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Scratching the polymethyl methacrylate and photo resist samples using atomic force microscopy

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1. Introduction

For the evaluation of scratching, adhesion, friction, wear and indentation processes, the atomistic mechanisms and dynamics of the interactions of two materials, when they are brought in to contact, separated, or slid with respect to each other, need to be understood. At most solid–solid interfaces of technological relevance, the contact occurs at many asperities. Consequently, the importance of investigating single asperity contacts in studies of the fundamental micromechanical and tribological properties of surfaces and interfaces has long been recognized

By scaling this atomic force microscopy (AFM) cantilever down in size to a few nanometres and combining it with conventional scanning probe techniques, one can facilitate nano lithography with nanometre resolution. In the more common AFM scratching techniques, the tip is scanned under strong loading forces to remove the substrate or resist. This technique utilizes the principle of ploughing in the same way as the traditional tool: material is removed from the substrate in a well-defined way, leaving behind deep trenches with the characteristic shape of the plough used. The advantages of applying a nano scratching for lithography are obviously the precision of alignment, the no damaging definition process compared to electron or ion-beam structuring techniques, and the absence of additional processing steps, such as etching the substrate [1-4]. The computational techniques for simulating tip-surface interactions and interfacial properties have allowed systematic investigations of interfacial problems occurring during adhesion, friction, scratching, wear, nano indentation, and thin-film lubrication at sliding surfaces [3, 6]. The surface force apparatus (SFA), the scanning tunnelling microscopes (STM), atomic force and friction force microscopes (FFM) are widely used in micro or nano tribological studies. The SFA was developed in the late 1960s and is commonly employed to study both static and dynamic properties of molecularly thin films sandwiched between two smooth surfaces.

The STM, developed in 1981, allows imaging of electrically conducting surfaces with atomic resolution, and has been used for imaging of clean surfaces as well as of lubricant molecules. The AFM is also useful for investigations of scratching, wear and indentation, detection of transfer of material, fabrication and machining. Meanwhile, significant progress in understanding the fundamental nature of bonding and interactions in materials, combined with advances in computer based modelling and simulation methods, has allowed theoretical studies of complex interfacial phenomena with high resolution in space and time. Such simulations provide insights into atomic-scale energetic, structure, dynamics, thermodynamics, transport and rheological aspects of tribological processes [5, 6].

The aim of this work was to investigate theoretically and experimentally the possibility to use the AFM instrumentation to produce the micro-nanosize patterning on the soft polymers, like polymethyl- methacrylate (PMMA) and photo resist, by surface scratching using standard Scanning Probe Microscopy cantilevers

2. Contact model

A number of mechanical theories (Hertz, DMT, BCP and others), is used for creating a two body contact model. Which one theory to choose – it can be determined on a point of investigation and experiment conditions.

A Johnson – Kendall – Roberts (JKR) contact model was chosen for its universality (describes pressure distribution on a sample surface, the depth of identification, contact area). Adhesion forces can be described also, using the above mentioned model. For a complex estimation of two body contact results (acc. JKR theory) a characteristic of A_c is used, which is expressed as

$$A_c = \pi\left(\frac{R_e}{K}\left(L + 6\pi R_e\gamma + \sqrt{12\pi R_e\gamma L + \left(6\pi R_e\gamma\right)^2}\right)\right)^{\frac{2}{3}} \qquad (1)$$

where $R_e = RR_s/\left(R + R_s\right)$ is the effective contact radius; R is the radius of a tip; R_s is the radius of a dint; K is the reduced module of elasticity of contact surfaces; L is the applied load; γ is the Dupre energy of adhesion.

The reduced modulus of elasticity K is described from material characteristics of contacting bodies as

$$K = \frac{4}{3}\left[\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}\right] \qquad (2)$$

where E_1 and E_2 are modules of elasticity of materials of contacting surfaces; ν_1 and ν_2 coefficients of Poisson's.

The contact model of the AFM sample, as a system of two springs and two dashpots is shown in Fig. 1, expressing energy storage or stiffness of the springs. The cantilever moves a distance d in response to the displacement of the sample. The dashpots Q_c and Q_i express energy dissipation and correspond to the energy dissipation. One spring and dashpot combination represents the AFM cantilever of tip-sample interaction, as represented in Fig. 1.

Energy storage is represented as the spring constant with stiffness k_c and k_j (cantilever and interaction, respectively). Note that k_j may vary and it depends on the position of the tip relative to the sample. The cantilever moves a distance d in response to the displacement of the sample. The dashpots Q_c and Q_l express energy dissipation. For example, when the tip is far from the sample, the stiffness is zero, but when the tip is indented into the sample, the stiffness is high. The spring stiffness representing the interaction between the tip and the sample is usually significantly larger. Damping of the cantilever is described by a second-order differential equation of the form

$$m^*\ddot{d}(t)+2m^*Q_c\dot{d}(t)+k_c d(t)+P\left[d(t)\right]= \\ =k_c z(t)+2m^*Q_c\dot{z}(t) \quad (3)$$

where $P\left[d(t)\right]$ describes the force acting on the tip resulting from tip-sample interaction.

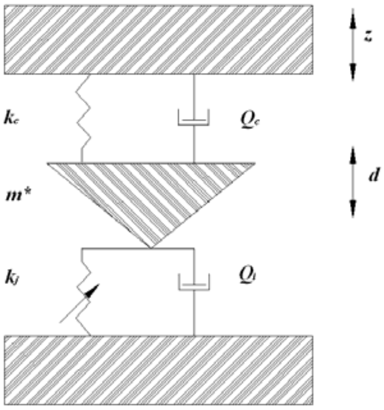

Fig. 1 Principal scheme of microlever-sample system: m^* is the micro cantilever effective mass; k_c and k_j are the spring constants; Q_c and Q_i are the dashpots which express energy dissipation; d and z are the moving directions of the tip and micro lever

It is convenient to rearrange equation (3), to put linear terms on the left-hand side, after, the term, describing nonlinear interaction between the tip and the sample on the right-hand side, expressing as

$$m^*\ddot{d}(t)+2m^*Q_c\left[\dot{d}(t)-\dot{z}(t)\right]+k_c\left[d(t)-z(t)\right]= \\ =-P\left[d(t)\right] \quad (4)$$

Two separate functions are needed, one to describe the attractive force away from the contact, and the other one to describe the net force in contact.

3. Scratching the surface

To carry out scratching, the microscope Quesant (model Q-Scope™ 250) was driven in to so-called “contact mode” and used in a similar technique introduced by Jung et al. to modify polymers [7] (Fig. 2).

After a mechanical contact between the tip and the sample surface, there is a repulsive force between them. This force is used as the feedback parameter (by maintaining constant force through adjustment of the sample height while the tip scans the surface) to obtain AFM image (Fig. 3). The tip was mechanically contacted with the sample surface at an applied force. This applied force is evaluated from a force-distance curve, which has been measured when the tip was brought to and then retracted from the sample surface.

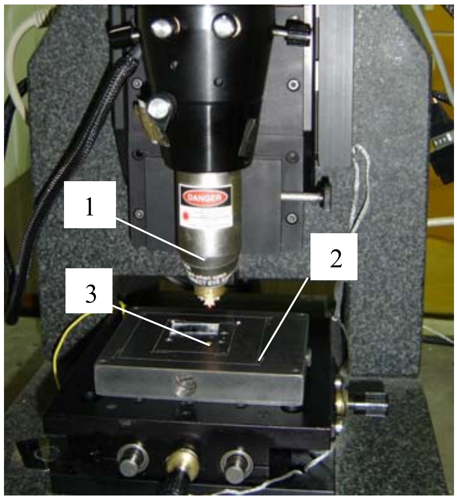

Fig. 2 Experimental stand: *1* - AFM Quesant measuring head; *2* - XY nano positioner; *3* - sample

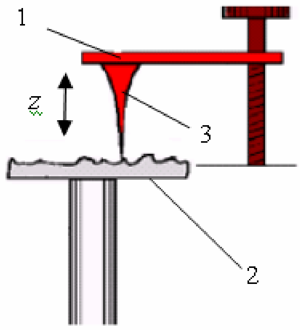

Fig. 3 AFM scheme of micro–nano surface modification procedure: *1* - microlever; *2* - sample; *3* - tip; z - moving direction of the tip in regard to the sample surface

A spring constant of 0.5 N/m of the cantilever, was used in contact regime. As the tip was mechanically contacted with the surface, topographic image was measured also. Following this, nano-lithography process was demonstrated on the photo resist surface by controlling the applied force on the micro lever. When scratching a sample with an AFM tip a constant force was applied to the surface by the probe at the end of the cantilever.

Measuring the force with the cantilever, its deflection was directly measured. In the contact mode AFM, the tip was mechanically contacted with the sample surface with a defined $17e^{-10}$ nN applied force. This applied force was estimated from force-distance curve, which was obtained by extending the tip to the surface to make contact between the tip and the surface followed by retracting the tip from the surface. The force-distance curve, shown in Fig. 4, was obtained using a soft silicon nitride cantilever (a spring constant 0.5 N/m) with an attached tip whose apex radius about 20 nm.

There is no interaction between the tip and surface when the tip is far away from the surface. When the tip is brought close to the surface there is an attractive force between them. Usually, the force gradient is much larger than the spring constant of the cantilever, so that the tip is snapped to the surface to make contact between the tip and surface. Further the tip results force to the surface. This repulsive force is usually used as the feedback parameter for the AFM system to obtain surface morphology.

There are used repulsive forces of $17e^{-10}$ nN for the contact mode in the experiment presented in this paper. In retracting cycle, for the adhesion, the tip did not depart from the surface until the force used to pull the tip from the surface exceeded the adhesion force between them. This pull-off force is considered as a measure of the adhesion force between the tip and surface. Adhesion force is related to the surface energy of the sample surface.

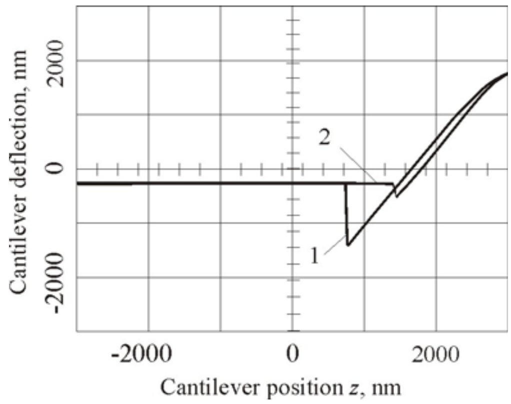

Fig. 4 Force-distance curve of PMMA: *1* is the approach characteristic; *2* is the detractive characteristic

4. Experimental set-up

After the tip has approached the surface (Fig. 5, a), the oscillation amplitude reaches its set pint of 70-80% of the initial value. The resulting tapping force is not high enough to indent the resist significantly. Once the drive amplitude increases, the control unit pushes the tip (Fig. 5, b) closer to the sample so the oscillation amplitude is kept constant at the preset value. As the result the tip more strongly taps against the sample surface (Fig. 5, c,d,e) so, the PMMA and the photo resist are plastically deformed [8].

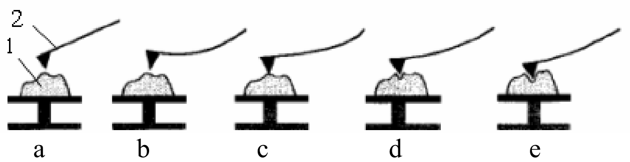

Fig. 5 Relative positions of the tip and the sample surfaces related to the added force during the all cycle down-up of micro lever and sample. *1* is the sample; *2* is the micro lever and tip

A PMMA was used as a versatile polymeric material that is well suited for many imaging and non-imaging microelectronic applications. The scratching process on the polymethyl methacrylate and photo resist of 1 µm thickness films for both films, placed on oxidized Si (001) plate, was performed.

The PMMA film was prepared by depositing a solution of 0.1 g of PMMA in 10 ml of dychloretanum on a Si slide, centrifuged for a 15 s at 1200 rpm and letting the film slowly evaporate within 3 h. The photo resist 1 ml was deposited on another Si slide also, centrifuged at 1200 rpm and letting the film slowly evaporate within 3 h also.

Both film thicknesses were about 1 µm. Commercially available cantilever (Park Scientific Instruments, USA) length 85 µm, width 18 µm, thickness 0.6 µm, resonance frequency 120 kHz and spring constant 0.5 N/m was used. All experiments were performed at room temperature in air.

The tip of the cantilever was not damaged during the experiment and no adsorption of polymer and photo resist occurs. The pressing force, in both sample cases, pushed the cantilever into the sample was $17e^{-10}$N .

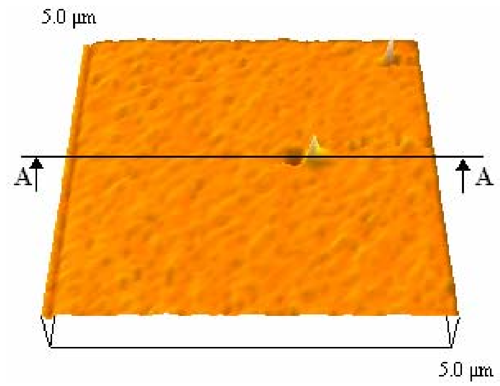

Fig 6 PMMA sample after 50 cycles of grind

Comparing the PMMA and photo resist samples the surfaces view from the top are shown in Figs. 6, 8 and the profile diagrams are shown in Figs. 7, 9.

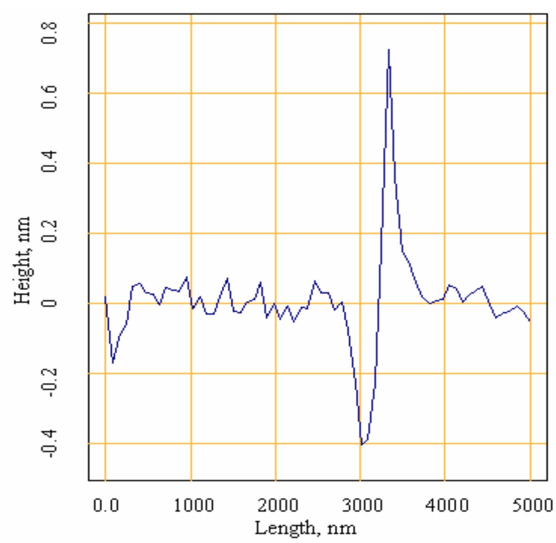

Fig. 7 The height diagram of PMMA after 50 cycles grinds (Fig. 5, layer A–A)

As the same experimental conditions where kept for both materials, the deformation depends only on physical parameters of the material. The shape of the dint is not always the same even if it surface is scanned after 50 cycles of interactions. But, in that experiment the main interesting point of the dint was how deeply the tip has penetrated into the sample surface.

The reason of a lot of dints is a heterogeneous surface where there are the regions of different hardness

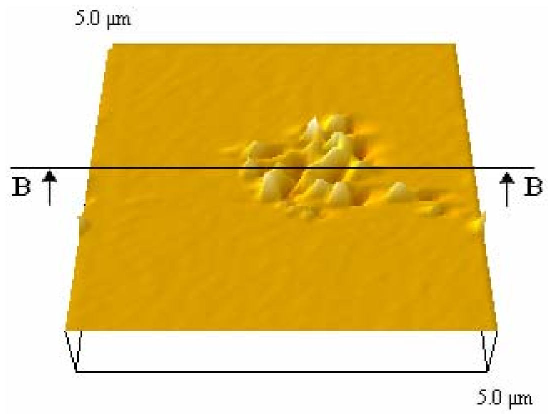

Fig 8 Photo resist sample after 50 cycles of grind

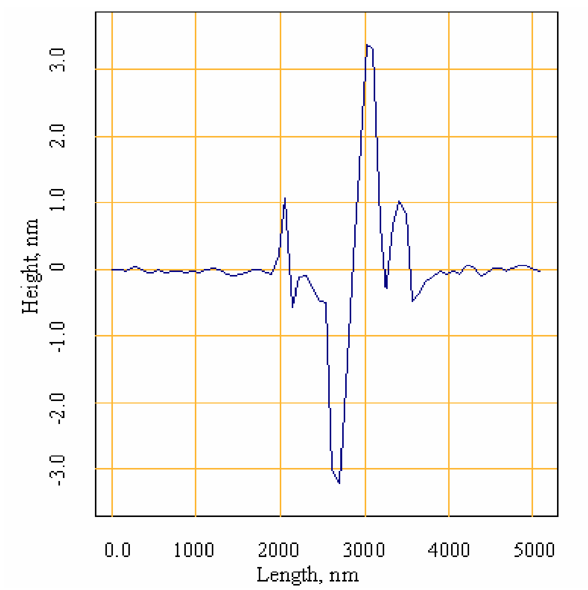

Fig. 9 Height diagram of photo resist after 50 cycles grind (Fig. 7, layer B–B)

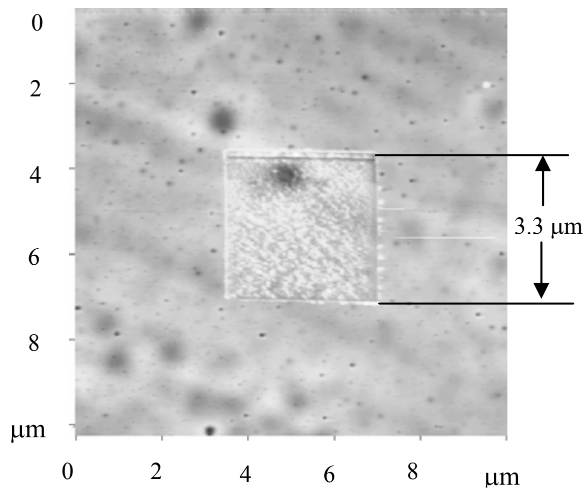

Fig. 10 A notch, formed in photo resist film (top view)

and friction in a very small area (1 µm). Using a microlever positioning at XY plane, herewith keeping step, which is not bigger than a double radius of the probe, it is possible to form a lithography picture. An accuracy of notches specifies metrological characteristics of the nano positioner. Fig. 10 shows a notch, formed in photo resist film, using nano positioner, with sensitivity of piezo drives of 35 nm, with a possibility to recover the step of positioning in XY plane in to flextensional piezoelectric actuator [9].

Scratch tests serve as highly accelerated tests to see what kind of loads the coatings can withstand. In real situations, the conditions are closer to that of the wear tests, where prolonged use at constant load occurs.

5. Conclusions

AFM enables the direct machining the sample surface by means of cantilever tips of the atomic force microscope. This can be achieved using “Static” (Scratching) and **“**Dynamic Ploughing” modes**.** The AFM is employed in contact mode to pattern a sample surface or some layer on them, e.g. single resist layer and subsequently use it as an etch mask. It has been proved that, while cutting a furrow into the resist by static ploughing, torsion of the cantilever may lead to edge irregularities. Additionally, depending on the local stiffness of the sample, while imaging the surface before or after the modification, further modifications may occur due to dragging of the surface. When the AFM is operated in contact mode, not only deep scratching but also several regimes from frictionless sliding to permanent wear are observed, depending on the applied load. In this way, AFM has been successfully used to characterize micro wear processes on materials of technological interest, as silicon for magnetic head sliders, polymers for electronic packaging and liquid crystals displays etc.

The results of the investigation can be used forming various complicated microlithography structures in optics and microelectronics.

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POLIMETILMETAKRILATO IR ŠVIESAI ATSPARIŲ BANDINIŲ BRAIŽYMAS PANAUDOJANT ATOMINĖS JĖGOS MIKROSKOPIJĄ

R e z i u m ė

Straipsnyje analizuojamos atominės jėgos mikroskopo (AJM), mikropaviršių topografijos, trinties, adhezijos ir kitų charakteristikų tyrimo įrankio panaudojimo galimybės dangų mechaniniam modifikavimui submikrometriniame lygyje. Naudojant zondą, kurio užaštrinimo spindulys 20 nm, AJM sistemoje atlikti mechaninio dilimo tyrimai ir mikroišdrožų formavimas polimetilmetakrilato (PMMA) ir fotorezisto plėvelėmis padengtuose bandiniuose. AJM mechaninė litografija įgalina formuoti lokalinius paviršių ypatumus, AJM mikrokonsole mechaniškai paveiktas dangų paviršius lengviau modifikuojamas nei nepaveiktas. Tyrimo rezultatai gali būti panaudoti formuojant ar modifikuojant elektronines bei biologines nanostruktūras

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SCRATCHING THE POLYMETHYL METHACRYLATE AND PHOTO RESIST SAMPLES USING ATOMIC FORCE MICROSCOPY

S u m m a r y

This paper analyses the Atomic Force Microscope (AFM) probe as a well established tool for the characterization of the topography, friction, adhesion forces and surface as the modification tool from a micrometer level down to a sub-nanometre level. Micro scale scratches and wear resistance tests using an atomic force microscope have been conducted on polymethyl methacrylate (PMMA) and photo resist coatings. AFM lithography results in the formation of extremely small features. The areas, mechanically-scratched using AFM cantilever, are better susceptible to modification than the same but unscratched surfaces going to be practice to nano electronic and biological structures.

К. Немчяускас, Г. Сенюнас, В. Снитка

ИСПОЛЬЗОВАНИЕ МИКРОСКОПА АТОМНЫХ СИЛ ПРИ ФОРМИРОВАНИИ ВЫРЕЗОВ В ПОЛИМЕТИЛМЕТАКРИЛАТЕ И СВЕТА НЕПРАНИЦАЕМЫХ ПОВЕРХНОСТЯХ

Р е з ю м е

В статье анализируется возможность использования микроскопа атомных сил (МАС), инструмента исследования топографии, трения, адгезии и других характеристик микроповерхностей для механической модификации в субмикронном уровне. Используя зонд с радиусом заострения 20 нм, в системе МАС исследовано механическое истирание и процесс формирования микровырезов в образцах, покрытых полиметилметакрилатом и фоторезистом. Механическая литография при помощи МАС дает возможность формировать локальные особенности поверхностей с высокой точностью. Механически обработанные МАС зондом покрытия модифицируются легче, чем необработанные. Результаты исследования могут быть использованные при формировании электронных и биологических наноструктур.

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