Tribological studies on fracture and erosion of nanostructures

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We present a variety of scanning force microscope experiments concerning fracture and wear mechanisms of microfabricated nanotowers. The scanning force microscope tip is used as a tool to apply well-defined forces to the surface of the patterned substrate that consists of a two-dimensional array of nanotowers. Detailed studies reveal two different wear mechanisms: erosive wear of the nanotower from the top and fracture of the structure at its bottom. Using optimized parameters, a controlled removal of individual nanotowers and the ability to create predefined patterns on the nanometer scale can be achieved.

KEY WORDS: atomic force microscope; nanostructure; silicon dioxide; fracture; modification; erosive wear

1. Introduction

Scanning probe microscopy (SPM) techniques are increasingly used for tribological studies of engineering surfaces at scales ranging from micrometers to atoms and molecules [1]. The scanning force microscope (SFM) allows nanotribological investigations with simultaneous measurements of topography and friction forces. Successive scans give insight into surface modifications and wear. These techniques have been used to study adhesion and friction [2], scratching and wear [3], indentation [4], and for nanofabrication and nanomachining purposes [1]. Forces involved in the sliding of nanocrystals [5] or carbon nanotubes [6] on substrates can be examined by this means. Dissipation and cohesive energies of C₆₀ have been determined in such nanometer-scale experiments [7].

Beyond tribological studies SPM techniques have been used for surface modification experiments. Writing patterns in polymers [8] or producing lines [9,10] and dots [11,12] in semiconductor surfaces could be achieved by these means. The positioning of atoms [13] and molecules [14], nanocrystals [5] and particles [15] has been performed successfully.

We present a variety of new modification experiments with microfabricated nanotowers which give access to tribologically relevant parameters of fracture and wear on the nanometer scale. Using an SFM tip as a tool, forces are applied to the surface of the patterned substrate resulting in different types of modification of the towers. Using optimized SFM parameters a controlled removal of individual nanotowers and the ability to create predefined patterns on a nanometer scale can be achieved.

2. Experimental

We used a Topometrix Explorer SFM in contact mode with silicon nitride tips (Microlevers by Park Scientific Instruments). The calibration of the cantilevers was carried out

by the method described by Hutter and Bechhöfer [16]. The sample consisted of SiO₂ towers on a silicon (100) surface; the towers were arranged in a square order with a periodicity of 680 nm and a height of 120 nm. The experiments were performed in bidistilled water.

For the preparation of the samples an oxidized Si (100) wafer (120-nm oxide layer) was cleaned with Microposit Remover 1165 and covered with Primer Solar (0.1 ml) and photoresist S1805 (0.1 ml, both from Shipley). The surface was structured by laser interference lithography (HeCd laser with $\lambda = 442$ nm and $P = 80$ mW). The development was performed with a mixture of Microposit Developer MF-319 (70 ml) and DI water (10 ml). After the etching process in buffered hydrofluoric acid, the photoresist and the light exposed structure were removed with Microposit Remover 1165 [17].

The sample was imaged in contact mode with a normal force of 4 nN ("imaging mode"). Fracture and modification of individual nanotowers were achieved by two different techniques: increasing the scanning force ("static modification mode") or increasing the scanning force and exciting cantilever oscillations additionally ("dynamic modification mode"). The oscillation frequency and amplitude have been selected to be 1.75 kHz and 25 nm, respectively (figure 1) [18].

3. Results and discussion

In a detailed series of surface modification experiments, the relevant parameters have been identified and two different types of surface modification processes observed. In the following, these two processes will be called "fracture" and "erosion". Fracture is described in figure 2: (a) shows an unmodified sample with SiO₂ nanotowers arranged on a silicon substrate. Applying an increased force in dynamic modification mode to the tower in the position marked by the dark

Figure 1. Diagram of the modes used for imaging and modifying the sample: The sample is imaged in contact mode with a force loading of 4 nN (“imaging mode”). Fracture of individual nanotowers can be achieved by two different techniques: increasing the scanning force (“static modification mode”) or increasing the scanning force and exciting cantilever oscillations additionally (“dynamic modification mode”) [18].

Figure 2. Selective removal of SiO₂ nanotowers using scanning force microscopy (SFM): (a) SiO₂ nanotowers with a lattice constant of 680 nm and a height of 120 nm on a Si substrate produced by laser interference lithography. (b) Applying an increased force in dynamic modification mode to the tower indicated by the dark cross in (a) results in fracture and removal. The residual surface area after fracture and removal is shown in (c). The roughness of the residual surface is <2 nm. A comparison of this value with the original tower height (120 nm) indicates a breaking of the structure at the bottom end.

“X” results in fracture and removal (figure 2(b)). Figure 2(c) shows the residual surface area after fracture and removal. The roughness of the residual surface is <2 nm. A comparison of this value with the original tower height (120 nm) indicates a breaking of the structure at the bottom end. This removal process was observed in the dynamic as well as the static modification mode. The SiO₂/Si interface has been ob-

Figure 3. Gradual erosion of nanotowers: (a) The two towers in the middle row have been exposed for different durations to dynamic modification mode. The cross-section (b) (indicated by the arrows in (a)) shows the gradual decrease of structure height and width. The monotonic dependence of the height decrease on the time of exposure and the number of oscillations, respectively, is shown in (c).

served to be of critical importance as a well-defined “weak link” for this fracture process [18].

Besides the breaking of the towers at their bottom end, a second removing process (“erosion”) was observed using the dynamic modification mode. In figure 3(a) the two towers in the middle row have been dynamically modified for durations increased in two steps from left to right. The cross-section (b) (indicated by the arrows in (a)) shows the gradual decrease of structure height and width. The degree of erosion is monotonically dependent on the time the tip is located at a tower (figure 3(c)). The top x -axis relates the residual tower height with the number of oscillations, which we identify as the individual events of “tip-attacks”.

In the following we discuss the forces involved in the static and dynamic modification processes: In dynamic modification mode the force applied to the towers was set to a calibrated value of 8 nN with an additional modulated force amplitude of ± 1 nN. In static modification mode, the threshold value for fracture has been determined to be 13 nN [18]. Thus, the modulation of forces with lower peak values leads to lower thresholds for tower removal than in the corresponding static case. In the dynamic modification process, the number of individual “attacks” is in the order of several

Figure 4. Erosion of a selected nanotower: (a) Unmodified tower (left) with the corresponding cross-section (right) indicated by the bright line. After a modification experiment performed at the position marked by the dark “X”, the shape of this selected tower is changed (b). Due to the erosion process the maximum height of the tower is decreased from 120 to 100 nm. Beyond the expected modification at the marked position the total half of the nanotower shown in the lower part of the image has been eroded. Here, the height decrease is doubled with respect to the upper half. (c) Considering this diagram of the expected modification and a lateral force increase on surfaces with positive slope [20], a mechanism for the observed modification can be proposed (see text).

ten thousands with forces slightly below the observed static modification threshold force. In macroscopic tribological studies this phenomenon is generally described as “fatigue”. Highly repetitive load/unload cycles lead to failure at a lower threshold than that measured for static events [19]. In the described case, dynamic fracture of a nanotower can be initiated at about 70% of the maximum load required for static modification. These results are to be compared to fracture mechanics experiments on a larger scale.

In figure 4, the shape of a tower is investigated after dynamic modification. Figure 4(a) shows an unmodified tower (left) with the corresponding cross-section (right) indicated by the bright line. After a modification experiment performed at the position marked by the dark “X”, the shape of this selected tower is changed (figure 4(b)). Due to the erosion process, the maximum height of the tower is decreased from 120 to 100 nm. Beyond the expected modification at the marked position, the total half of the nanotower shown in the lower part of the image has been eroded. Here, the height decrease is doubled with respect to the upper half. In accordance with the observations of Ogletree [20] we propose the following mechanism: First a ditch is formed by erosion

Figure 5. Nanopattern generated using the described dynamic modification method after detailed optimization of all relevant parameters: Individual nanotowers have been directly accessed and removed.

at the marked position. Then the increased lateral force F_L exerted by the tip at the positive slope of the ditch leads to partial fracture of the residual tower and the observed “asymmetric” shape (figure 4(c)). Thus, this “asymmetric” shape is a result of the dynamic modification combined with the subsequent imaging which also applies small forces to the sample.

Using similar parameters and the same tip, both fracture and erosion of the nanotowers have been observed reproducibly in dynamic modification mode. The position of the tip with respect to the “attacked” nanotower, *e.g.*, as marked by a white “X” and a dark “X” in figure 4(a), determines the type of surface modification. An attack in the center of the tower (dark “X”) solely induces erosion. Moving the tip from the center to the edge of the tower (white “X”), increases the probability of fracture. The maximum fracture probability is achieved when positioning the tip with its apex straight beside the tower marked by the white cross in figure 4(a). Fracture is then induced by the edge of the tip.

Using a combination of imaging mode and dynamic modification mode, nanotowers can be removed in a controlled way. After optimization of all relevant parameters in dynamic modification mode, individual nanotowers can be directly accessed and removed. Using this technique nanometer scale patterns can be generated [18]. Figure 5 shows an example of a complex pattern produced by this technique. The structure was written and subsequently imaged by the same tip. There is no difference in image quality before and after writing the structure. This confirms that there is little tip damage due to the modification procedure. This observation is also supported by scanning electron microscopy (SEM) analysis of tips before and after dynamic modification mode experiments. The tip apex of a new tip is below 50 nm, which is the resolution limit of the SEM. The manufacturer specifies the radius of curvature to be in the order of 20 nm. After modification of several hundreds of nanotowers, the size of the tip apex is increased to ~ 100 nm,

which is still sufficient for imaging structures of the given size. The foremost tip asperity, which is sharpened in the cantilever manufacturing process, is observed to be removed after such intense use. One may assume a slower increase of the tip apex in subsequent experiments with the same tip. The tip material Si_3N_4 is about three times harder than the sample material SiO_2 ($14.4 \times 10^3 \text{ N/mm}^2$ for Si_3N_4 and $4.4 \times 10^3 \text{ N/mm}^2$ for SiO_2). Thus, some degree of degradation has to be expected.

4. Conclusion

We have presented investigations on fracture and erosion of nanotowers using SFM techniques. Our method can be applied to any system that uses a tip with a higher hardness than the sample. A second system requirement is given by the experiences from the results in figure 4: A superposition of modification and imaging effects should be avoided. Thus, the force in imaging mode has to be so small that a modification can be excluded.

Due to the decreasing size of mechanical devices, fracture mechanics has to be reinvestigated to clarify whether size-effects have to be considered. Our experiments show that cyclic application of defined forces can lead to similar failure to that observed with static forces of a higher value. This feature is known as “fatigue” for macroscopic experiments. In the context of our results one may speculate about “fracture mechanics deviation” from large scale down to the onset of atomic and molecular scale mechanisms. Future applications may include micromechanical data storage using structures with an integrated interface as a well-defined breaking point. The presented experiments open up new pathways for the investigation of the fundamentals of fracture and wear on the nanometer scale and its applications.

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