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Nanoscale friction and wearing of octadecyltrichlorosilane covered silicon surface

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Abstract. Silicon wafers were silanized by plasma hydroxylation and chemical vapour deposition of octadecyltrichlorosilane [OTS, $CH_3(CH_2)_{17}SiCl_3$]. Then, the OTS covered silicon samples were used in atomic force microscopy (AFM) measurements of wearing and friction at nanoscale. Wearing experiment performed by 1000 cycles of forwards and backwards movements of sharp AFM tip revealed formation of a wearing track with a depth that was much smaller than the thickness of OTS coating, which confirmed a very good wearing property of OTS coating. Friction versus normal loading force experiments performed with the same AFM tip revealed a nonlinear dependence of friction force on the normal loading force in agreement with prediction of Bowden and Tabor's theory of friction and an increase of friction with the moving speed. Dependence of friction force on the sliding speed is attributed to a transfer of kinetic energy from the moving AFM tip to individual molecules of OTS coating.

1. Introduction

In their seminal work published in 1954, Bowden and Tabor [1] pointed towards the microscopic foundations of friction. They treated friction as result of elastic deformation of interlocking spherical asperities with the result that the macroscopic friction force is proportional to the total contact area of individual asperities on surfaces of the macroscopic bodies. Increase of the normal loading force determines increase of the real contact area of surface asperities and, therefore, this theory predicts a nonlinear dependence of friction force on normal loading force, in contradiction with Amontons' first law of friction. The experimental investigation of microscopic nature of friction has been facilitated by the inventions of surface force apparatus [2] and atomic force microscope (AFM) [3] and such studies laid foundations of nanotribology [4]. The development in the early 1990's of the AFM technique of friction force microscopy (FFM) allowed many studies of friction at level of single asperity contacts, since the nanoscale sharp tip of the AFM probe is considered as physical model of a single asperity. However, besides asperity interlock origin, friction may result from a mixture of complex processes as plastic deformations, material plough, local welding, molecular interactions between surfaces in relative motion, or by viscous movement of surface adsorbed molecules [5].

In this paper wearing and friction at level of single-asperity contact between octadecyltrichlorosilane (OTS) covered silicon wafers and a sharp silicon AFM tip is studied by atomic force microscopy techniques. Deposition of octadecyltrichlorosilane (OTS) molecular layers is commonly used in electronic industry and in various applications that require modification of silica surfaces as in biosensors, micro electro mechanical systems (MEMS) and actuators [6]. Most MEMS components are manufactured from silicon at nanometer or micrometer sizes [7]. The smallness of these components and gaps formed by their surfaces determines undesired high surface forces [8]. Use of common lubricants in MEMS is impossible because of capillary forces. Therefore, use of self assembled monomolecular coatings (SAM) of silane molecules is an important method for reducing capillary and friction forces in MEMS. In this context, covering with OTS SAMs confers to silica surfaces a hydrophobic character with an important reduction of adhesion and friction forces between moving parts of MEMS [9]. Macroscopic tribology measurements in ball-plane geometry on OTS SAM revealed relatively low friction coefficient at small normal loading force, increase of friction with the sliding velocity and poor wearing properties at relatively large normal loading forces [10]. These measurements may be affected by the poor quality of the OTS SAM, the experiments showing transfer of OTS material from plane substrate to the ball probe of the trybometer. However, the trybologic properties at nanoscale of OTS coatings have not been investigated so far. In the present study we show that OTS coated silicon have good wearing property at nanoscale, the wearing track formed after one thousands wearing cycles having a depth much smaller than the thickness of OTS coating. Also, it was notice a decrease of friction force during first cycles of wearing. The friction versus normal loading force measurements revealed a nonlinear dependence that confirms proportionality relationship between friction force and real contact surface area. Also, the molecular origin of friction force is proved by dependence of friction on the sliding speed, a noticeable increase of friction with the sliding speed being observed.

2. Materials and methods

2.1. Materials

Octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCl_3$, OTS, > 90%) and ethanol (> 99.8%) were purchased from Sigma-Aldrich and used as received. Distillate water was freshly purified and deionised using an Ultrapure Academic Milli-Q system. Single side polished N-type silicon <100> wafers (0.5 mm in thickness) were procured from Sigma-Aldrich. Silicon AFM probes HQ:NSC35/No Al were purchased from Micromasch.

2.2. Deposition of OTS molecular layers

Before OTS depositions, the silicon substrates (1 cm × 1 cm) were cleaned by sonication in pure ethanol and distillate water to remove large dust particles from surfaces. Then, the substrates were loaded on the chamber of plasma and chemical vapour deposition reactor. Depositions were made in two steps:1) cleaning and chemical activation of silicon surfaces by hydroxylation under the action of discharge plasma and 2) exposure of activated surface to OTS vapour. In first step, the silicon substrates were loaded on small stainless steel cathode and the chamber was vacuumed down to 10^{-2} Torr for about 30 minutes. Activation of silicon surface was done by exposing the substrate for 2 minutes to the negative glow plasma of a d.c. luminescent discharge (voltage around 380V and current intensity around 5 mA) in air and water vapour mixture at low pressure (0.3 Torr). In the second step, OTS coatings were fabricated by chemical vapour deposition (CVD) at room temperature in the same reactor chamber by exposing the plasma-activated silica surfaces to OTS vapour for 24 hours. Then, the OTS coated silica substrates were baked in atmospheric air at 100°C for another 24 hours. Then, the probes were used for AFM friction and wearing measurements. Figure 1 shows an AFM topography image of OTS covered silicon surface and the probability distribution of surface height values. The topography image shows a very smooth OTS coating, which can be attributed to a good packing of OTS molecules in a SAM. The probability distribution has a Gaussian shape with a full width at half maximum (FWHM) of 0.19 nm. This computes for the OTS coating a root mean square (RMS) roughness value of 0.16 nm if it is considered that RMS value of noise in the AFM height data of 0.1 nm

2.3. Atomic Force Microscopy wearing and friction measurements

AFM force wearing and friction measurements were performed by a commercial AFM apparatus (XE 100 from Park Systems, South Korea) with silicon AFM probes (HQ:NSC35/No Al from Micromasch). The force constant of the AFM probes were determined by thermal noise method and the curvature radius of the AFM tip was determined by analysis of high-resolution images of the sharp edges of a standard grating probe (TGG1 from NT-MDT, Russia). The topography images of the OTS modified surfaces were obtained by AFM scans in tapping mode using the same silicon AFM probe. The friction force was computed by analysis of lateral force loops recorded during lateral forwards and backwards movements of the AFM tip (see Fig. 2 for an example). The friction force versus normal load curves were obtained by scanning an area of 2 µm × 2 µm of OTS surface with different speed and normal force values.

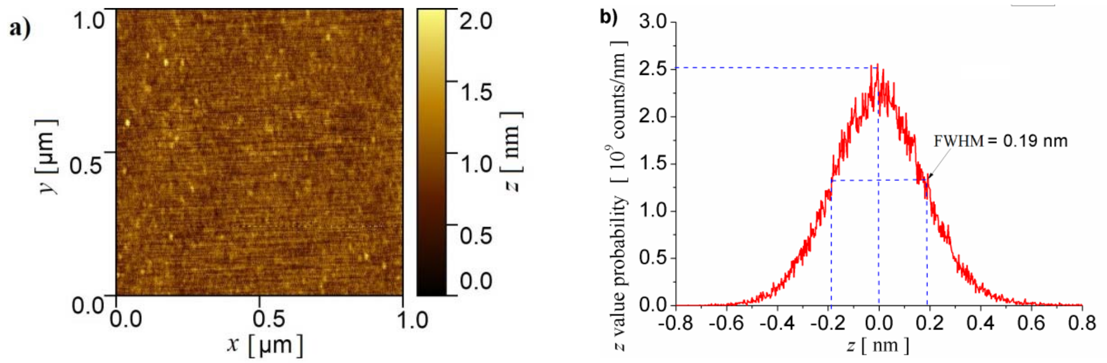
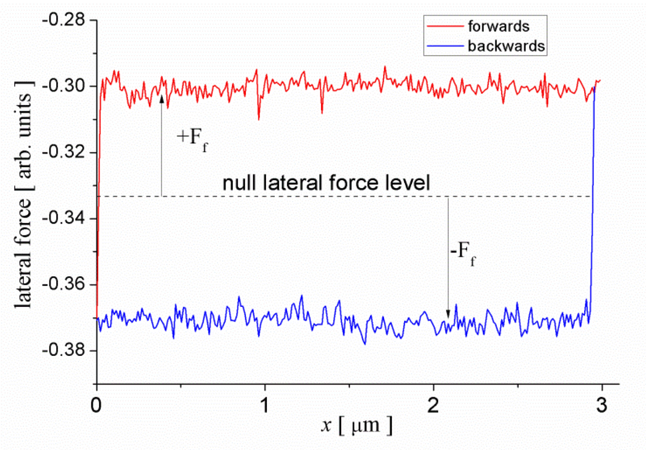


Figure 1. a) AFM topography image (1 µm×1µm) of OTS coated silicon and b) probability of surface height (z) values in the topography image showing a FWHM value of 0.19 nm.

Figure 2. Example of a friction loop, i. e. lateral force versus linear displacement of the AFM tip during forward and backward movements along a path with length of 3 µm. Due to friction, the lateral force is displaced with, F_f, above the null lateral force level during forward movement and with $-F_f$ below the null lateral force level during backwards movement. The area enclosed by friction loop determines the mean value of friction force.



3. Results and discussion

3.1. Wearing experiment

Figure 3 shows the wearing track formed on the surface of OTS coating after 1000 wearing cycles. This experiment was performed by moving a sharp silicon AFM tip (curvature radius of 17 nm) under a normal load of 50 nN forwards and backwards in 1000 cycles along a path with length of one micron. The large width of wearing track (estimated to about 100 nm from the height profile of the wearing track in Figure 3 b)) is due partly to a drift in *y* position of the AFM tip during wearing measurements and partly to tip-sample convolution effects. Estimation of the tip-sample contact area to about 100 nm^2 indicates a compressive stress applied to OTS surface during wearing of 0.5 GPa. The depth value of 0.8 nm of the wearing track is much smaller than the thickness of OTS coating (estimated to about 2.4 nm for OTS SAM). This means that the wearing track is formed by alignment and bending of OTS molecules along the wearing track without their removal from the substrate. This is also indicated by variation of friction force during wearing cycles depicted in Figure 4, which shows decrease of the friction force during first 200 cycles and almost a constant value afterwards. In spite of formation of the wearing track and corresponding increase of tip-sample contact area, the friction force decreased noticeably during first wearing cycles because the loss of energy in interactions between OTS molecules and AFM decreased during formation of the wearing track.

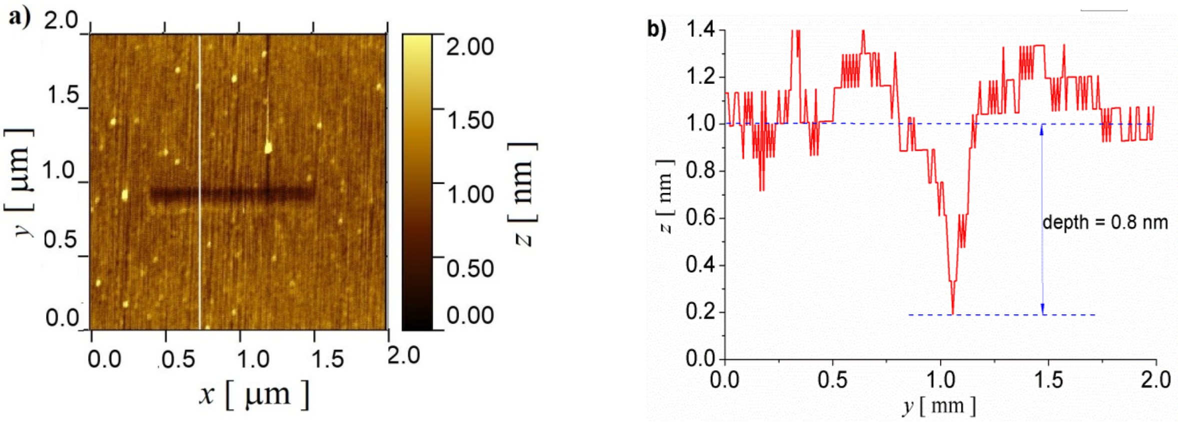


Figure 3. a) AFM topography image of wearing track formed during 1000 cycles of forwards and backwards sliding movements of an AFM tip under a normal loading force of 50 nN along a path with length of 1 μm. b) Height profile of the wearing track along the scanning line showed in the AFM topography image.

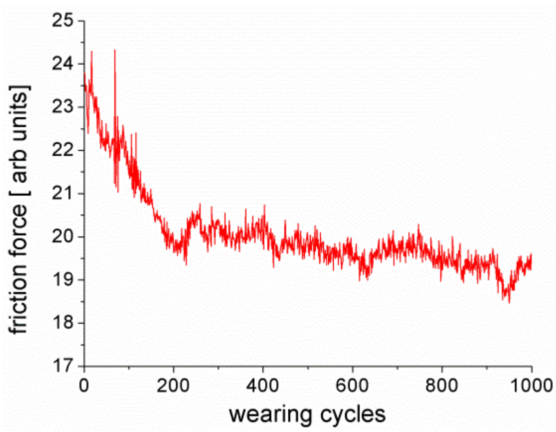


Figure 4. Variation of friction force during 1000 cycles of forwards and backwards sliding movements of an AFM tip under normal loading force of 50 nN along a path with length of 1 μm.

3.2. Friction experiment

Figure 5 shows friction versus normal force curves recorded at different sliding speed values. The curves shows a nonlinear dependence of friction force on normal loading force, the friction force decreasing to zero while the normal force is negative (pulling) with absolute value close to tip-sample adhesive force, F_{ad}, which in this experiment was around 17 nN. When the normal pulling force is equal to F_{ad}, the AFM tip detaches from the surface and friction and normal forces jumped to zero. The continuous black lines on the graph are fits of the experimental data with prediction of Bowden and Tabor's theory of friction, which for elastic deformations of surfaces foresee a dependence of friction force to 2/3 power of normal force ($F_f \alpha N^{2/3}$). The relative good agreement of the experimental data with theory predictions confirms that the deformation of OTS coating is elastic. It should be mentioned that the normal force is sum of externally applied force (through the AFM cantilever) and tip-sample adhesion force, F_{ad}. Dependence of friction on sliding speed reveals the molecular origin of friction in this particular case. In the process of friction, the AFM compresses the molecular layer of OTS molecules, each molecule being deformed elastically and released by sliding movement of the tip. In this process the tip transfers also kinetic energy to molecules by collisions and this kinetic energy increases with the tip sliding speed.

4. Conclusion

In summary, high quality OTS coatings were obtained on silicon substrates by plasma activation (hydroxylation) of substrate surfaces and chemical vapour deposition. The OTS covered surfaces were used in AFM wearing and friction measurements at level of a single-asperity contact.

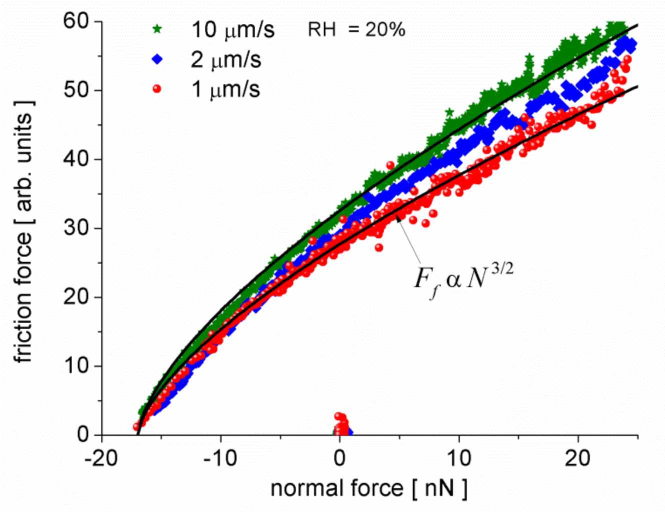


Figure 5. Dependence of friction force on normal loading force at different values of sliding speed

Wearing experiment performed by 1000 cycles of forwards and backwards movements of sharp AFM tip (curvature radius of 17 nm) under a normal applied force of 50 nN revealed formation of a wearing track with a depth that was much smaller than the thickness of OTS coating. This indicated a very good wearing property of OTS coating. The AFM friction investigation revealed a good agreement of experimental data with prediction of Bowden and Tabor's theory of friction, which confirms that friction rise from elastic deformation of the layer of OTS molecules. Dependence of friction force on the sliding speed revealed also a kinetic mechanism of friction, each molecule being collided by the moving tip with a transfer of kinetic energy.

5. References

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