CO₂ release and flash release. In Figure 4.9, the techniques are presented with the intermediate steps form start to finish. For all three processes the sacrificial silicon-oxide is removed by HF or BHF. The advantages of the flash release to the other two techniques are that it uses just two processing liquids, consequently the contamination during release is minimized, and that no special equipment is required.

![Figure 4.9. Release techniques used for the comparison of the yield of cantilevers.](image)

Differential interference contrast technique (DIC) has been used to compare the yield of the three release processes. Pictures in Figure 4.10, show that the last set of successfully released cantilevers with freeze-drying is 675 µm long and those not released are pulled down (C1 to C3); the supercritical CO₂ release is successful up to a length of 455 µm (till C7), while
the flash release freed all the cantilevers with length up to 1 mm. Small deflection of the long cantilevers, induced by the stress gradient in the doped polycrystalline-Si layer, can be observed in Figure 4.10.(c) and Figure 4.11. The gap between the tip and substrate decreases as the width of the cantilever increases, but the tip is not touching the substrate yet for 1 mm long and 100 µm wide cantilevers.

![Figure 4.10](image-url)

**Figure 4.10.** The released cantilevers with: (a) freeze-drying – up to 675 µm; (b) supercritical CO₂ releasing – up to 455 µm; (c) flash releasing – up to 1 mm. The widths of the cantilevers are 10, 50 and 100 µm for each set with different length.

![Figure 4.11](image-url)

**Figure 4.11.** SEM photographs of flash released cantilevers on tilted table (upper picture - along the cantilevers; lower pictures – at the tip). C1 and C2 sets of cantilevers are 1 and 0.9 mm long respectively. For wider cantilevers the gap between the tip and substrate decreases due to larger stress gradient.

Returning to the theoretical considerations in the previous section, experimental evidence has been sought for the generation of very high pressure in close proximity of the wafer. Etched cavities were used for this purpose, which can be regarded as clamped membranes. Through etch-holes the sacrificial oxide was removed and the etchant was substituted with DI water, then the flash release was carried out. The expected behavior of the membranes was that they break if high pressure builds up, but the way they broke denoted extremely high pressures, which can be a couple of hundreds of bars. Close examination
revealed that the polycrystalline-Si was broken along the clamping, specifically where the membranes were still resting upon silicon-oxide (Figure 4.12.).

![before flash releasing](image1.png) ![after flash releasing](image2.png)

**Figure 4.12.** Top views of sacrificially underetched membrane-like structure (cavity) before and after flash releasing. It consists of 2 µm thick B-doped polycrystalline-Si on 2 µm thick sacrificial silicon-oxide. Close-up of the broken membrane (SEM table tilted 60°) shows that the membrane is sheared at the clamping perimeter.

The polycrystalline-Si membranes were blasted and propelled so that no remains were found by examination with optical microscope. Analytical calculation according to [23] showed that pressure larger than 70 bar is required to simply break such a membrane, but this would happen along a fracture line and definitely not along the clamping perimeter.

The reason why cantilevers and bridges survived the flash release and membranes did not is that during the phase explosion the pressure difference becomes extremely large only between the two sides of the membrane. The membrane obstructs the diffusion of the high-pressure vapor into the air from the bottom-side, while it can freely diffuse on the topside.

The yield of the flash release of complex MEMS devices has been proved by successful operation of the microtribosensor (sketch in Figure 3.9.), in both directions (in- and out-of-plane) in environmental conditions and under vacuum. Figure 4.13. shows the SEM photograph of the actuated micromechanism on a 45° tilted table, representing the critical part of the tribosensor shown in Figure 4.7. for exemplification of complex structures consisting of multiple doped polycrystalline-Si layers built up on multiple sacrificial silicon-oxide.

Apparently the process looks simple, but mistakes, which are crucial to the release of the microstructures, can easily be made. The most important three that have been observed experimentally are: (1) if the sacrificial etchant is not completely substituted with DI water, then the high temperature enhances the etch-rate of the vapor HF, so that the wafer will be completely stripped of functional layers such as Si₃N₄ for electrical isolation; (2) if the position of the wafer is not horizontal, then the water flows down from the wafer, which might cause stiction of the structures before the wafer reaches its place in the oven; (3) fast handling is required, otherwise the wafer heats gradually up and ordinary boiling occurs which destroys all the microstructures on the wafer.
The high temperature during the release process does not affect the structures considerably due to growing of a silicon-oxide layer around the Si or polycrystalline-Si structures, since the oxidation rate at 600 °C is still low. The reported thicknesses of the silicon-oxide grown in dry and wet conditions are approximately 1.5 and 1.7 nm respectively for an oxidation time of about 450 seconds [24]. The period while the wafer is at 600 °C in the oven is even shorter for the flash release, consequently the silicon-oxide layer grown during the release process is not much thicker than the native silicon-oxide layer that forms on Si or polycrystalline-Si surfaces when the MEMS devices are stored.

4.5. Conclusions

The process development for a microtribosensor, which can provide coupled and decoupled in- and out-of-plane motions for various tribological investigations, has been presented.

The change of residual stress of undoped sacrificial silicon-oxides has been investigated. By choosing appropriately the combination of LPCVD and PECVD silicon-oxides, the residual stress can be minimized. Annealing PECVD, LPCVD or a combination of PECVD and LPCVD silicon-oxide layers at 1100 °C gives almost identical compressive residual stress, which is an indication that different silicon-oxides have similar morphology after cooling them down from temperatures that exceed their softening point.

Perfect directional profiles have been obtained for etching multilayer-stacks with the optimized Bosch process. Directional etching allows stopping on a particular layer with both, SF₆-based ICP plasma and the Bosch processes. This can be achieved by using low ion energy, controlling the uniformity of the layers or with etch-stop methods such as additional stopping layers or endpoint detection with the bias voltage.

A novel timesaving and cost-effective release technique has been developed which gives good yield for complex MEMS devices that consist of multiple structural layers built up on multiple sacrificial layers. The physical nature of the release technique has been discussed and it has been shown that extremely high pressure builds up in close proximity to the structures by phase explosion.
Chapter 4

There are three important requirements for successful releasing: good substitution of the sacrificial etchant, fast handling of the wafer and appropriate temperature of the oven.

From the comparison of three release techniques: freeze-drying, supercritical CO₂ release and the flash release, it turns out that the latter gives better yield for cantilevers. Moreover, contamination during releasing is minimized.

The limitation of the technique due to high pressure that builds up during the process does not allow releasing MEMS devices that contain enclosed cavities.

The developed processes enable the fabrication of complex MEMS devices such as the microtribosensor, consisting of multilayer-stacks and multiple locally doped polycrystalline-Si layers.

4.6. References


Fabrication of complex MEMS


Chapter 4

Nomenclature

\( A \) – heated area of the Si wafer
\( \epsilon \) – specific heat of Si
\( h \) – convection heat transfer coefficient of air
\( h_p \) – Planck’s constant
\( I_n \) – rate of homogeneous nucleation
\( k \) – Boltzmann’s constant
\( m \) – mass of the H\(_2\)O molecule
\( M \) – molecular weight of H\(_2\)O
\( N_i \) – molecular density in molecules/cm\(^3\)
\( p, p_l, p_g \) – pressure (\( l \) - liquid, \( g \) - gas)
\( p_s(T) \) – temperature dependent pressure in units of atmosphere
\( r_c \) – critical radius of the bubbles
\( T, T_\infty \) – temperature (\( \infty \) - far field)
\( T_c \) – critical temperature of water
\( V \) – volume of Si wafer
\( v_r \) – recession velocity
\( W_{\text{min}} \) – minimal energy for nucleation
\( \alpha \) – vaporization coefficient
\( \gamma \) – surface tension
\( \lambda \) – collision frequency
\( \rho, \rho_{Si} \) – density of water and Si respectively
\( \tau_i, \tau_h \) – time (\( i \) - inserting, \( h \) - heating)

Note: values of the parameters are taken from [20]
Chapter 5

Characterization of polycrystalline-Si based electrothermal actuators

Abstract

Polycrystalline-Si microactuators based on electrothermal principles exhibit many interesting features but their practical use is severely limited by permanent damage that may occur due to accidental overheating. Under these conditions polycrystalline-Si structures will display irreversible structural changes ranging from slight geometrical deformations to complete damage. In this chapter an approach is presented to avoid permanent structural deformation of Boron-doped polycrystalline-Si based electrothermal actuators by overheating. The method allows distinguishing reversible and irreversible actuation conditions, which is demonstrated in ambient environment and under vacuum. It enables full utilization of the capabilities of B-doped polycrystalline-Si based electrothermal actuators with reproducible performance.

5.1. Introduction

Electrothermal actuators are used for applications requiring large forces and low actuation voltages such as micromotors [1-3], exploiting their main advantages compared to electrostatic actuators. However, very high local temperatures obtained by Joule heating limit the utilization of electrothermal actuators, thus in certain cases they have to be avoided. At relatively high electrical power, actual values being determined by design and environmental conditions, the actuator changes its neutral position and materials properties, resulting in irreversible change of the geometrical shape. The phenomenon has been reported by different authors, calling it “plastic deformation” [4] or “back bending” [1, 2] and it is explained as a result of a reflow or recrystallization of the material at high temperatures [1] or caused by the stress in the hot arm when the temperature rises to above the brittle-to-ductile transition (approx. 660 °C for polycrystalline Si) [4].

To the best of our knowledge the only indication to actuate the B-doped Si or polycrystalline-Si based electrothermal actuators with reproducible performance is to operate them below the intrinsic temperature of the doped Si or polycrystalline-Si [5]. At this temperature the intrinsic and dopant carrier concentrations are equal. The dopant concentration of polycrystalline-Si at which the number of active carriers saturates is approximately $2 \cdot 10^{20}$ [6]. According to [7], higher dopant concentration causes higher
intrinsic temperature. This can be well above the temperature limit at which plastic deformation initiates due to Joule heating.

Our concern about reversible and irreversible actuation regions of electrothermal actuators originates from investigations on the microtribosensor that requires large in- and out-of-plane forces for adhesion, friction and wear studies of various material-couples [8-10]. The design of the actuators composing the microtribotester has been presented in chapter 3. The main structural material of the actuators is polycrystalline-Si since its electrical properties can be controlled by the amount of Boron diffused into the polycrystalline-Si and because it is suitable for all types of electrothermal actuators no matter which is the working principle [11-18].

The experimental method presented focuses on the onset of the deviation from the neutral position of the B-doped polycrystalline-Si based electrothermal actuators, operated at relatively high electrical power.

5.2. Distinction of reversible and irreversible actuation regions

In order to distinguish the reversible and irreversible operating regions, experiments have been carried out on electrothermal actuators with the working principle from all three categories mentioned in section 3.5.3. The design rules as well as their simulated and experimental performance have been reported earlier in [8, 9], where also the importance of taking the temperature dependence of the properties of the materials into account has been shown. The actuators presented are all surface micromachined, only the embedding in complex MEMS devices needs special requirements [10]. They were fabricated in one and the same batch. The thicknesses of the layers are: polycrystalline-Si – 1.6 µm, Si₃N₄ – 0.25 µm, and silicon-oxide – 0.8 µm (where applicable). The gap between the substrate and the free structures is 2 µm. The measured resistivity of the B doped polycrystalline-Si was 3·10⁻³ Ωcm at room temperature, which corresponds to a doping concentration of approximately 8·10¹⁹ atoms/cm³ [6]. The resistivity of highly doped polycrystalline-Si approaches the resistivity of highly doped single-crystal Si [6], thus the estimated intrinsic temperature of the polycrystalline-Si with a doping concentration of 8·10¹⁹ B atoms/cm³ [7] is approximately 1300 K.

Figure 5.1. Schematic of the electrical circuit used for device characterization.

The actuators were driven by voltage control. The schematic of the electrical circuit used for
device characterization is presented in Figure 5.1. Resistance and operational power were calculated from the voltage of the source and the measured current. The serial resistance of the electrical connection was very low compared to the resistance of the actuators, therefore it was neglected in the interpretation of measurements.

A micrometer mounted on an optical microscope was used for the measurement of the vertical displacements in ambient conditions, while under vacuum, the measurement of the out-of-plane displacement is based on pictures recorded during actuation on a scanning electron microscope table tilted relative to the horizontal plane (Figure 5.2). In-plane displacements have been measured directly with an optical microscope in ambient conditions and based on SEM photographs under vacuum. The measurements are presented for different actuators in ambient conditions or/and under vacuum in order to emphasize that the distinction method of reversible and irreversible actuation regions is applicable for operation in both conditions.

The measurement procedure is the following: I – identification of the initial neutral position of the actuator; II – actuation at a certain electrical power, then measurement of the displacement and electrical resistance after 1 minute; III – electrical power switched off and measurement of the neutral position after 1 minute. Subsequently, the actuation power is incremented and the measurement cycle is repeated (II and III) till the failure of the actuator occurs. The results are collected in the maximum tip displacement vs. electrical power and electrical resistance vs. electrical power graphs for each type of actuator.

5.2.1. Bi- and trimorph actuators

The sketch and the geometrical characteristics of the bimorph actuator characterized are given in Figure 5.3. and Table 5.1. respectively.

Measurement data obtained in step III form curve (a) of the displacement vs. power graph (Figure 5.4.), representing the change of the neutral position of the actuator, while
curve (b) shows the maximum displacement of the tip for the range of actuation powers, and it consists of measurement data from step II.

The curves are drawn through the measurement points for guidance of the eye. The effective displacement provided by the actuator for a certain power is the difference between curve (a) and (b).

Table 5.1. Geometrical characteristics of the bimorph actuator.

<table>
<thead>
<tr>
<th>Geometrical characteristics</th>
<th>Dimensions [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>legs</td>
<td>352 x 4</td>
</tr>
<tr>
<td>connection of the legs at tip</td>
<td>20 x 13</td>
</tr>
<tr>
<td>contact pads</td>
<td>100 x 100</td>
</tr>
</tbody>
</table>

Figure 5.3. Sketch of the bimorph actuator: top-view (upper graph) and cross-view (lower graph).

Figure 5.4. Maximum tip-displacement vs. electrical power and electrical resistance vs. actuation power graphs of the bimorph actuator (under vacuum). (a) neutral position of the tip; (b) maximum tip-deflection.
The shift of the initial neutral position of the actuator from the horizontal position “0” after fabrication (Figure 5.4.) is caused by the stress gradient across the bimorph structure (Si$_3$N$_4$ on top of polycrystalline-Si). By increasing the actuation power the displacement becomes larger and larger. From measurements performed for a range of actuation powers it turned out that the actuator could not regain its initial neutral position after a certain threshold value (2.5 mW for the device with geometrical characteristics listed in Table 5.1.) had been exceeded, and by applying higher electrical power the neutral position shifted more and more till the failure of the actuator occurred due to reaching the melting temperature of the polycrystalline-Si.

By analyzing the graphs presented in Figure 5.4. it can be observed that the change of the neutral position of the actuator initiates when the value of the electrical resistance during operation of the device reaches a maximum. This is also confirmed by measurements on the trimorph actuator (Figure 5.5.), with geometrical characteristics listed in Table 5.2., carried out under vacuum.

![Figure 5.5. Sketch of the trimorph actuator: top-view (upper graph) and cross-view (lower graph).](image)

![Figure 5.6. Maximum tip-displacement vs. electrical power and electrical resistance vs. power graphs of the trimorph actuator (under vacuum). (a) neutral position; (b) maximum tip-deflection.](image)
Table 5.2. Geometrical characteristics of the trimorph actuator.

<table>
<thead>
<tr>
<th>Geometrical characteristics</th>
<th>Dimensions [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>legs</td>
<td>330 x 20</td>
</tr>
<tr>
<td>silicon-oxide</td>
<td>312 x 12</td>
</tr>
<tr>
<td>connection of the legs at tip</td>
<td>4 x 5</td>
</tr>
<tr>
<td>contact pads</td>
<td>118 x 110</td>
</tr>
</tbody>
</table>

In this case the shift of the initial neutral position from the horizontal is negative (Figure 5.6.) due to combination of highly compressive silicon-oxide, tensile Si₃N₄ and almost stress-free B-doped polycrystalline-Si. The electrical resistance vs. actuation power graph shows the same trend as the one of the bimorph actuator.

5.2.2. Hot-leg/cold-leg actuator

It is one of the most used in-plane electrothermal actuators due to the simple one-mask fabrication process (Figure 5.7.) and because large deflection (up to 15 µm) and force ranges (up to 10-12 µN) can be achieved.

![Figure 5.7. Sketch of hot-leg/cold-leg actuator (top-view).](image)

In the maximum tip-displacement vs. actuation power graph (Figure 5.8.) the “back bending” mode that corresponds to the descending branch of the resistance vs. actuation power graph can be observed.

Table 5.3. Geometrical characteristics of the hot-leg/cold-leg actuator.

<table>
<thead>
<tr>
<th>Geometrical characteristics</th>
<th>Dimensions [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>hot leg</td>
<td>320 x 2</td>
</tr>
<tr>
<td>cold leg + flexure</td>
<td>275 x 20 + 45 x 2</td>
</tr>
<tr>
<td>connection of the legs at tip</td>
<td>5 x 2</td>
</tr>
<tr>
<td>contact pads</td>
<td>115 x 110</td>
</tr>
</tbody>
</table>

Two regions can be distinguished where this particular actuator does not change its neutral position for certain intervals of actuation powers: below 30 mW and above 60 mW. Although the “back bending” zone can be used efficiently to assemble micromechanisms after fabrication [2], we have not succeeded identifying measurants or input parameters that could clearly distinguish the “back bending” regime from the region where failure occurs.
Operating the actuators on the ascending branch of the electrical resistance vs. actuation power graph ensured reproducible actuation performance.

![Figure 5.8](image.png)

**Figure 5.8.** Maximum tip-displacement vs. electrical power and electrical resistance vs. actuation power graphs of the hot-leg/cold-leg actuator (ambient conditions). (a) neutral position of the tip; (b) maximum tip-deflection.

### 5.2.3. Double-clamped parallel-beams

This actuator consists of two double-clamped beams of bimorph structure (polycrystalline-Si and Si$_x$N$_y$ – Figure 5.9.). The stress gradient through the structure determines the preferential buckling direction once the beams are resistively heated. The two 300 µm long and 4 µm wide beams separated by a 4 µm gap are clamped at both sides but electrically connected only at one end.

![Figure 5.9](image.png)

**Figure 5.9.** Sketch of the double-clamped parallel-beams.

A comparison of the electrical resistance vs. actuation power graph for tests performed in
ambient condition and under vacuum is presented in Figure 5.10. The measurements suggest that the thermal power loss due to conduction through air and primarily to the substrate is about 90% for actuation at the same performance, and in both cases the same phenomenon occurs. The maximum deflection of the middle of the beam measured in ambient conditions was larger than in vacuum (difference of ~1-2 µm) due to conduction through air, which changes the temperature distribution along the beams [19].

![Graph of electrical resistance vs. actuation power](image)

Figure 5.10. The electrical resistance vs. actuation power graphs for double-clamped parallel-beams: (a) under vacuum, (b) in ambient conditions.

Even though the beam is double-clamped there is a change of the neutral position of the middle of the beam when it is actuated at high electrical powers (Figure 5.11.). The change of the neutral position initiates where the electrical resistance vs. actuation power graph reaches the peak.

![Graph of deflection vs. actuation power](image)

Figure 5.11. Maximum deflection at the middle, and change of the neutral position of double-clamped beam due to so-called “plastic deformation” under vacuum.

5.3. Thermal characterization of microstructures in the near-infrared domain

Preliminary measurements with near-infrared camera (wavelength <1.1 µm) have been performed in order to estimate the temperature at which permanent deformation initiates. The camera was mounted on an optical microscope and images for different values of the actuation power have been recorded in ambient conditions. The calibration of the
temperature measurement was done on identical actuators (structures and materials) placed on a heater element that could be heated up to 1000 °C. It is extremely important to calibrate the measurement for the same material as the actuator consists of, since thermal radiation coefficients are both material and surface dependent. Due to 1.1 µm maximum wavelength of the camera the lowest detectable temperature was limited to about 450 °C for the double-clamped parallel-beams. In Figure 5.12, images grabbed with the near infrared camera are presented. For symmetry consideration and sufficient optical magnification each picture shows half-length of a pair of actuated double-clamped beams. Figure 12(a) represents the actuator operated at 65 mW for which the estimated maximum temperature was 610 °C and the measured out-of-plane displacement of the middle of the beam was 6 µm. The last measurement within the reversible actuation region was performed at 75 mW (Figure 12(b)), which corresponds to a maximum temperature of about 770 °C and gives 7 µm deflection. Taking into account the limited precision of the temperature measurement technique we can estimate that the permanent deformation for this particular device initiates at local temperatures around 800 °C, clearly far below the intrinsic temperature of our highly doped polycrystalline-Si.

Figure 5.12. Temperature measurement on double-clamped beams with near-infrared camera (half-length of a pair of double-clamped beams is presented for symmetry consideration): (a) – actuator operated at 65 mW; (b) – actuation at 75 mW.

5.4. Discussion

The actuators have also been operated with AC square wave signals. The maximum frequency at which they could be actuated in ambient conditions was limited to 17 Hz due to thermal inertia, but this value is design dependent. Operation of the actuators in the reversible region for a few thousand cycles (several minutes) did not lead to irreversible
behavior.

Modifications or combinations of the presented actuators can lead to better control and/or larger operating variety of the devices. For instance a lever that connects two pairs of double-clamped parallel-beams can provide three operation modes: upward and downward motions of the lever-tip when the two pairs of parallel-beams are actuated at different electrical powers, or crane-like motion of the lever by actuation of both pairs of parallel-beams identically. Figure 5.13. shows the neutral position of the device and the three different operating modes.

The performance of the device was simulated with FEM and presented in section 3.5.3. Measured deflections of the lever-tip are in good agreement with the simulations. The downward actuation of the tip is limited by the fabrication, the magnitude of the motion of the lever-tip is determined by the thickness of the sacrificial silicon-oxide, which was 2 µm in our case. This operating mode could potentially be used for closing micro-valves due to large force and actuation flexibility.

![Figure 5.13. SEM photographs of a parallel-beams/lever electrothermal actuator on a 45° tilted table: top left – neutral position; top right – lever tip actuated downwards; bottom left – lever tip actuated upwards; bottom right – crane-like motion of the lever.](image-url)

The maximum upward deflection of the lever-tip, measured in ambient conditions by a micrometer mounted on an optical microscope, was 28 µm. However measurements in vacuum showed that the actuation in reversible regime is limited to 17 µm. The crane-like actuation can provide a lever-tip deflection equal to the deflection of the individual beams (up to 11 µm). Large deflection and force ranges can be obtained by varying the ratio of the lengths of the lever-arms. Experiments also showed that differential actuation of the pairs of
parallel-beams is possible in any intermediate position.

![SEM photographs of actuated actuators](image)

**Figure 5.14.** SEM photographs of actuated (a) bimorph actuator, (b) trimorph actuator, (c) double-clamped parallel-beams and (d) B-doped polycrystalline-Si hot-leg/trimorph cold-leg (on tilted SEM table).

**Failure of the electrothermal actuators**

Figure 5.14. shows the SEM photographs of different electrothermal actuators tested under vacuum. It has been discussed that reproducible performance can be obtained when the electrothermal actuators are operated within the range of electrical powers for which the trend of the electrical resistance is increasing. Above this electrical power threshold the actuators can be operated till the physical limitation is reached. The electrical circuit breaks open when the temperature due to Joule heating exceeds locally the melting temperature of the material from which the circuit is made of. Examples of failure of electrothermal actuators are presented in Figure 5.15.

Although it was expected that reaching the melting temperature of the polycrystalline-Si locally would cause the failure of all polycrystalline-Si based electrothermal actuators, an interesting failure mode of the trimorph actuator was observed during testing. In reality, the failure of this type of actuator is caused by the softening of the silicon-oxide at high temperatures and the subsequent sudden increase of its thermal expansion [20]. As a consequence, the softened silicon-oxide breaks the polycrystalline-Si/\(\text{Si}_x\text{N}_y\) interface (Figure 5.16). Further heating results in melting of the polycrystalline-Si beam which connects the two symmetrical trimorph legs.
5.5. Conclusions

It has been shown that the change of the neutral position of B-doped polycrystalline-Si based electrothermal actuators coincides with operational powers at which the electrical
Characterization of electrothermal actuators

resistance vs. actuation power graph reaches a maximum. This can be used beneficially to
distinguish the reversible and irreversible actuation zones no matter which is the working
principle of these actuators and in which environment they are operated. Although this
finding was experimentally observed specifically for B-doped polycrystalline-Si actuators, we
do expect that comparable behavior may be observed for other (poly-) crystalline
semiconductor based actuators. Contrarily, metal-based actuators will not show the same
characteristic.

Due to fabrication process dependence of the properties of the materials this
experimental method is appropriate to obtain full capacity of the electrothermal actuators
with reproducible performance. It is important to mention that one actuator from each
specific design has to be characterized beyond the reversible limit, thus sacrificed, before
other identical actuators can be used at full performance. The method requires only a very
simple measurement set-up, whereas other methods may be more complex. The
discrimination of the reversible and irreversible actuation regions based on optical
microscopy may require sophisticated set-ups, because initially the permanent deformation is
small. This may be hard to detect by simple optical/mechanical techniques like micrometers
attached to a microscope (e.g. for out-of-plane motion).

The observed changes in electrical resistance for the devices presented are attributed
to structural change of the material since the doping levels are very high, thus the intrinsic
temperature is much higher than the temperature at which the onset of structural changes are
found.

5.6. References

Academic Publisher (1998).
400-403 (2003).


The microtribosensor

Abstract

The fabrication and preliminary testing of the microtribosensor, which provides decoupled in- and out-of-plane motions for adhesion, friction and wear investigations under different loading conditions, is presented in this chapter. Although the fabricated MEMS device delivers the designated motions, the amount of wear generated by rubbing the test surface to the substrate cannot be quantified due to mechanical and/or physical limitations. These restrictions are discussed and an alternative solution is proposed, which is presented in the next chapters.

6.1. Fabrication and testing of the microtribosensor

The microtribosensor, for which the design is presented in section 3.4., was fabricated using the processes described in chapter 4. The MEMS device shown in figure 6.1. consists of a coupled hot-leg/cold-leg actuator for generating in-plane motion, two trimorph actuators to provide out-of-plane (pull-off) motion and placed symmetrically to the longitudinal axis of the shuttle carrying the test surfaces, an electrostatic parallel-plate actuator for applying normal load on the test surfaces, and a spring system.

Figure 6.1. Scanning electron microscope image of the fabricated microtribosensor.
The fabrication of the device is complex due to different actuators that had to be embedded in the same process. The actuators do not only differ in working principle but they are also micromachined from different structural layers. The fabrication of the microtribosensor requires nine masks. Various structural and functional layers are laid down on multiple sacrificial silicon-oxide layers.

Although different combinations of in- and out-of-plane actuators have been tried out, only a selective description of the fabrication process of the microtribosensor, shown in Figure 6.1., will be given. It is important to mention that all out-of-plane actuators presented in section 3.5.3. and 5.2. can be embedded in the same fabrication process.

A cross section along different structures is indicated in Figure 6.2., in order to allow identification of different process steps during the fabrication of the microtribosensor. The schematic of the fabrication is presented in Figure 6.3. A 0.25 µm thick Si$_x$N$_y$ layer is deposited onto a p-type, polished $<100>$ single-crystal Si wafer for electrical isolation purpose. Then, a 2 µm thick silicon-oxide layer (combination of PECVD and LPCVD) is deposited and patterned with the first mask to serve as sacrificial layer for the trimorph out-of-plane actuators (a). The silicon-oxide layer is removed from everywhere on the wafer but not under the legs of the trimorph actuators. The first, 1.6 µm thick, structural LPCVD polycrystalline-Si layer is deposited (b), then it is locally doped with Boron using a 0.5 µm thick LPCVD silicon-oxide layer as doping mask (c). The local doping is needed for electrical conduction of the polycrystalline-Si layer where the trimorph actuators will be patterned, for the bottom electrode of the parallel-plate actuator, and for the electrical connection to one of the legs of each hot-leg/cold-leg actuator. The masking silicon-oxide used for solid source dotation is removed from the wafer and then a 0.8 µm thick PECVD silicon-oxide layer is deposited from which the stripes are patterned on the polycrystalline-Si legs of the trimorph actuators (d).

Figure 6.2. Sketch of the tribosensor. A-A is the section for which the fabrication process can be identified in Figure 6.3.
Figure 6.3. Fabrication process of the microtribosensor. The schematic shows the process steps for section A-A in Figure 6.2.
A 0.25 µm thick SiNx layer is deposited for electrical isolation of the bottom electrode of the parallel-plate actuator, and for protection of the silicon-oxide stripes on the legs of the trimorph actuators during sacrificial release (e). The geometry of the trimorph actuators is obtained by patterning the SiNx/polycrystalline-Si stack with RIE (f). A second, 2 µm thick, sacrificial silicon-oxide layer is deposited by a combination of LPCVD and PECVD techniques. This layer will define the vertical distance between the shuttle and the trimorph actuators in neutral position. The molds of the test surfaces, which will be contacting the substrate during tribological investigations, are patterned (g). Subsequently, the silicon-oxide layer is removed from the trimorph actuators, but it is left just partially at their tip in order to assure a gap between the shuttle and the trimorph actuators (h). In the same process step the silicon-oxide layer is removed also for the contact pads of the electrodes of the parallel-plate actuator, of the coupled hot-leg/cold-leg actuator and for the clamping of the suspension. Further, the SiNx is removed where the contact pads have to be electrically connected to the bottom electrode of the parallel-plate actuator, and for one of the electrodes of each hot-leg/cold-leg actuator (i). The SiNx is also removed from the contact pads of the trimorph actuators. A second, 2 µm thick, structural polycrystalline-Si layer is deposited (j), from which the shuttle carrying the test surfaces, the in-plane actuator and the suspension will be patterned. The polycrystalline-Si layer is doped locally with Boron using a 0.5 µm thick LPCVD silicon-oxide mask (k). The doped regions are where the in-plane actuator and the top electrode of the parallel-plate actuator will be located, but in such a way that there is no electrical connection between them and their operation is completely decoupled. The hot-leg/cold-leg actuators are all fed from the same contact pads, but there is no electrical connection between them at their tips, although they are mechanically coupled. After stripping the doping mask, the in-plane actuator, the shuttle, the suspension and the contact pads are patterned by RIE (l). Finally the structures are released (m) with the flash release technique [1].

Testing of the microtribosensor revealed that the designated in- and out-of-plane motions could be performed either coupled or decoupled. Figure 6.4. shows two captures of the microtribosensor, when it is in neutral position (left) and when the in-plane actuator is operated at 0.18 W electrical power (right). It can be observed that the thin (hot) legs of the hot-leg/cold-leg actuators are bent due to differential linear expansion of the thin and the thick legs, caused by Joule heating. The suspension is deformed due to the motion generated by the in-plane actuator.

The microtribosensor was tested for adhesion mode operation in ambient environment and under vacuum. In this mode only the out-of-plane actuators are operated. First the test surfaces are brought into contact with the substrate by the electrostatic parallel-plate actuator (Figure 6.5.(a)), then the test surfaces are pulled off the substrate by the electrothermal out-of-plane actuators (Figure 6.5.(b)). The vertical motion of the shuttle carrying the test surfaces can be observed by contrast change in that particular region of the image.

Different designs were used for out-of-plane actuators (chapters 3-5), for which the successful actuation has already been shown. However, other actuators, reported in literature, can also be embedded in the fabrication process.
The single-material out-of-plane actuator patterned from two structural layers vertically separated by a certain distance can provide downward or upward motions, depending on the electrical circuit that is operated [2]. In this case both structural layers consist of B-doped polycrystalline-Si, which form an inner and an outer electrical circuit.

Figure 6.4. Actuation of the microtribosensor for friction mode. (a) neutral position; (b) in-plane actuator operated at 0.18 W. It can be observed that the thin (hot) legs of the hot-leg/cold-leg actuators are bent due to differential linear expansion of the thin and the thick legs, caused by Joule heating. The suspension is deformed due to the motion generated.

Figure 6.5. Actuation of the microtribosensor for adhesion mode. (a) test surfaces in contact with the substrate due to actuation of the parallel-plate electrostatic actuator; (b) test surfaces pulled off the substrate by the out-of-plane actuators. The contrast change of the shuttle is caused by height difference.
Chapter 6

The inner circuit is located 2 µm below the outer circuit. By operation of the inner circuit the motion of the tip of the actuator is upwards, while the actuation of the outer circuit generates downward motion. Figure 6.6. shows the close-up of the out-of-plane actuator operated under vacuum, pulling the shuffle off the substrate.

![Image](image_url)

Figure 6.6. Actuation of the microtribosensor for adhesion mode under vacuum. The test surfaces are pulled off the substrate by out-of-plane actuators located symmetrically to the longitudinal axis of the shuttle.

6.2. Deficiencies of the microtribosensor

Although the MEMS device was carefully designed to enable adhesion, friction and wear investigations, shortcomings hindered its full-scale usage in specific measurements. It has been shown that in- and out-of-plane motions can be generated, thus the quantification of pull-off and friction forces can be done indirectly from the electrical power when the force-deflection-electrical power characteristics of the electrothermal actuators are known.

![Image](image_url)

Figure 6.7. Device for determination of the force-displacement-electrical power characteristic of the in-plane electrothermal actuators. The position of the force sensor can be changed and then fixed by electrostatic attraction to the substrate.
The calibration of in- and out-of-plane actuators can be carried out with test structures presented in Figure 6.7. and 6.8. respectively.

![Figure 6.7. and 6.8.](image)

Figure 6.8. Device for determination of the force-displacement-electrical power characteristic of the out-of-plane electrothermal actuators. The spring constant of the suspension of the plate can be changed by electrostatic attraction of a part of the suspension to the substrate.

The most important shortcoming of the microtribosensor is the difficulty to quantify wear generated by the test surfaces upon rubbing a substrate. Although small windows were designed on the shuffle beside the test surface (Figure 6.6.), it was not possible to identify wear with optical interferometry on the substrate. Furthermore, the substrate was not accessible to Atomic Force Microscope (AFM) probes via the windows. The access to the substrate can be enabled only by peeling off the structures after wear is generated, which means that it is not possible to resume testing with the same device. Even by peeling off the structures, the worn spots were extremely difficult to locate on the substrate with an MMAFM-2 equipment.

![Figure 6.9.](image)

Figure 6.9. Detection of wear using scanning electron microscopy. Surface modification is generated by the test surface upon rubbing a substrate. Left – structures peeled off the substrate; right – close-up of the spot where the test surface rubbed the SiN$_3$ substrate. The direction of the wear patterns is along the direction of the reciprocatory motion of the in-plane actuator.
Furthermore, it cannot be obtained the reference topography of the same spot before wear is generated, thus the subtraction of topography images (before and after wearing) is impossible.

Despite these problems, it was demonstrated by scanning electron microscopy that wear is generated on the substrate (Figure 6.9.). Nevertheless, it is impossible to quantify the amount of wear using just SEM images, because the contrast change in the pictures can be caused not only by height difference but also by the presence of dissimilar materials due to possible material transfer to the substrate during rubbing.

6.3. Practical solution to quantify wear

Micro- and nano-scale wear can be quantified with good precision if the surface topography is known before and after wear generation. Thus, the modified topography can be subtracted from the reference one and the amount of wear can be determined. Since atomic force microscopy enables surface topography measurement and also surface modification [3], it has been considered as a serious contender of the microtribosensor. It is also possible to resume testing (topography modification and characterization) with AFM, once it has been interrupted. However, existing techniques of using atomic force microscopy in tribological applications also have some deficiencies, which will be discussed in the following chapters. Improvement of the surface topography modification and characterization technique, as well as the development of specific probes for surface modification in dry condition and with local lubrication will be presented.

6.4. References


Chapter 7

Introduction to Atomic Force Microscopy

Abstract

In this chapter, the reader is introduced to the atomic force microscopy. The basics are presented, which are important to understand the interpretation of the results in the following chapters.

7.1. General introduction on Atomic Force Microscopy

Scanning Probe Microscopy (SPM) is a very important technique in surface science. It comprises Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), but also very dedicated techniques such as Electric Force Microscope (EFM), Magnetic Force Microscopy (MFM), Electrochemical Microscopy (ECSTM) etc.

The focus point of this work is the use of AFM for surface topography characterization and modification. The AFM was developed by Binnig et al. [1] to measure small forces, based on the design of the STM [2]. A short introduction to the principle is presented. More detailed information can be found in [3,4].

The main parts of the AFM are: the optical head, the piezoelectric tube scanner and the
feedback controller (Figure 7.1.). The optical head contains a laser diode that generates an optical beam, which is directed by a prism onto the topside of the cantilever of an AFM probe. Due to inclined mounting of the AFM probe into a probe-support that is fixed onto the optical head, the path of the laser beam reflected by the cantilever will be different from the incoming one (Figure 7.2).

[Image of optical head with laser diode, photodetector, and cantilever]

Figure 7.2. The path of the optical beam.

The cantilever bends when the surface topography changes, thus the direction of the reflected beam changes accordingly. A four-quadrant photodetector, embedded in the optical head, gives a certain electrical signal, which depends on the direction of the incoming laser beam. The advantage of the four-quadrant detector is that differential signal readout is possible between the upper two (1+2) and lower two detectors (3+4) or between the left (1+3) and right pairs of detectors (2+4), depending on the operation mode. The first case is used for topographic measurements, while the second mode depicts the torsional behavior of the cantilever when the AFM probe-tip, located on the cantilever, is in contact with a sample surface. This information is related to the transverse friction forces that are encountered during scanning.

The piezoelectric tube scanner is providing the X-Y-Z relative motion between the AFM probe and the sample. There are two different constructions of the AFM. The probe can be mounted onto the piezoelectric tube scanner incorporated in the optical head, in which case the scanning motion is performed by the AFM probe. In the other case the probe is mounted into the optical head, and the sample, fixed onto the piezoelectric tube scanner, completes the scanning motion. For both constructions the piezoelectric tube produces a raster scan pattern as shown in Figure 7.3. The fast scan axes for topography imaging and friction mode operation are along, and orthogonal to the longitudinal axis of the AFM-probe respectively (Figure 7.4).

Data registered for scanning along the solid and the dashed lines are separated and
presented in two different images, called the trace and retrace image. It is possible to disable the slow scan axis, thus scanning occurs along one single line for a certain number of scan cycles.

![Figure 7.3. Schematic of the X-Y motion generated by the piezo tube scanner.](image)

The differential signal from the upper and lower photodiodes modifies with the topography change. This is used as feedback signal to control the vertical position of the piezo tube scanner in such a way that the deflection of the cantilever remains constant. The contact force between the probe-tip and the sample surface is also constant in this operating mode, called “height mode”. The vertical motion of the piezo tube scanner is directly related to the scanned topography and the image is obtained by converting the electrical signal to height information.

Contact force calibration is used to investigate the interaction between the AFM probe-tip and a sample surface by approaching and retracting the probe-tip from the sample. As a result, a force curve is created from the electrical signal generated by the photodetector (Figure 7.5.), which is a measure of the tip-sample interaction. When the probe-tip and the sample surface are relatively far from each other, then the signal is constant. As the piezo tube extends and the sample approaches the probe-tip (A), the cantilever bends towards the sample due to dispersion forces and the tip jumps into contact with the sample (B). The piezo tube still extends even after the tip contacted the sample, which can be observed as positive deflection in the so called force curve (deflection curve, based on which the contact
force is calculated), because the cantilever is pushed upwards by the piezo tube. After the piezo tube reaches the upper limit (C), then it starts to retract, trying to separate the sample from the probe-tip. First the bending of the cantilever is reduced and then the cantilever bends the other way around (negative deflection), because the tip is still in contact with the surface due to capillary and dispersion forces. At point (D) the spring force of the cantilever equals the attractive forces, and then the cantilever jumps back to its initial non-contact position, where the signal is constant. Knowing the spring constant of the cantilever, the pull-off force can be calculated from the force calibration curves [3].

![Contact force calibration (force curve).](image)

The application field of the AFM in micro/nanoscale research is extremely large. Recent developments enable nanolithography and nanopatterning [5, 6], however the main utilization relies on characterization of surfaces (e.g. tribological studies [4]) and determination of materials properties [7-9]. Besides, there is increased interest in using the same tool simultaneously for different purposes, which is a driving force to develop multi-cantilevered probes [10, 11].

7.2. Foreword to AFM-based surface modification

The following chapters deal with development of new AFM-probes and new surface modification and characterization techniques. The aim was to enable quantification of surface topography modification in each and every moment of the experiments, without changing the contact conditions. This is only possible if the acquired image contains information about the modified and unmodified (reference) surface at the same time. With currently available AFM-probes it is not possible to implement this technique, hence new AFM-probes were designed and fabricated. Another idea to include fluidic functionality in the AFM-probes was also explored and the progress of the development is presented. If fluid can be transported through the cantilever of an AFM-probe to a well-defined location, where relative motion can be generated between two surfaces, then tribological experiments with local lubrication could be carried out. The device with fluidic functionality can be used potentially for other
applications, such as writing different patterns by depositing or removing materials.

7. 3. References


Chapter 8

Multifunctional tool for in-situ characterization of surface modification

Abstract

An innovative technique has been developed to enable in-situ monitoring of mechanical surface modification. The method is based on using a test surface and a sharp tip located on two different cantilevers, one for mechanical surface modification and the other for in-situ detection of surface topography change. The device can be used in standard atomic force microscope, the image obtained during scanning contains information about a region with modified and a region with unmodified (reference) topography. Surface topography modification (e.g. wear) or the change of different parameters (e.g. friction force) can be followed as they occur due to the reference region in the image or in each scanning line. This is important for fundamental understanding of wear and for reliability studies of MEMS and NEMS. The characterization technique and typical results are presented.

8.1. Introduction

Since the information on which the images are based contains aspects of the interaction between the scanning tip and the scanned surface, the AFM has extensively been used for tribological investigations including adhesion, friction, and wear of various materials for different loading conditions with or without lubrication [1-6]. State-of-the-art nanoscale wear studies [4-6] use the same tip for wearing and measuring. Wearing is done at a high load while subsequent imaging is done with the same probe on a larger area, applying a smaller load. A typical result, which can be obtained by this technique, is shown in Figure 8.1. In the middle part of the zoom-out image a darker area can be observed where wear was generated at high normal load. A reference surface is needed for wear characterization, where the topography is not modified during rubbing. This can be considered the surface surrounding the worn part in Figure 8.1. Since zoom-out and change of the load have to be made frequently, the contact conditions are changed practically each time for repeated surface modification and characterization cycles.

The in-situ technique presented provides information about modified and unmodified topographies at the same time, and allows a wider range of possibilities for surface modification without compromising image quality.
8.2. The principle of the in-situ characterization technique

The design of the tool, called \textit{wear-AFM probe}, has to meet the following requirements: (i) to enable in-situ friction and wear investigations for a wide range of loading conditions for various material-couples, (ii) to be usable in any standard AFM equipment without modifications, (iii) to allow detection of subnanometer change of surface topography.

The wear-AFM probe consists of two cantilevers separated by a given distance that allows to a certain extent overlap of the scan ranges of the two tips (Figure 8.2.): a test surface located on a so called multifunctional cantilever which generates the change of the surface topography along its scanning range, called rubbing range, and a sharp tip placed on another so called detection cantilever for in-situ monitoring of the surface topography along its scanning range (detection range). The minimum separation distance between the cantilevers is limited by the diameter of the laser beam that needs to be focused only on the top of the detection cantilever (as shown in Figure 8.2.), assuring that any motion of the multifunctional cantilever does not influence the reflection of the laser beam onto the photodiodes. The scan area of the detection tip determines the size of the images captured during frame scanning. The topography image consists of a part where no or little wear is created due to very low loading of the detection tip against the surface, and a part where wear is generated in a controlled way, which is defined by the overlap between the detection and the rubbing ranges.

The ratio of the normal loads as exerted by the multifunctional tip/surface and the detection tip is determined by the geometrical characteristics (angle, height, width, thickness) and material properties of the cantilevers.

In principle, the multifunctional cantilever can be positioned either in front or behind the detection cantilever by adjusting the ratio between the heights of the tip/surface and the

Figure 8.1. Wear characterization technique: imaging a larger area is necessary to quantify wear generated at high normal load.
geometrical characteristics of the cantilevers. The option for more than two cantilevers for adding extra functionalities is not excluded but is not practical because the overlap region of the scan ranges of the tips and/or surfaces is diminished, and it may be difficult to control the applied normal load on the tips/surfaces separately using standard AFM equipment.

The multifunctional cantilever can perform other functions than wearing the surfaces. It is relatively easy to incorporate a heater [7], which would enable us to study surface modification by local heating or to monitor wear processes at elevated temperature. It is also possible to study the tribological interaction of various pairs of materials by coating the test surface, located on the multifunctional cantilever, with a certain material. Improvement of the force control on the test surface can be made using active multifunctional cantilevers [8], which allows controlling of the contact force in a wide range and not only predefined by the properties of materials and the geometry.

8.3. Design of the wear-AFM probe

The material chosen for the fabrication of the cantilevers is Si$_x$N$_y$, due to its excellent mechanical properties. The thickness of the cantilevers is chosen in such a way that their elastic properties resemble to that of the commercial ones, in order to allow contact and tapping mode operations with standard AFM equipment. Trapezoidal shape was adopted for the multifunctional cantilever, in order to decrease the distance between the test surface and the detection tip. The detection cantilever is V-shaped, like most of the contact mode AFM-
probes made of Si$_x$N$_y$. The multifunctional cantilevers are 200 µm long, with beam width from 10 to 20 µm, while the detection cantilevers are about 170 µm long and are either 10 or 15 µm wide. The thickness of the cantilever beams was chosen to be between 0.4 and 1 µm, which gives spring constants in the interval of 0.011 and 0.340 N/m and resonance frequencies of the first vibration mode in the range of 95-235 kHz for the multifunctional cantilever. The spring constants of the detection cantilevers, corresponding to the given geometrical characteristics, are between 0.018 and 0.430 N/m and the resonance frequencies range from 133 to 295 kHz. The support of the cantilevers is Pyrex, chosen from technological reason, because of the good Si/Pyrex etch selectivity in KOH when the sacrificial Si substrate has to be removed to obtain freestanding structures clamped on the support.

8.4. Fabrication of the wear-AFM probe

The fabrication process of the device is based on the fabrication of a single-cantilever AFM probe [9] with additional techniques for specific functionalities. The flow chart of the fabrication process is presented in Figure 8.3.

A 100 nm thick LPCVD Si$_x$N$_y$ is deposited at 800 °C on a <100> single-crystal Si wafer and it is patterned by Reactive Ion Etching (RIE) [10] (a). The mold of the test surface that is located on the multifunctional cantilever is obtained by etching the exposed Si surface with the Bosch process [10] (b). The Si$_x$N$_y$ layer is stripped in 50% HF solution and a new Si$_x$N$_y$ masking layer is deposited, and then patterned with RIE (c) in order to obtain the mold of the detection tip by etching the exposed Si in 25 wt% KOH:H$_2$O solution at 75 °C (d).

The Si$_x$N$_y$ is removed (e) and a new Si$_x$N$_y$ is deposited (f) from which the cantilevers are patterned using RIE (g). The backside Si$_x$N$_y$ layer is patterned by RIE so that a Si$_x$N$_y$ ring remains, which will be used later on as etch-stop layer to inhibit Si etching at the edge of the wafer. The Si ring prevents the AFM probe-strips falling apart when the Si substrate is removed in KOH (Figure 8.4.).

The support of the cantilevers is from a 500 µm thick Pyrex wafer. The Pyrex wafer has to be bonded to the Si wafer, on which the cantilevers are patterned. In order to facilitate the release of the cantilevers in a later stage, the adhesion between the Pyrex wafer and the Si$_x$N$_y$ layer must be avoided along the cantilevers. Strong bond is desired at other places to ensure that the Si$_x$N$_y$ cantilevers are well clamped on the Pyrex support. A thin Chromium (Cr) layer deposited and patterned so that it covers just the cantilevers is the typical solution for this problem [9]. For simplicity we adopted another approach, avoiding Cr processing before and after bonding. The alternative is partial dicing (250 µm) of the backside of the Pyrex wafer (h), so that the part where material is removed to be aligned right above the cantilevers.

Difficulties in anodic bonding of Si$_x$N$_y$ directly to Pyrex were observed, but they were overcome by thermal oxidation of the topside Si$_x$N$_y$ [11] at 1100 °C in humid environment for 30 minutes. Perfect bonds were obtained with no air inclusions (i), which can partly be attributed to the thin Si-oxinitride interface and partly to the diced lines in the Pyrex through
which the air can escape.

Figure 8.3. Fabrication process of the wear-AFM probe for in-situ characterization of surface topography modification. (a) RIE patterning of the Si$_3$N$_4$ etching mask for the mold of the test surface, (b) RIE etching of the <100> single-crystal Si substrate for the mold of the test surface, (c) RIE patterning of a freshly deposited Si$_3$N$_4$ etch mask layer for obtaining the mold of the detection tip, (d) KOH etching for the mold of the tips, (e) removal of the Si$_3$N$_4$ mask, (f) deposition of the Si$_3$N$_4$ layer for the wear-AFM probe cantilevers, (g) patterning the wear-AFM probe cantilevers and patterning the backside Si$_3$N$_4$ ring, (h) dicing of the Pyrex wafer above the cantilevers to inhibit bonding, (i) anodic bonding of the Pyrex and Si wafers with Si-oxinitride interface, (j) dicing of the Pyrex wafer to enhance breaking apart the probes after fabrication, and dicing of the Pyrex wafer to free the topside of the cantilevers, (k) releasing the cantilevers in KOH bath, (l) deposition of a thin gold layer onto the top of the probe to enhance optical reflection, and optional deposition of a certain material on the test surface by shadow masking technique.

The Pyrex part of the wafer-stack is partially diced (300 µm) in the direction perpendicular to the probe-stripes in order to enhance breaking apart the probes after fabrication. The Pyrex is also partially diced along the probe-stripes right above the cantilevers, thus the topside of the cantilevers becomes free (j). The wafer-stack is immersed into a KOH bath in order to completely release the cantilevers (k). It is highly important to clean the wafer-stack after the Si substrate is removed. Inappropriate cleaning will cause adherence problems when a gold layer is deposited on top of the probes (l) for enhancing the reflection of the incoming laser beam to the photodiodes. We used a HCl:H$_2$O$_2$:H$_2$O (1:1:5) vol% solution at 85 °C for cleaning, after 2 hours of its preparation. This was necessary to avoid damaging of the cantilevers, because bubbles generated in the solution due to chemical reaction can break the
free-hanging cantilevers.

Figure 8.4. Top image – Si₃N₄ ring at the edge of the wafer to hold together the wear-AFM probe-stripes. Bottom image – close-up of the wear-AFM stripes.

The probes were left for 12 hours in DI water and then dried in air. The fabricated wear-AFM probe is shown in Figure 8.5. The test surface on the multifunctional cantilever can be coated optionally with a chosen material (e.g. Cr) by a shadow-masking technique (l).

Figure 8.5. Fabricated wear-AFM probe.
If the test surface is substituted with a sharp pyramidal tip on the multifunctional cantilever, then it can be fabricated in the same process step as the detection tip (c) and (d). Different sizes of pyramidal pits can be obtained in the same etching step due to good selectivity between etch rates of single-crystal Si in various crystalline orientations [14, 15]. The size of the pyramidal pit depends on the Si surface exposed to the etchant and it is limited by the <111> planes. The undercut remains relatively small in 25 wt% KOH:H₂O solution at 75 °C due to an etch ratio of 80:1 in <100> and <111> directions respectively. Such a fabricated device is presented in Figure 8.6.

Figure 8.6. Fabricated wear-AFM probe with pyramidal multifunctional tip (instead of test surface) and pyramidal detection tip.

8.5. **Experimental investigations**

This section focuses on typical results of the measurement technique at nanoscale. Due to the inclined mounting of the device into an AFM equipment it is possible to exert dissimilar normal forces on a sample surface with the two cantilevers. Larger force can be applied with the multifunctional cantilever than with the detection cantilever for the configuration shown in Figure 8.2.

The test surface is much larger than the detection tip, thus the pressure exerted by the tip can be larger than that applied by the test surface in case the latter is entirely in contact with the sample.

However, due to the inclined mounting of the probe the friction force that appears between the sample and the test surface during scanning will cause a torque that rotates the test surface, making the contact occur along the leading edge. As the scanning motion is reciprocatory, the leading and trailing edges of the test surface change as the direction of motion alternates from forward to backward (trace and retrace in Figure 7.3.). Scanning a
sample with a rectangular shaped surface instead of a sharp tip has proved this principle, the asperities encountered appeared as ridges with length approximately equal to the edge of the test surface (Figure 8.7.). The smaller the test surface the larger the contact pressure, but it is possible to further reduce the contact edge by using circular test surfaces instead of rectangular ones. In these conditions the pressure exerted by the edge of the test surface can be larger than that applied on the detection tip.

![AFM image of a sample scanned with a rectangular surface instead of sharp tip. Asperities encountered during scanning appear as ridges due to line contact.](image)

**Figure 8.7.** AFM image of a sample scanned with a rectangular surface instead of sharp tip. Asperities encountered during scanning appear as ridges due to line contact.

### 8.5.1. Experiments carried out with circular test surface

An experimental test was carried out for prove of principle of the in-situ surface modification and characterization technique. A smooth (Ra~0.4 nm) polished <100> single crystal-Si surface was used for monitoring the wear for every scan cycle in the overlapping region and where just the detection tip scans. The detection tip was loaded with 25 nN against the Si surface, which according to the calculations [12] based on the geometrical characteristics of the multifunctional cantilever and the properties of Si₃N₄ (Young’s modulus 300 GPa), resulted in a loading of the rubbing surfaces with 0.625 µN against the sample surface. The rubbing surface was circular shaped with a radius of 4 µm (Figure 8.8.) and the scan frequency along the fast scan axis was 2 Hz on a frame of 50x50 µm².

A mark has been traced, prior the wear experiment, in the region where just the detection tip scans and another one where also the rubbing surface operates, designated C and A respectively (Figure 8.9.). Track B is where the overlap region ends and it is generated during the experiment. The section where the profiles of the surfaces are compared after different number of scan cycles is marked with a white line, and the evolution of the depth of the tracks is given in Figure 8.10. It can be observed visually in Figure 8.9. that track B generated during the experiment is getting deeper for each and every scan cycle and the depth of groove A in the overlap region is continuously decreasing. After six scan cycles track A is almost “erased”, while the depth of track C does not change noticeably. The results
emphasize that the wear in the area where just the detection tip scans is insignificant compared to the change of the depths of tracks A and B, showing the viability of the in-situ measurement principle.

Figure 8.8. Close-up of the wear-AFM probe with circular test surface and pyramidal detection tip (after being used).

Figure 8.9. In-situ wear test on smooth surface. Images captured after the first and sixth scan cycles. Marks A and C were generated before the test, while track B is created during in-situ wear test, representing the end of the rubbing range.

Figure 8.10. The change of depths of the wear tracks defined in Figure 8.9.
In order to investigate in-situ detection of wear for rougher surfaces, a Si wafer roughened by reactive ion etching ($R_s \sim 14.5$ nm) was used as sample. The detection tip, and the circular test surface of 4 µm radius were loaded with 25 nN and 0.8 µN against the sample. In Figure 8.11, the results of repeated scanning of a 35x35 µm² area are shown. The section profiles are compared along the fast scan axis after the first, sixth and fourteenth scan cycles (Figure 8.12).

Figure 8.11. Images of the 1st, 6th, and 14th scan cycles of the Si sample (trace images). Section profile, marked with a line, is where the profiles are compared for the 1st, 6th, and 14th scan cycles.

Figure 8.12. Comparison of the profiles for the 1st, 6th, and 14th scan cycles for the same section of the Si sample. There is slight topography change where just the detection tip scans, but in the overlap region the modification is significant.

It can be observed that the modification where only the detection tip scans is very small compared to that in the overlap region, where also the rubbing surface operates. Since
the loading of the detection tip can be minimized, for few scan cycles the topography change in the region scanned just by the detection tip can almost be neglected. In the overlap region the topography modification is significant due to rubbing with the highly loaded test surface, and the comparisons between successively taken images show that the material is continuously redistributed.

8.5.2. Experiments carried out with rectangular test surface

The configuration of the device used for these experiments is shown in Figure 8.5. Three different experiments are presented: the first shows the result of repeated scanning of a sample along a single line, by disabling the slow scan axis (orthogonal to the longitudinal axis of the probe cantilevers); the second experiment is an in-situ adhesion measurement, which shows that the pull-off force changes in the worn region compared to that in the non modified area; and the third experiment demonstrates that in-situ friction and wear measurements can be performed simultaneously to determine when a thin coating layer is removed from a substrate.

(a) In-situ wear experiment along a single line

If the slow scan axis is disabled and scanning occurs along a single line, then the image is built up from topography information of subsequent scan cycles. A smooth Si surface (R\text{a} \approx 0.4 \text{ nm}) was chosen as sample and the test surface on the wear-AFM probe was square shaped with 5 \mu m sides. The load on the detection tip was optimized so that the surface is not damaged due to scanning with the tip, while the force applied on the edge of the square test surface was 0.4 \mu N.

![Figure 8.13](image)

Figure 8.13. In-situ wear test on a smooth (R\text{a} \approx 0.4 \text{ nm}) Si surface. The (trace) image is built up from subsequent scanning along a single line (slow scan axis disabled). The depth of the wear track increases, as the scanning proceeds, from 0.2 \text{ nm} in the 1st scan to 1.3 \text{ nm} in the 256th scan line.

In Figure 8.13, it is shown that the depth of the wear track increases from 0.2 \text{ nm} in the first scan to 1.3 \text{ nm} for the 256th scan cycle. The 0.2 nm deep track after the first scan cycle is
attributed to removal of the native oxide layer which forms on the Si sample in ambient environment. The sample was dipped into a 1% vol. HF:H₂O solution before the experiment, so that the native oxide formed on the Si surface by the inception of the in-situ wear testing was thinner than usually. About 1 nm thick native oxide layer forms on Si surfaces stored in ambient environment for few days. Increasing the contact pressure on the edge of the rubbing surface by reducing the size of the geometrical feature results in deeper wear track due to ploughing, e.g. a circular test surface with 4 µm radius gives a 7 nm deep track already for the first scan cycle in similar scanning condition.

(b) In-situ adhesion measurement

The effect of the surface modification on adhesion strength (pull-off force) can also be investigated in-situ at any place within the detection range. In order to show this capability, a polished <100> single-crystal Si wafer with an average roughness of 0.2 nm, and covered by native oxide, was subjected to in-situ wear test. A 30x30 µm² frame was scanned once, resulting in a 0.6 nm deep wear-track at the end of the rubbing range (Figure 8.14). At this depth it is supposed that we are still in the native oxide layer, which is approximately 1 nm thick.

Figure 8.14. A polished single-crystal Si wafer with an average roughness of 0.2 nm kept in ambient environment, then subjected to in-situ wear test for one complete scan cycle, resulting in a 0.6 nm deep wear-track in the overlap (worn) region.

A first adhesion test was performed in both, modified and unmodified regions, right after the frame scanning was completed. The obtained force curves are presented in Figure 8.15. for both, the worn and not worn regions. The triangles formed by the retraction of the pyramidal tip from the sample surface show that the adhesion changes with the surface modification. After scanning the surface the second time, the adhesion test was repeated. In the not worn area the force curve remained almost the same, but in the worn region, which was at this time 1.3 nm deep, the adhesion further decreased. The drastic change of the force curve suggests that the native oxide layer was removed, because it resembles the force curve obtained for a hydrophobic Si sample surface that was dipped into a 1% HF:H₂O solution to remove native
oxide before testing.

The nature of the surfaces (hydrophilic/hydrophobic) influences the pull-off force, since the capillary forces are the most important forces which have to be counteracted by the cantilever spring in these types of tests.

(c) Simultaneous in-situ friction and topography measurements

An important application for thin-film coated materials is to determine when the coating is worn away. Scanning in raster pattern (Figure 7.3.) allows registering a slight torsional behavior of the cantilever besides the bending. This makes possible that besides the topography image, the friction data can be recorded simultaneously on a second channel, which can provide additional qualitative information on the scanned surface. In the following experiment it will be shown that it is possible to determine when a thin coating layer is removed from a substrate.

A polished <100> single-crystal Si wafer was coated with 5 nm thick Platinum (Pt) by sputtering, and then the sample was subjected to in-situ wear test. In Figure 8.16.(a) the topography of a 40x40 µm² area is shown after one complete scan cycle, the region where the
rubbing surface operates being modified. Figure 8.16(b) shows the in-situ friction signal image in which two regions can be distinguished where the friction signal is uniform. The region where the signal is different corresponds to the region where rubbing occurred and the topography was modified. The friction signal suggests that the Pt film is worn away, which is confirmed by the step height of 5.1 nm in the topography image.

In summary, in-situ friction and adhesion investigations are mostly important for coated materials or for samples from which the native oxide or organic layers are removed due to rubbing.

Figure 8.16. In-situ wear and friction measurement on a Pt coated Si wafer. (a) - topography image of a 40x40 µm² area in which wear due to rubbing in the overlap area can be observed; (b) - friction signal of the same area obtained simultaneously with the topography image, which shows that the 5 nm thick Pt coating is worn in the first scan cycle, because the friction signal has completely modified in the overlap region.
8.5.3. Experiments carried out with sharp multifunctional tip instead of a test surface

The applied load on the sample surface by the sharp multifunctional tip (Figure 8.6.) is more concentrated than in the case of the test surface. Subsequently, the contact pressure increases several times and the ploughing of the material becomes more significant. The tip collects the material, forming bulges, which are disposed randomly on the surface within the overlap area. The same Pt coated Si sample was used as for the experiments presented in Figure 8.16, in order to illustrate such a scenario.

The pyramidal tip cannot carry the worn material to the end of its scanning range like a rectangular surface, because the friction force between the bulges and substrate causes a torque due to which the material is pushed aside by the moving tip. Another interesting effect is that the bulges are elongated in the direction of scanning. Figure 8.17. shows that within the first frame scan on the Pt coated sample bulges form, which are disposed mostly in the overlap area. Subsequently, the bulges can be transported by the detection tip along its scanning range, which indicates that the worn material does not strongly adhere to the surface. The situation becomes worse for scanning the second time, and the hills formed can easily reach 0.5-0.6 µm height.

![Figure 8.17. In-situ wear experiment on a Pt coated Si wafer carried out with sharp multifunctional tip instead of test surface (left - first frame scan; right - second frame scan). The height of the hills reaches 0.5-0.6 µm. The material bulges can be transported by the detection tip along its scanning range.](image)

8.6. Conclusions

The wear-AFM probe developed extends the possibilities of nanoscale tribological investigations with standard AFM equipment, allowing in-situ detection of topographic surface modification as generated in a controlled manner by a tip or surface located on the multifunctional cantilever.
Chapter 8

The prove of principle was demonstrated and it was shown that the rubbing pad (test surface) can generate significant topography modification (wear), whereas the detection tip causes little or no damage during in-situ wear investigations. Surface modification with subnanometer vertical resolution can be detected due to in-situ comparison between modified and unmodified regions contained in the same image. Another major advantage of the technique is that different tribological phenomena can be observed during wear experiments, e.g. how the material redistribution occurs along the wear-track, how the friction and adhesion change due to material removal.

Further improvement of the tool (e.g. by adding active force control and embedding heaters) can expand the application field of the technique.

8.7. References

In-situ AFM-based characterization

Chapter 9

Design and fabrication of a Micromachined Fountain Pen for AFM-based fluidic applications

Abstract

A tool is presented that enables chemical, chemical/mechanical or physical surface modifications based on Atomic Force Microscopy, using continuous liquid supply. The device consists of a reservoir micromachined into the AFM probe support that is connected to fluidic channels embedded in a V-shaped cantilever. Via the channels the fluid reaches the pyramidal tip, which upon contact with a substrate transfers fluid to its surface. The design and the fabrication process of the tool are presented, and then the fluid transport to the sample surface is demonstrated. In-situ characterization of surface modification is possible when two cantilevers are used, like in the case of the wear-AFM probe, one for fluid enabled surface modification and the other for detection.

9.1. Introduction

Since the AFM was developed [1] its application is ever increasing, recent developments enable nanolithography [2, 3] or different biochemical and biophysical applications at nanoscale [4-6]. Our concern was to develop a modified AFM probe with integrated fluidic channels running over the cantilever beams, which can replace the pulled glass capillaries used in the localized chemical and electro-chemical experiments [7, 8], and which enables the use of standard AFM equipment for these experiments. The probe may extend the possibilities of dip-pen lithography [2] and so called nanoscale dispensing [3] as the amount of ink available for writing is significantly increased, and the mass of the probe is only slightly and reproducibly changed, which is important for resonant operations. The possibility to provide continuous fluid flow to the AFM probe-tip might also be important for nanoscale in-situ tribological studies of lubricated surfaces with a design similar to the wear-AFM probe.

The concept of fluid transport via channels embedded in cantilever was proposed previously [9]. In our design the sharpness of the tip of the fountain pen is not affected by the micromachining due to a different fabrication approach than that described in [9]. It is extremely important to have sharp tips for applications such as nanolithography, localized etching and electrochemical deposition.
The device may be combined with a previously developed tool for in-situ characterization of surface modification [10], thus providing additional functionality.

9.2. Design of the Micromachined Fountain Pen

Two different designs have been considered for which the cross sectional views along the multifunctional cantilever and the probe support are illustrated in Figure 9.1. The integrated fluidic channels are encapsulated between two structural thin films from which the multifunctional cantilever of the Micromachined Fountain Pen (MFP) is patterned. The channels connect the reservoir to a pyramidal tip located at the end of the cantilever. The first type of MFP, shown in Figure 9.1.(a), can be fabricated in batch process because the fabrication process is based on conventional photolithography (1 µm resolution) with which the outlet holes of the fluidic channels can be opened at the base of the pyramidal tip. However, with techniques such as ion beam lithography or Focused Ion Beam (FIB) milling smaller outlet holes can be made. The latter permits milling the outlet holes at any place along the facets of the pyramidal tip or even at the tip of the pyramid, with the drawback that the last process steps cannot be done in batch. Figure 9.1.(b) shows a schematic of this configuration.

The material chosen for the fabrication of the cantilevers is Si₃N₄ due to its excellent mechanical properties and because its hydrophilic nature facilitates fluid transport in capillaries. Due to good chemical resistance of the Si₃N₄ to a large variety of chemicals, the application field of the MFP is hardly limited by the fluids that have to be transported via the channels. The thickness of the cantilevers is chosen in such a way that their elastic properties resemble to that of the commercial ones, in order to allow contact and tapping mode operations with standard AFM equipment. Trapezoidal shape was adopted for the multifunctional cantilevers, in which the fluidic channels are embedded, in order to decrease the distance between the detection and the multifunctional tips. The multifunctional cantilevers are 200 µm long, 15 µm wide, and 0.6 µm thick, which give a spring constant of
0.055 N/m and a resonance frequency of about 140 kHz for the first vibration mode. The height and the width of the fluidic channels are 0.25 and 2 µm respectively. The same design of the detection cantilever was used as in the case of the wear-AFM probes.

9.3. Fabrication of the Micromachined Fountain Pen

The fabrication process of the device is based on the fabrication of the wear-AFM probe presented in the previous chapter, combined with techniques for the fluidic functionality.

The flow chart of the fabrication process is presented in Figure 9.2. A 100 nm thick LPCVD Si₃N₄ layer is deposited at 800 °C on a polished <100> single-crystal Si wafer (a), and it is patterned by RIE [11] (b) in order to obtain the molds of the detection and the multifunctional tips by KOH etching of the exposed Si (c). In single-crystal Si different sizes of pyramidal pits can be obtained in the same etching step due to good selectivity between etch rates in various crystalline orientations.

![Fabrication process of the micromachined fountain pen](image)

Figure 9.2. Fabrication process of the batch processed micromachined fountain pen.

The masking Si₃N₄ layer is stripped in 50% vol. HF:H₂O solution (d) before a new Si₃N₄ layer
is deposited on the Si wafer (e). This film is designated to be half of the thickness of the cantilevers (300 nm), constituting the first layer of the two which are encapsulating the fluidic channels. Opening the outlet holes of the fluidic channels (f) is the following step for the MFP fabricated in batch process. Photolithographical patterning is possible at the base of the pyramidal pit, but it is difficult if not impossible to pattern well defined holes on the facets of the pyramid due to accumulation of photoresist in the etched pits. We used Olin 908-17 positive photoresist for photolithography and RIE etching of Si$_x$N$_y$ [11]. This process step is not required for the configuration shown in Figure 9.1.(b), because milling the outlet holes by FIB can be done as one of the last processing steps.

The fluidic channels are fabricated with a sacrificial polycrystalline-Si technique [12]. The geometry of the channels is defined by micromachining a 0.25 µm thick LPCVD polycrystalline-Si film deposited at 590 °C (g). Due to the nature of the process the deposition is double-sided, therefore the backside polycrystalline-Si layer is removed by RIE, while the front side is protected by photoresist from accidental damage. Subsequently, the fluidic channels are patterned form the front side polycrystalline-Si layer by RIE (h).

A second 300 nm thick LPCVD Si$_x$N$_y$ layer is deposited (i) to cover the polycrystalline-Si lines. The detection and multifunctional cantilevers are patterned from the stack of two Si$_x$N$_y$ layers using RIE (j), while the polycrystalline-Si lines remain completely encapsulated. The backside Si$_x$N$_y$ layer is patterned by RIE so that a Si$_x$N$_y$ ring remains, which will be used later on as etch-stop layer to inhibit Si etching at the edge of the wafer (see section 8.4.). The Si ring prevents the AFM probe-stripes falling apart when the Si substrate is removed in KOH. The inlet holes of the fluidic channels that make connection to the reservoir are patterned by RIE (k), these openings are also used as etch holes when the polycrystalline-Si lines have to be removed.

The support of the cantilevers is from a 500 µm thick Pyrex wafer, the same material as used for the wear-AFM probes. Processing the Pyrex can be regarded as the second module of the MFP fabrication. The fluidic reservoirs are powder blasted into the Pyrex wafer [13] using alumina particles of 29 µm size (l).

The Pyrex wafer, constituting the support of the cantilevers, has to be bonded to the Si wafer on which the cantilevers were patterned from Si$_x$N$_y$. In order to facilitate the release of the cantilevers in a later stage, adhesion between the Pyrex wafer and the Si$_x$N$_y$ layer must be avoided along the cantilevers. Strong bond is desired at other places, because the Si$_x$N$_y$ layer seals the bottom side of the fluidic reservoir machined into the Pyrex. Instead of a Cr layer deposited onto the cantilevers to inhibit bonding in those areas [14], we used the alternative of partial dicing (250 µm) of the backside of the Pyrex wafer (m), similar to the fabrication of the wear-AFM.

The anodic bonding of the Si$_x$N$_y$ structural layer to the Pyrex wafer (n) was carried out similarly as described in the case of the wear-AFM probes, specifically by using a Si-oxinitride interface [15]. The Pyrex part of the wafer-stack is partially diced (300 µm) orthogonal to the probe-stripes in order to enhance breaking apart the probes after fabrication. The Pyrex is partially diced also along the probe-stripes right above the cantilevers, thus the topside of the cantilevers becomes free (o). The wafer-stack is immersed into a KOH bath in order to completely release the cantilevers (p). This is also the process step where the fluidic channels
are etched free by removing the sacrificial polycrystalline-Si lines via the inlet and outlet holes. The cleaning of the wafer, containing the probe-stripes, was similar to that of the wear-AFM probes in HCl:H₂O₂:H₂O (1:1:5) vol% solution after 2 hours of its preparation. The probes were left for 12 hours in DI water and then dried in air. The last fabrication step for the batch processed MFP was sputtering of a 30 nm thick gold layer onto the topside of the cantilevers to enhance optical reflection.

The probes with FIB opened outlet hole need an additional layer on the backside of the cantilevers, where the tips are located, in order to avoid charging during FIB milling. We chose a 15 nm thick sputtered Cr layer, which can be removed by wet etching after the holes are drilled into the Si₃N₄ structural layer. For this configuration the inlet hole, patterned in step (k), is located relatively far from the pyramidal tip, hence the sacrificial polycrystalline-Si line is just partially removed by KOH during releasing of the cantilevers. It means that the sacrificial polycrystalline-Si line remains encapsulated between the two Si₃N₄ layers along the cantilever and at the tip. This can be used favorably as end-point detection when the outlet of the fluidic channel is milled into the first Si₃N₄ layer. The rest of the sacrificial polycrystalline-Si line is removed by KOH, subsequent to the wet etching of Cr.

The MFP probes are presented in Figure 9.3., where two different configurations can be distinguished. The design with two reservoirs has the advantage that two dissimilar fluids can be used in combination or separately, with the drawback that fluid manipulation is more difficult with ordinary syringe, unless the AFM probe-holder comprises hollow channels that connect directly to the reservoirs when the probe is mounted into an AFM.

![Image](image1.png)

Figure 9.3. Fabricated MFP probes: left – with one reservoir connected to both channels embedded in the two legs of the V-shaped multifunctional cantilever; right – with separate reservoirs for the two channels.

In Figure 9.4, the top and bottom views of the MFP cantilevers are shown. The photolithographically defined outlet holes are located at the two opposite sides of the pyramidal tip, and they are indicated by white arrows in the inset.

The outlet holes can be milled everywhere on the pyramidal tip with FIB. Two examples are illustrated in Figure 9.5 and 9.6., particularly a probe with the outlet hole at the tip of the pyramid and another with holes milled at the base of the pyramidal tip, similar to the batch processed MFP.
Although the configuration with two cantilevers is advantageous in many applications, because one tip is used for surface modification and the other for detection of the changed topography, it is possible to use the MFP with just one cantilever for both purposes.

Figure 9.4. Top and bottom views of the MFP cantilevers. The fluidic channels (250 nm high, 2 µm wide) are embedded in the multifunctional cantilever. The close-up image shows that the sharpness of the multifunctional tip is not affected by the photolithographically defined outlet. The outlet holes of the channels are shown with arrows in the inset.

Figure 9.5. Outlet hole milled at the tip of the pyramidal multifunctional tip by FIB.

Figure 9.6. Outlet holes milled at the base of the pyramidal multifunctional tip by FIB.
(modification and detection), when the outlet hole of the fluidic channel is opened on the facets or at the base of the pyramidal tip (Figure 9.7).

![Figure 9.7. Top view of an MFP probe with one cantilever.](image)

### 9.4. Proof of principle

The fluid transport from the reservoir to the tip of the multifunctional cantilever was tested in different ways. The first test was carried out before the cantilevers were coated with gold, in order to allow optical inspection. Prior to testing the devices were annealed in an oven heated to 280 °C, in ambient environment, for functionalizing of the fluidic channels by eliminating possible organic contaminants deposited onto the channel walls. The reservoir was fed with a water droplet and the capillary filling of the channels was observed by color change when the fluid column advanced towards the tip (Figure 9.8).

![Figure 9.8. Capture of the capillary filling of the fluidic channel. The tested MFP has two reservoirs, one for each channel. When just one reservoir is filled, the fluid column advances only in the channel that is connected to it. The moving meniscus can be followed by the color change of the filled part of the channel.](image)
Chapter 9

We observed with optical microscope that the water flowed instantaneously in treated channels, which is in correspondence with a driving capillary pressure of several bars [16]. The filling speed decreased with time, so that after storing the samples for three days or more the heat treatment had to be repeated in order to retrieve the initial filling speed. The regeneration of the MFP probes was also tested at higher temperatures (400-450 °C), but the gold layer deposited onto the probes, to enhance optical reflection, was considerably damaged.

The fluid transport in the gold-coated MFP probes was checked with the resonance frequency shift of the cantilever with water filled channels compared to that with empty channels. The cantilever was excited by the piezo-stack of an MMAFM-2 manufactured by Digital Instruments, in tapping mode operation. By exciting the cantilevers with dry channels (no fluid in the reservoir) for a certain frequency range (0-500 kHz) in tapping mode, two resonance modes were found (shown by the dashed line in Figure 9.9). After inserting a water droplet with a syringe into the reservoir, the experiment was repeated and a shift in resonance frequency was observed for both modes as the continuous line shows in Figure 9.9. The frequency shift due to additional fluid mass [17] for both resonance modes is according to the computation. Considering the cross-sectional areas of the cantilever and the densities of water and Si$_x$N$_y$, a 3.2 % increase of the mass of the cantilever was expected, which is in correspondence with the observed 1.6 % shift in the resonance frequencies.

![Figure 9.9. Dynamic response of the cantilever versus frequency: dashed line – dry conditions (empty channels); continuous line – with water filled channels. The frequency shift is caused by the additional mass of fluid.](image)

The change of tip-substrate adhesion strength was measured to demonstrate that via the pyramidal tip fluid transport occurs to a sample surface. There is a significant increase in adhesion when the channel is filled with water compared to dry contact conditions. Figure 9.10, shows the force curves for Si$_x$N$_y$ pyramidal tip and native oxide covered single-crystal Si substrate for dry conditions and water filled channels. The device used for the pull-off test was the one shown in Figure 9.4. The laser beam was focused on the topside of the outer cantilever with a calculated spring constant of 0.055 N/m [18].

The surface of the polished single-crystal Si sample was hydrophilic in nature due to the presence of native oxide. For water filled channels the pull-off force increased four times
due to the capillary forces in fluid mediated contact, which convincingly shows that the water reached the tip-substrate interface. For a spherical tip of radius $R$ the contact force is given by $4\gamma R \cos \theta$ [19]. Good agreement with the measured pull-off force was found assuming a contact angle of 20°, a tip radius of 30 nm (typical for this fabrication process) and taking the surface tension of water. The measured and calculated values of the pull-off force are 8.3 and 8.2 nN respectively.

9.5. Conclusions

A device was presented which enables continuous fluid supply from one or two fluid reservoirs for localized applications based on atomic force microscopy.

The combination of the in-situ surface modification and characterization technique with the micromachined fountain pen further extends the field of AFM-based applications.

The tool was designed in such a way that it is suitable for standard AFM equipment without any modification.

Different configurations of the MFP were presented together with the fabrication process. The tool can be fabricated in batch process if the outlet holes of the fluidic channels are photolithographically defined, enabling an economically viable fabrication which may have a profound impact in AFM-based lithography and in other applications.

Fluid flow was observed in the channels with optical microscope and evidence of fluid transport from the reservoir to the pyramidal tip has been shown by resonance frequency

![Figure 9.10. Comparison of the adhesion strength for dry and wet Si$_x$N$_y$ tip on polished single-crystal Si sample. The pull-off forces calculated based on the force curves are 2.1 and 8.3 nN respectively. Testing conditions: relative humidity 45%, temperature 20 °C. The signal waviness is an artifact due to interference of the measuring laser.](image)
shift. It has also been demonstrated by pull-off force measurements that fluid transfer occurs from the pyramidal tip of the MFP probe to a substrate.

In the following chapter the capabilities of the micromachined fountain pen are demonstrated in various applications, such as fluid enabled material removal and deposition.

9.6. References


Chapter 10

Applications of the Micromachined Fountain Pen

Abstract

In this chapter the applications of the micromachined fountain pen are presented, such as fountain pen lithography, electrochemical metal deposition as well as in-situ characterization of fluid enabled surface modification. The continuous fluid supply facilitates new applications or extends several AFM-based surface modification techniques. Another advantage is that the same AFM equipment can be used for various applications. Future applications are identified and discussed, which show the possible impact of the micromachined fountain pen in nanoscale science.

10.1. Fountain Pen Lithography

The application field of the AFM is ever increasing, since ongoing development of probes and instrumentation enables new possibilities. The main constraint of the technique in fluid-based localized surface modification was the limited quantity of fluid that could be used. Therefore, these applications were mostly carried out with pulled glass capillaries (nanopipettes) thus far [1-4]. The concern to overcome this limitation emerges from the requirement of dedicated instrumentation to control nanopipettes and to reduce the critical dimensions of the patterns created. The trend of the research carried out in this direction shows the necessity to use standard equipment such as AFM for fluid-based localized surface modification. Starting with dip-pen lithography [5], different approaches have been tried such as using inking wells, so that after the available fluid on the tip is consumed, the tip can pick ink up and continue the operation [6]. Feeding the probes with an increased quantity of fluid was the other option, which could be achieved either by putting a fluid droplet on the backside of the cantilever carrying a hollow tip [7] or by transporting the fluid from a reservoir to the tip by fluidic channels [8].

The micromachined fountain pen presented in the previous chapter is able to supply liquid for relatively long operation compared to dip-pen technique. Lithography experiments were carried out with the tool in order to test its capabilities. The configuration of the MFP used in the tests was the one presented in Figure 9.4., with photolithographically defined outlet holes at the base of the pyramidal multifunctional tip. The laser beam was focused onto the topside of the multifunctional cantilever for both purposes, creating and detecting the patterns.
Two kinds of fountain pen lithography applications are presented, patterns created by depositing and by removing material.

10.1.1. Fountain Pen Lithography by SAM adsorption on Au substrates

The state-of-the-art technique of using scanning probe microscopy for deposition of Self-Assembled Monolayers (SAM) on a gold substrate is the dip-pen lithography [5]. The technique uses a solid-state substrate and an AFM probe-tip coated with molecules which have chemical affinity for the substrate. The medium to transport the molecules from the probe-tip to the sample surface is the water droplet, which forms at the tip-substrate interface when the relative humidity is above a certain threshold. Although the inking well [6] provides supply for the tip used for patterning, the operation has to be interrupted each time when the tip runs out of ink, thus the change of contact force and alignment problems emerge by resuming the operation. The operational time can be extended without these problems by using the MFP probe. Containing a fluidic reservoir in the probe support which can be filled with a certain fluid by syringe or via fluidic connections from the probe holder to the probe support, the MFP becomes suitable for patterning purposes, performing like a fountain pen.

For proof of concept two tests were carried out with inks having different chemical composition. In the first experiment 1-octadecanethiol (ODT) dissolved at 0.1 mM in CH$_2$Cl$_2$ was used as ink on a 20 nm thick sputtered gold surface. The ink forms a self-assembled monolayer when brought in contact with a gold surface.

Figure 10.1. Friction image of pattern (lines) generated with ODT (dissolved at 0.1 mM in CH$_2$Cl$_2$) on a gold sample by 5 scan cycles (each) with a contact force of 1 nN at a speed of 4 µm/s. The ODT lines exhibit lower friction force than Au.

Each line in Figure 10.1. was generated by 5 scan cycles in the direction orthogonal to the longitudinal axis of the cantilever, while the slow scan axis was disabled. The contact force
was 1 nN and the scanning speed 4 µm/s. Figure 10.1. is the friction image obtained by frame scanning using the same tip as for SAM writing.

The second experiment was carried out with 1-octadecanethiol dissolved at 0.1 mM in C₂H₅OH on the same sputtered gold substrate. The scan conditions to create the pattern were identical with the previous experiment and the lines were also generated by 5 scan cycles (Figure 10.2.). The detection was done using the same tip immediately after pattern generation in the friction force operating mode of the AFM.

The thinnest lines generated by adsorption of SAM on gold surface were 0.5 µm wide. We estimate that the width of the lines is determined by the diffusion and wetting due to continuous ink flow, beside the well-known effect of the sharpness of the tip and the roughness of the sample surface. Optimization of the tip geometry, ink flow-rate (through the size of outlet holes, viscosity and wetting properties of the ink), and smoothness of the sample surface could further decrease the critical width.

Figure 10.2. Friction image of pattern (cross) generated with ODT (dissolved at 0.1 mM in C₂H₅OH) on a gold sample by 5 scan cycles with a contact force of 1 nN at a speed of 4 µm/s.

Theoretical studies on the size of the meniscus formed by capillary condensation between a flat surface and an AFM-tip showed that the ultimate size of the meniscus can be 2 nm in the case of the sharpest possible tip for which the contact diameter would be equivalent to the diameter of just one molecule [15]. This determines the resolution of the dip-pen lithography, technique in which the relative humidity plays an important role. For fountain pen lithography the vapor saturation is high around the tip-substrate interface due to continuous fluid transport on the sidewalls of the AFM-tip. The ultimate size of the meniscus for the most favorable case can roughly be compared with that of the meniscus formed between the tip and substrate due to capillary condensation in relatively high vapor saturation. For a tip radius of about 30 nm the estimated minimum width of the stable liquid meniscus is approximately 40-50 molecular diameters in this condition (~20 nm for water which has a molecular diameter of about 0.37 nm).
10.1.2. Patterning by fluid assisted material removal

This technique is used for correcting masks or creating masking layers for fabrication of micro/nanostructures, and it belongs to the top-down nanotechnology approach. Reported state-of-the-art fountain pen nanochemistry [2] is carried out with a cantilevered quartz micropipette by etching patterns in chromium (Cr) with a cyanide-based etchant. The fluid was pressure driven and the environment around the sample surface had to be controlled in order to avoid formation of globules when the etchant fluid reaches the Cr substrate.

The advantage of using MFP is that the fluid does not need to be pressure driven and formation of globules on the sample surface has not been observed during operation, so that no special environment had to be created around the sample.

Fluid assisted material removal can be chemical when the fluid reacts with the sample material and the resulting product is removed without further mechanical intervention of the tip (e.g. by suction when one channel is used to supply fluid and the other to remove the resulting product) or chemical-mechanical when the fluid reacts with the sample material dissolving it or softening it, and subsequently removing it by mechanical action of the tip. The pure chemical removal of material is theoretically possible with the fabricated MFP, but practically it is an ambitious future work since the suction of the reaction product raises further technical challenges. The chemical-mechanical material removal is a straightforward technique, therefore it is presented here for proof of principle.

The patterns were created with fluidic contribution and then the detection of the patterns was done by frame scanning with the same tip after it dried. Chromium was chosen for sample material due to its hardness, so that at a few nN contact force it cannot be scratched mechanically with a Si$_3$N$_4$ tip.

![Figure 10.3. Lines etched with Chromium etchant Selectipur® into sputtered Cr. Line at 90° orientation to the longitudinal axis of the cantilever etched by three scan cycles with 5 µm/s speed at 5 nN contact force – 25 nm deep and 0.8 µm wide. Line at 45° orientation etched by one scan cycle under the same conditions – 14 nm deep and 0.35 µm wide.](image_url)
A 25 nm thick Cr layer sputtered on a polished <100> single-crystal Si substrate was used as sample surface and the fluid was Chromium etchant Selectipur® (MERCK 111547) with ammonium cerium (IV) nitrate as main active component.

Two lines were etched into the Cr film, as shown in Figure 10.3. A line at 90° orientation to the longitudinal axis of the cantilever was etched by three scan cycles with 5 µm/s speed at 5 nN contact force, and another at 45° orientation by just one scan cycle under the same conditions. The first line was 25 nm deep and 0.8 µm wide (the tip reached the Si substrate on which the Cr was sputtered), while the second was 14 nm deep and 0.35 µm wide.

The example shows the potential of the MFP in lithography, although further optimization has to be made to reduce the critical size of the patterns created with fluidic contribution.

10.2. AFM-based electrochemical metal deposition

Since an electrical circuit can be closed by an electrical conductive fluid, the MFP should enable AFM-based electrochemical metal deposition from electrolyte solution.

State-of-the-art nanoelectrochemical depositions are carried out with pulled glass capillaries [3], requiring special instrumentation. The goal was to create micro/nano structures by electrochemical deposition using standard instrumentation such as AFM equipment. The use of dip-pen technique [5] and nanodispensing [7] in AFM-based electrochemical metal deposition is limited by the small amount of liquid that can be used as electrolyte and the problems related to closing the electrical circuit via the electrolyte solution.

The working principle of the electrochemical AFM-based metal deposition is presented in Figure 10.4.

Figure 10.4. Principle of the AFM-based electrochemical metal deposition with MFP probe. The cross section of the MFP probe illustrates the transport of the electrolyte from the reservoir to the sample surface.
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The cathode, where material is deposited, has to be an electrical conductive material. The anode is a gold layer on the topside of the MFP probe, which also enhances the optical reflection of the laser beam onto the photodiodes. The wall of the truncated cone-shaped reservoir is also covered by gold due to the nature of the sputtering process, thus the electrical circuit is closed via the electrolyte as long as the reservoir is not completely empty.

A DC source was used for the voltage driven experiments and the complementary electrical circuit was realized with platinum wires, which were glued to the substrate (cathode) and to the metallic support of the MFP probe (anode). Due to the small dimensions of the channel its electrical resistance is high ($\gg 10 \, \text{M} \Omega$ for practical solutions). Therefore, for sufficiently high driving voltages, the writing current is mainly determined by the channel resistance. More in detail, the channel resistance is given by:

$$R = \frac{l}{\kappa A}$$  \hfill (10.1)

where $\kappa \, \text{[S/m]}$ is the conductivity of the electrolyte, $l$ is the channel length, and $A$ is the cross sectional area of the channel.

In the experiments CuSO$_4$ dissolved at 1 mM in deionised water was used as electrolyte. The measured conductivity of the electrolyte solution was 176 $\mu$S/cm. Eq. (10.1) returns a channel resistance of approximately 110 G$\Omega$ for a 2 $\mu$m wide, 0.25 $\mu$m thick and 1 mm long electrolyte column in the channel. The electrochemical deposition was carried out at 10 V DC, which according to the channel resistance results in ~90 pA electrical current. Assuming a density of the deposited Cu of 8920 kg $\cdot$ m$^{-3}$ this corresponds to a deposition rate of $3.3 \times 10^6$ nm$^3$ $\cdot$ s$^{-1}$ [16].

The deposition procedure was the following:

i) insertion of electrolyte into the fluidic reservoir with a syringe;

ii) approaching the substrate with the pyramidal tip in contact AFM mode. The settings correspond to approximately 10-15 nN contact force for dry conditions.

iii) adjusting settings so that for dry contact condition the tip would snap off, but in reality the capillary forces present in the meniscus formed between the pyramidal tip and the substrate keep the tip in close proximity of the substrate;

iv) switching DC source on and starting pattern generation by scanning.

Three experiments were performed to show the proof of principle of AFM-based nanoelectrochemical metal deposition. In all three cases Cu structures were created from CuSO$_4$ electrolyte solution on different substrates.

The first experiment was carried out to create a Cu pattern on a 100 nm thick gold layer sputtered on a $<100>$ single-crystal Si wafer. It was intended to write “UT” by five scan cycles on each line (slow scan axis disabled). The result was analyzed by frame scanning of a larger area (Figure 10.5). The lines created by scanning orthogonal to the longitudinal axis of the cantilever resulted in Cu structures, while generation of lines by scanning along the longitudinal axis of the cantilever was not successful. This might be explained by the location of the outlet holes (Figure 9.4. and 9.6) at the two opposite sides of the pyramidal tip, which makes that fluid transport from the base to the tip of the pyramid occurs via those two facets.
Further investigation is needed to determine the reason why lines orthogonal to the longitudinal axis of the cantilever can successfully be created, while in the other direction not. One of the possibilities is to change the design of the micromachined fountain pen, so that the outlet holes are opened at the base of all four facets, but other parameters such as contact force, scan velocity and fluid flow rate can also play an important role.

The volume of the deposited Cu was estimated by using the section analysis along one of the 20 µm long lines (Figure 10.5). The lines were smeared laterally due to frame scanning at a too large contact force. The volume calculated from the geometrical characteristics of the deposited Cu line and that calculated using the deposition rate, scan velocity, number of scan cycles and length of the line are in good agreement. The theoretical volume of Cu deposited is $1.65 \cdot 10^9$ nm$^3$, while in reality the estimated volume is $1.5 \cdot 10^9$ nm$^3$.

![Figure 10.5](image1.png)

Figure 10.5. Lines created by 5 scan cycles in the direction orthogonal to the longitudinal axis of the cantilever, at 0.4 µm/s scan speed. The section analysis shows the height difference along the line. The hills at the two ends of the line indicate that material is transported by the tip and is accumulated at the end of the scan range. The height difference in the middle of the line can be caused by smearing during frame scanning due to high contact force.

For the second experiment a 30 nm thick Cr layer sputtered on a <100> single-crystal Si
wafer was used as cathode, on which 20 \( \mu \text{m} \) long Cu lines were deposited (Figure 10.6.). The electrochemical deposition was carried out by scanning once in the direction orthogonal to the longitudinal axis of the cantilever, at 0.4 \( \mu \text{m/s} \) scan speed.

The obtained lines were examined by frame scanning at relatively low contact force due to the reduced hardness of the Cu compared to the Cr substrate. High scan velocity and/or large contact force damaged the deposited Cu lines as it could be seen in Figure 10.5. The average height of the smallest lines that could be deposited with this technique was 3 nm, while the width was varying between 250-300 nm. In this case the theoretical volume that should have been deposited is almost a factor of 10 larger than the calculated one from the geometrical characteristics of the line, which might be caused by the lower flow-rate of the electrolyte due to possible clogging of the outlet hole and/or fabrication imperfections, but also by the use of a different substrate (Cr instead of Au).

The third experiment was carried out to demonstrate that three-dimensional structures can be created by successive scanning on a particular region. A 100 nm thick gold layer sputtered on a <100> single-crystal Si wafer was used as substrate.

Copper structures were created by two subsequent scan cycles on a 1x1 \( \mu \text{m}^2 \) frame at 0.4 \( \mu \text{m/s} \) scan speed. The fast scan axis was orthogonal to the longitudinal axis of the cantilever.

After first time scanning the result was analyzed by frame scanning of a larger area. Deposition of Cu was observed, as the section analysis in Figure 10.7. shows. The base of the structure is larger than the scanned area, which can be explained by the diffusion of the electrolyte solution on the substrate. The height of the structure was 28.1 nm after the first deposition. After the tip was repositioned on the initial 1x1 \( \mu \text{m}^2 \) frame, a second scanning was carried out, resulting in a hill with a height of 75.3 nm. Like in the previous case, the theoretical volume of Cu that should have been deposited is also several times larger than that calculated from the measurement of the geometrical characteristics of the structure.

Preliminary tests show promising results, but further optimization has to be carried out on fluid flow rate, electrolyte concentration and composition, electrical current density

![Figure 10.6. Three 20 µm long Cu lines deposited onto a 30 nm thick sputtered Cr layer at 0.4 µm/s scan speed. The average height of the lines is 3 nm, while the width is varying between 250-300 nm.](image)
Applications of the MFP

and choice of substrate material. The reasons why the theoretical volume of material that should be deposited is different from reality has to be investigated, and further work has to be done on the improvement of the resolution and the reproducibility of the deposition technique.

Nanoelectronics is one of the possible applications of the technique, but potential applications can emerge in the fields where metallic structures have to be created with bottom-up approach, although this requires further reduction of the deposition rate.

10.3. In-situ characterization of surface modification due to localized fluid dispensing

In-situ characterization of surface modification is possible when two cantilevers are used, like in the case of the wear-AFM probe, one for fluid enabled surface modification and the other for detection. The test presented in this section is intended to show this capability. The outlet hole of the fluidic channel was FIB milled at the tip of the pyramid, as shown in Figure 10.7. 3-D copper structure created by two complete scan cycles on a 1x1 μm² frame. The substrate was sputtered Au and the scan speed was 0.4 μm/s. The section analysis shows the height of the structure deposited by the first and second scan cycle. The width of the structure at the base is 1.25 μm and the maximum height was 28.1 nm after the first and 75.3 nm after the second scan cycle.

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Figure 9.5. A 100 nm thick sputtered Cr layer was used as sample surface and the fluid was Chromium etchant Selectipur®. Frame scanning was performed using the working principle presented in Figure 8.2, for dry condition and with fluidic contributions. The scan speed was 80 µm/s, while the contact force on the detection and multifunctional tips were 5 nN and 0.6 µN respectively. High scan speed was used in order to limit the diffusion of the etchant during operation.

In Figure 10.8.(a) it can be observed that no surface modification was identified by the detection tip in the overlap region for dry condition, which demonstrates that the sample surface is hard enough not to be mechanically modified by a Si₃N₄ tip. The surface of materials less hard than Si₃N₄, such as single-crystal Si, is mechanically modified already during the first scan cycle due to relatively large contact force on the multifunctional tip when the detection tip slightly touches the sample [9].

Fluid (Cr etchant) was inserted into the reservoir with a syringe and the experiment was repeated. Within the first scan cycle we observed a step of about 16 nm high. In the operating range of the multifunctional tip the liquid dispensed on the sample attacks the Cr chemically and the tip removes the product mechanically. In Figure 10.8.(b) it can be observed that a sharp line differentiates the regions of modified and unmodified topographies, which also represents the end of the scanning range of the multifunctional tip. The surface of the etched area is smoother than the surface of the original sample, thus the process can be regarded as local chemical-mechanical polishing.

Although further tests have to be conducted in micro/nano tribology, it is obvious that the MFP probe allows tribological studies with local lubrication. This has been shown by taking the most unfavorable case, when the so-called “lubricant” chemically attacks the material.

![Figure 10.8](image)

Figure 10.8. In-situ characterization of surface modification. Left – in dry condition the multifunctional Si₃N₄ tip cannot mechanically modify the surface topography due to the hardness of the Cr. Right – when Chromium etchant is dispensed through the multifunctional tip, the fluid reacts with the Cr surface and the product is removed mechanically by the tip. The surface is significantly modified within the overlap area, while it remains almost unmodified in the rest of the image.
10.4. Conclusions

Successful operation of the MFP probes has been shown by carrying out various AFM-based applications requiring continuous fluid supply.

The utility of the MFP has been proven for lithographical application such as writing with self-assembled monolayers on gold surface, and by removing materials locally, in a controlled way. The critical size of the patterns created is limited by the spreading of the fluid on the sample surface. This effect is much more evident than in dip-pen lithography due to continuous fluid flow. Optimization of the ink flow rate by modifying the size of outlet holes, the viscosity and wetting properties of the ink, can push the performance of the AFM-based fountain pen lithography to match those of the dip-pen lithography.

AFM-based electrochemical metal deposition was carried out successfully using MFP. The proof of principle has been shown, and results such as deposition of copper features on chromium and gold surfaces demonstrate the possibility to create 3-D micro/nanostructures with bottom-up approach. Further investigations have still to be carried out to study the effect of different factors on the deposition, such as: concentration of the electrolyte solution, tip sharpness, flow rate of the electrolyte, current density, substrate material and environment.

The continuous fluid supply through a test surface or a tip located on the multifunctional cantilever allows in-situ investigation of fluid assisted surface modification when the laser beam is focused on the top of the detection cantilever. This has been proved by in-situ detection of chromium etching by a solution released at the multifunctional tip. Although the test had to be carried out at relatively high speed to avoid the diffusion of the chromium etchant on the sample surface, this experiment showed that the MFP enables in-situ nanoscale tribological investigations in dry and lubricated conditions.

10.5. New opportunities

Further research has to be directed to improve the performance and the reproducibility of the above-mentioned applications by optimizing the operation conditions. Investigation on the influence of the fluid flow rate, the properties of the fluid and sample material, and the effect of the tip geometry on the critical dimensions of the patterns generated by different applications has to be conducted.

Secondly, the possibility to use the MFP in other applications such as electroless deposition [10], electrochemical etching, different bio-chemical and bio-physical [12-14] applications has to be explored. The micromachined fountain pen also facilitates localized chemistry experiments using multi-component substances which are mixed at a hollow tip (Figure 10.9.). Experiments like sampling a cell (add and/or remove substances), applying different stimuli and monitoring the reaction of the cell, or trap and transport them, are in close reach with the developed device.

The active control of the fluid flow rate and flow direction by electroosmotic or
pressure driven fluid transport is another important issue that can improve the performance of the applications or which can even further enlarge the application field of the AFM.

With single or multiple cantilever tools characterized in that there are at least two channels embedded in the multifunctional cantilever having separate or joint outlet for the supply or removal of alike or dissimilar substances, it is possible to create local environment (such as gas curtains or to control the humidity locally) for different localized applications (e.g. etching, writing, deposition).

![Figure 10.9](image)

Figure 10.9. Top and bottom views of the MFP configuration for localized chemistry using multi-component substances.

Making active multifunctional cantilevers instead of passive ones is another direction that has been taken into consideration, e.g. the position of the cantilever could be controlled by applying electrical current [11].

## 10.6. References


Applications of the MFP


Summary

MEMS and AFM-based surface modification techniques and applications are presented in the dissertation. The starting point of the work was the investigation of tribology at microscale. Motivation of the work and general approach of the subject are presented in the introduction, followed by the background of microtribology. The most important historical progresses of tribology as science are pointed, on which the microtribology has been developed.

The requirements and the design of a microtribotester are presented in chapter three. These are based on adhesion and friction considerations for microstructures. Different in- and out-of-plane actuators, from which the microtribotester is built up, are designed and their performance is simulated by finite element method.

Chapter four comprises the work carried out on technological developments for fabrication of complex MEMS devices like the microtribosensor. It is composed of a part describing investigations on the change of residual stress of undoped sacrificial silicon-oxide at high temperature processing, a part consisting of studies carried out on optimization of reactive ion etching processes for thick silicon-oxide layers and Si$_3$N$_4$/polycrystalline-Si/silicon-oxide stacks. In the third part a novel release technique is described, which enables releasing complex MEMS structures consisting of multiple structural layers built up on multiple sacrificial layers, but which do not contain enclosed cavities.

Chapter five is based on characterization of electrothermal actuators and describes an empirical method of discriminating reversible and irreversible actuation regimes of electrothermal actuators, since their main disadvantage is the plastic deformation at high temperatures, which modifies their geometry and hence their initial neutral position.

In chapter six the fabrication process of the microtribotester is presented, and its successful operation is shown. The reason of continuing the work in the direction of atomic force microscope-based surface modification and characterization is also discussed.

Chapter seven is a prologue to the second major part of the dissertation. Basic notions related to atomic force microscopy are introduced in order to help in the interpretation of data presented in the following chapters.

A new in-situ AFM-based surface modification and characterization technique is described in chapter eight. The technique developed enlarges the possibilities of micro- and nano-tribological investigations using atomic force microscopy, since it enables in-situ wear, friction and adhesion studies for various material-couples and loading conditions.

In chapter nine further development of the AFM-probes is presented. In order to allow AFM-based fluid enabled surface modification, new probes were designed and fabricated, comprising reservoir(s) and fluidic channels in their structure. The proof of principle, based on experimental evidences, is also shown in this chapter.

Chapter ten focuses exclusively on new applications, which can only be carried out by using the AFM-probes with fluidic capabilities. In-situ AFM-based surface modification and
characterization technique can be used in combination with the new probes, hence tribological investigations can be carried out with local lubrication. The utility of the micromachined fountain pen has been proven for lithographical application, such as writing with self-assembled monolayers on gold surface and by removing materials locally, in a controlled way. The micromachined fountain pen improves techniques like dip-pen lithography due to continuous fluid flow, and surface modification carried out by using pulled glass pipettes up to now. Another application, the electrochemical deposition of metal features, demonstrates the possibility to create 3-D micro/nanostructures with bottom-up approach using standard AFM equipment. All these preliminary tests provide the evidence that the new AFM-probes considerably enlarge the field of AFM-based applications. Furthermore, other opportunities have been identified such as multicomponent chemistry and cell manipulation by using dedicated AFM-probes, which can be developed based on the micromachined fountain pen.
List of publications

Journals

Proceedings
- S. Deladi, G.J.M. Krijnen, M.C. Elwenspoek, “Parallel beams/lever electrothermal out-of-
List of publications


Posters

• S. Deladi, G.J.M. Krijnen, M.C. Elwenspoek, “Powerful electrothermal actuators developed for micro-tribosensors”, The sense of contact 5th workshop, 12-13 March 2003, Wageningen.


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