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Using scanning probe lithography to form planar microparticles with configuration anisotropy

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The experimental results of the formation of polymer masks for the creation of planar microparticles of a given shape by scanning probe lithography are presented. The problems associated with the nonlinearity of the probe movement during the mask formation are considered. The possibility of increasing the lifetime of the probe by changing the mask formation procedure and (or) changing the sample temperature has been demonstrated. Improving the quality of the resulting mask is achieved through the use of chemical etching.

Keywords: Atomic force microscopy, polymer masks, chemical etching.

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Introduction

Lithography is one of the modern methods for fabrication of micro- and nanostructures on the surface of solids [1]. Structures may be produced either directly from thin films deposited onto the surface or by deposition of a certain amount of material through a mask that was formed on the surface in advance. A thin polymer layer, which is modified at the needed sites by a certain type of radiation (visible, ultraviolet, or X-ray), is normally used to form a mask. The processed polymer is then removed by making use of the difference in rates of etching of modified and initial polymer materials, and deposition through the formed mask is carried out. After that, the mask and the excess material for structure formation are removed via etching (i.e., the so-called lift-off procedure is performed). In addition to irradiation, mechanical stimuli may be used (if one ensures their fine localization) for local modification of the surface of polymers and other materials. Such modification may be performed using scanning probe lithography (SPL) with a scanning probe microscope (SPM) acting locally on the surface [2,3]. A polymer material is removed mechanically in this case from predetermined regions by an SPM probe moving along a certain trajectory. It was found in [4] that SPL (and the lift-off process) allow one to form structures with lateral dimensions on the order of 1 nm. An SPM provides an opportunity to both form masks in a polymer and modify the formed structures directly or shape them from continuous films on the surface. However, this approach normally requires a significantly higher force of interaction between an SPM probe and the surface and may induce rapid dulling (or even breakdown) of the probe. The issue of preservation of sharpness of an SPM probe in the course of lithography is also relevant to the process of mask formation in a polymer, since the SPM probe shape affects the quality and accuracy of reproduction of structures. The indicated issue may be solved by reducing either the force of probe–surface interaction or the time of formation of a single mask.

The reproducibility of particle shape and size is another problem arising in the fabrication of masks for micro-nanoparticle formation by SPL. It is often caused by the nonlinear properties of an SPM piezo scanner [5,6]. Mathematical algorithms, which yield a solution with a limited accuracy, have been applied earlier to introduce a correction for this nonlinearity. In more recent studies, capacitance sensors, which provide a much better compensation for nonlinearity of the piezo scanner motion and allow one to control more accurately the SPM probe position relative to the examined surface, have been used for the purpose [7]. An SPL evidently cannot ensure such accuracy of mask fabrication that may be achieved in modern electron or X-ray lithography; however, its availability and affordability make SPL potentially suitable for application at the initial stages of exploratory research. In addition, SPM techniques provide an opportunity to examine the physical properties of formed micro- and nanostructures and correct their shape and size when necessary. This option may also be useful in scientific research [8–10]. Thus, the refinement of SPL methods and the examination of their potential for fabrication of various structures remain relevant. The present study is focused on the application of SPL methods in fabrication of arrays of identical ferromagnetic particles with lateral dimensions on the order of 1 μm and a thickness of approximately 40 nm (specifically, microparticles with configuration anisotropy induced by their exterior shape). These include square and triangular particles with axial symmetry and particles similar in shape to letters X and Y. The interest in such microparticles stems from their potential applications in straintronics devices [9].

1. Formation of masks for SPL fabrication of ferromagnetic microparticles

1.1. Sample preparation and research procedure

Poly(methyl methacrylate) (PMMA) produced by Acros Organics (Belgium) was the polymer used to form masks. Thin films on the surface of substrates were formed by spin coating. A solution of PMMA in chloroform (0.55%) was deposited for this purpose onto the substrate surface, which was then rotated at a rate of about 6000 rpm for approximately 10 s. Following the formation of a thin PMMA film, the substrate was dried for 1 h in air at a temperature of 90°C to remove the residual solvent from the film. The obtained films had a thickness of about 100 nm. Since the thickness of films is crucial for subsequent SPL lithography, it was monitored additionally by atomic force microscopy (AFM) in accordance with the procedure detailed in [8]. The root-mean-square roughness of PMMA films was 0.3 nm, which is close to the root-mean-square roughness of the used substrates.

Ntegra and Solver P47 SPMs were used to form masks and examine microparticles. Masks were formed by D300 (SCDProbes) cantilevers with a probe having the shape of a diamond pyramidal single crystal. The tip radius of the probe was 5–10 nm, and the tip angle was 10°. The same cantilevers were used to monitor the quality of masks. Optically polished glass, congruent lithium niobate, and single-crystalline atomically smooth silicon served as substrates for the formation of microparticles. Marks in the form of rectangular particles $5 \times 50\,\mu m^2$ in size, which were easy to distinguish using the system of optical positioning of the SPM probe, were created near each of the obtained microparticle arrays to facilitate their identification.

The method of electron-beam sputtering of a solid-state target in ultrahigh vacuum (UHV) was used to deposit metal onto the surface of a substrate with a masked formed on it. Nickel was sputtered using an Omicron Multiprobe P UHV setup under a pressure of 10^{-6} Pa. Following this procedure, excess metal and PMMA were removed in an ultrasonic bath in a chlorobenzene solution. The sample was then rinsed with distilled water and dried.

The magnetic properties of microparticles were examined by magnetic force microscopy (MFM). Multi75M-G (BudgetSensor) cantilevers were used. In MFM scanning, a signal proportional to the phase difference between the signal inducing oscillations of the MFM probe at the resonance frequency and the signal characterizing these oscillations was recorded. The measured signal is proportional to the gradient of the force of interaction between the probe and the magnetic field of the sample at a given point [11]. MFM measurements were performed in a single pass with the magnetic probe moving over the sample at a predetermined distance from it (this is done to suppress the influence of the magnetic moment of the probe on the obtained image).

1.2. Formation of a mask by raster lithography

An SPM may be operated in two primary modes in the course of mask formation. Let us examine the first mode: raster lithography. Just as in AFM scanning, the entire region of mask formation is presented in this mode as a set of points located at a certain distance (scan pitch) from each other. A template (raster grayscale image), which ideally has the same number of points as the region of mask formation, is prepared in advance in a graphics editor. The color of a point is proportional to the pressure exerted at this point during lithography. A template has to have only two colors to form a mask in a single pass: one representing zero influence and another color corresponding to the maximum pressure, which should be sufficient to pierce through the PMMA layer down to the substrate. A mask was formed in two ways: with capacitance sensors switched on and the nonlinearity of the piezo scanner motion compensated by a feedback system (first method) and with capacitance sensors switched off and the nonlinearity compensated exclusively by a mathematical algorithm (second method). A template in the shape of several squares of different sizes was used. The time of mask formation, the exposure time, and the pressing force acting on the PMMA surface were the same in both modes (600 min, 3 μs, and 300 nN). The force applied to the probe was rather high, since it was needed to pierce through the PMMA layer down to the substrate in a single exposure at any given point. Owing to this, the SPM probe tip radius could change (or the probe could be damaged) even in a single-pass mask formation process. Therefore, a new probe was used to form a mask in each of the two ways. The SPM probe forming a mask moved from left to right, shifting gradually from the bottom upwards. The result of mask formation with capacitance sensors switched off (second method) and the array of Ni microparticles produced using this mask are shown in Figs. 1, *a, b*. Since the SPM probe is positioned initially at the center of the scan, it shifts to the lower left corner at the start of lithography. and the greatest shape distortion of the obtained mask and microparticles is observed at the onset of scanning (Figs. 1, *a, b*). The lower rows of imaged microparticles have an elongated (rectangular) shape instead of the desired square one. According to the obtained data, the shape of microparticles becomes close to the predefined square approximately in the middle of the scan field (the upper three rows of microparticles in Figs. 1, *a, b*). When capacitance sensors were used (first method), the shape distortion of the obtained mask and microparticles produced based on it was significantly less intense (Figs. 1, *d, e*). A slight shape distortion is seen only in the bottom row of microparticles. According to the MFM images, the shape distortion of microparticles in the second mask formation method (without capacitance sensors) shortens the distance between them and induces ordering of the domain structure of neighboring microparticles (bottom row in Fig. 1, *c*); i.e., the obtained data suggest that neighboring microparticles interacted magnetically. The elongation of microparticles in

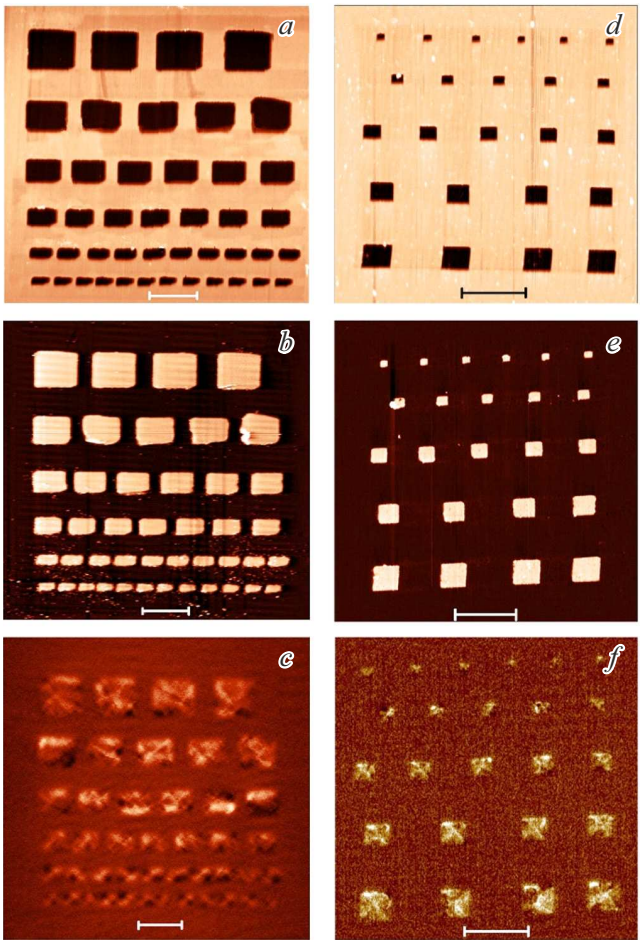

Figure 1. AFM image of the mask in PMMA (a) obtained using a Solver P47 SPM in the raster lithography mode. AFM (b) and MFM (c) images of Ni particles produced using this mask. AFM image of the mask in PMMA (d) obtained using an Ntegra SPM in the raster lithography mode. AFM (e) and MFM (f) images of Ni particles produced using this mask. The height of imaged relief is 70 (a), 40 (b), 90 (c), and 35 nm (d). The phase range in the image is 0.14° (e), 0.8° (f). The scale bar is 5 μm.

one direction also translates into a change in the size of magnetic domains. If a microparticle has a square shape, its magnetic structure is close to the classical four-domain one (the so-called Landau structure) that features triangular domains of the same size with the magnetization direction being parallel to the microparticle side at which they are located (Figs. 1, c,f).

If one takes into account the specifics of used SPMs in regard to the maximum number of points into which a single scan may be divided (1024×1024) and the effective lateral probe size (approximately 30 nm at a tip radius of about 10 nm), the maximum-size field on which a mask may be formed in a single pass is $30 \times 30\,\mu\text{m}^2$. The SPM scan field is more extensive and may be as large as $100 \times 100\,\mu\text{m}^2$, making it possible to form several masks within a single scan field. Therefore, we examined the issue of shape distortion of microparticles arising when the mask formation region is shifted relative to the center of the full available SPM scan field. A mask formation region located at the edge of the available SPM scan field was used for the purpose. Periodically positioned microparticles with configuration shape anisotropy were produced in this experiment. The lateral dimensions of microparticles were approximately 1μm. In the template drawn to form a mask, microparticles were positioned in rows one above the other. The AFM image of the mask formed in the second mode (with capacitance sensors switched off) is shown in Fig. 2, a. It can be seen that asymmetrical positioning of the mask formation region relative to the center of the full SPM scan field induces additional distortion in a microparticle array. In the initial scan region, the shape of microparticles is distorted, while the microparticles themselves are shifted relative to the others in a row (Figs. 2, a–c). Thus, sym-

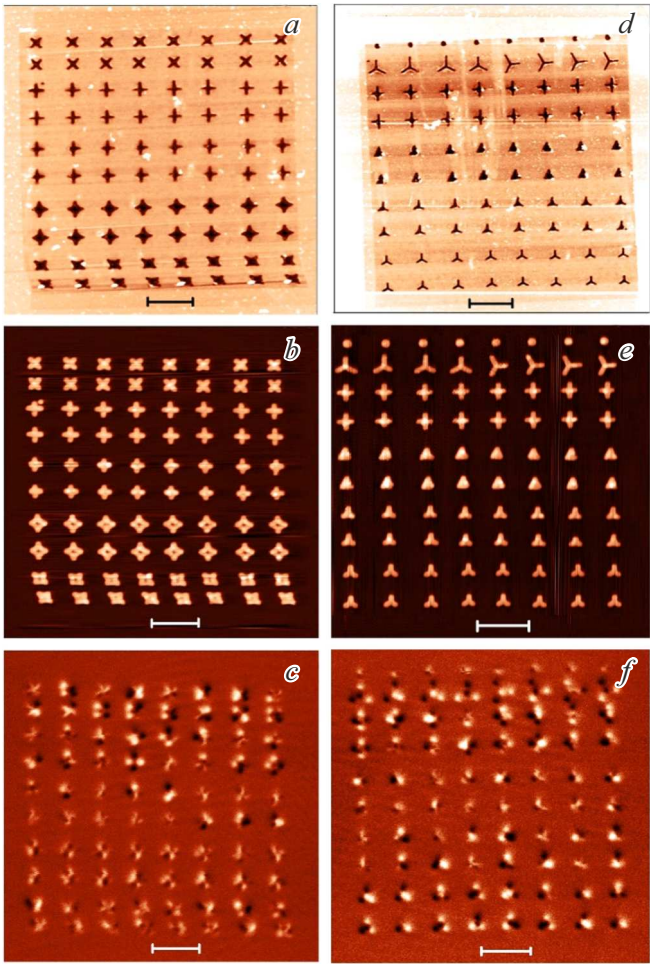

Figure 2. AFM image of the mask in PMMA (a) obtained using a Solver P47 SPM in the raster lithography mode. AFM (b) and MFM (c) images of Ni particles produced using this mask. AFM image of the mask in PMMA (d) obtained using an Ntegra SPM in the raster lithography mode. AFM (e) and MFM (f) images of Ni particles produced using this mask. The height of imaged relief is 150 (a), 45 (b), 90 (c), and 45 nm (d). The phase range in the image is 1° (e), 0.6° (f). The scale bar is 5 μm.

metrical positioning of the mask formation region relative to the scan center provides an opportunity to suppress the influence of distortion associated with nonlinearity of the piezo scanner motion. It is preferable in this context to shift the mask formation region using the SPM probe positioning system instead of shifting it with the piezo scanner.

The first method of mask formation (with capacitance sensors switched on) allows for a considerable suppression of distortion of the obtained microparticle array (Figs. 2, *d, e*). The shape of microparticles does not change in this case, and their positions in a row remain unshifted in the initial scan region. A slight shift of each subsequent row of microparticles relative to the previous one nay be attributed to the general drift of a sample in the process of mask formation. MFM images of the obtained array reveal a quasi-uniform magnetization structure that is expected of microparticles of this size (Figs. 2, *c,f*). The obtained AFM images in themselves do not allow one to make any conclusion regarding the probable magnetic interaction between microparticles; an additional examination of the behavior of microparticle magnetization in an external magnetic field is required.

It should be noted in summing up the experimental data on forming a mask for microparticle fabrication by raster lithography that the least distortion in a microparticle array is observed when a mask is positioned at the center of the full available SPM scan field and capacitance sensors are switched on. An ordered array of approximately one hundred submicrometer microparticles may be formed under these conditions.

1.3. Formation of a mask by vector lithography

Let us consider the second mode: vector lithography. Since a template for mask formation is set directly in the SPM control program in this mode, it is suitable only for microparticles of a simple shape (circle, ellipse, line, rectangle). An SPM probe does not scan over the entire field in this case; instead, it shifts to the initial point of a given figure, is pressed down into a PMMA film with a predetermined force, and starts moving along the contour of the figure. When such a motion sequence is implemented, squeezed-out polymer, which cannot be pierced through to the substrate at a preset force of probe–surface interaction, often accumulates in front of an SPM probe. If, for example, a simple line is being formed, this translates into variations of its width and possible discontinuities (Fig. 3, *a*).

It is difficult to determine the influence of nonlinearity of the piezo scanner motion on a mask of such a simple shape as a line; the quality in this case is specified primarily by the cantilever stiffness and a correctly adjusted probe–surface interaction force. Therefore, masks of circular and square shapes were formed for further studies. The shape of a mask formed with capacitance sensors switched off was often distorted (especially in the lower left corner of the scan, where the process was initiated; see Fig. 3, *b*). Figures were frequently left open, which may be attributed

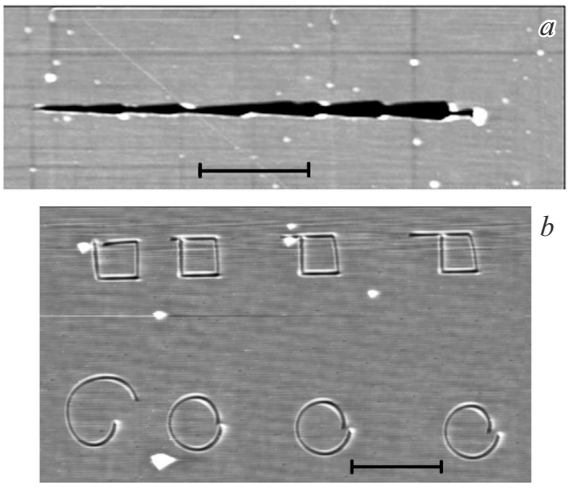

Figure 3. AFM images of a mask in PMMA in the form of a line (*a*) and contour figures (*b*) produced in the vector lithography mode in a single pass. The scale bar is 5 μm. Relief height: *a* — 100, *b* — 25 nm.

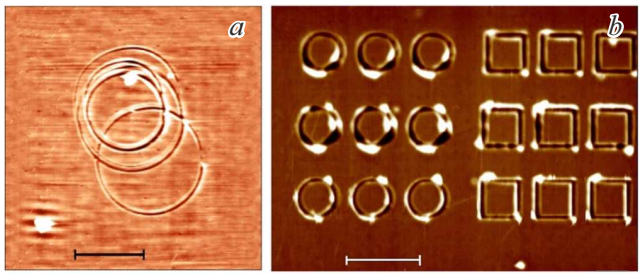

Figure 4. AFM images of a mask in PMMA formed in the vector lithography mode in several passes with capacitance sensors switched off (*a*) and on (*b*). The scale bar is 4 μm. Relief height: *a* — 14, *b* — 140 nm.

both to the piezo scanner nonlinearity and to an insufficient magnitude of the probe–surface interaction force that is too low to pierce through the accumulated polymer (Fig. 3, *b*). Another drawback of this approach consists in rapid breakdown of an SPM probe: in contrast to raster lithography where the force acting on the sample surface decreases considerably in moving from one point to the other, the pressing force in vector lithography remains constant and rather high throughout the entire mask formation process.

Therefore, it appears optimal for vector lithography to form a mask not in a single pass, but in several passes. The SPM probe–sample interaction force may be reduced in this case. A smaller amount of polymer will then be squeezed out in a single pass, and the procedure will just be repeated until the probe reaches the substrate surface. The key issue in this context consists in accurate matching of the probe motion trajectories in all passes. It was found experimentally that the SPM probe motion trajectory changes between passes if capacitance sensors are switched off (Fig. 4, *a*). In addition, the SPM probe itself often does

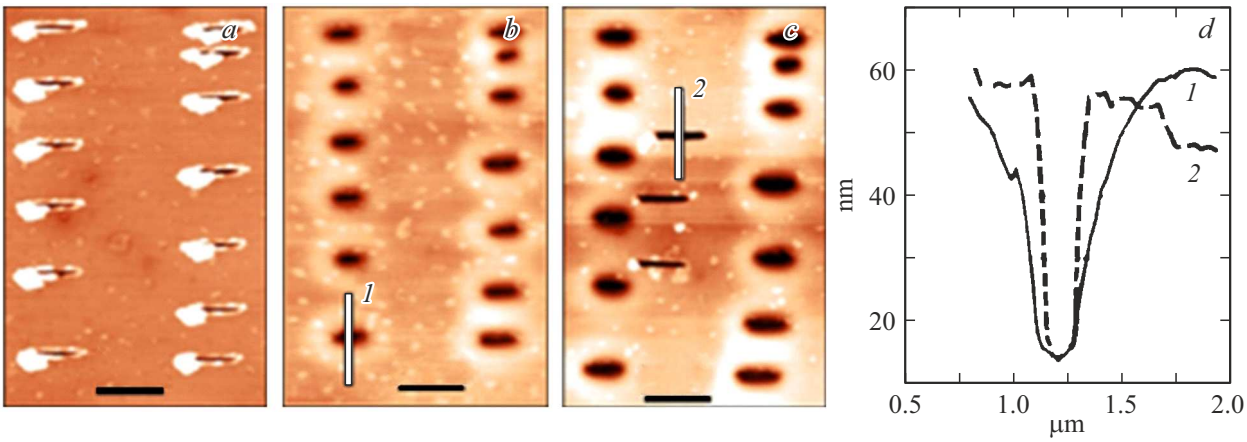

Figure 5. AFM images: *a* — mask in PMMA formed at room temperature and imaged prior to PMMA drying, relief height $(\Delta h) = 250$ nm; *b* — the same mask after heating to 90°C (PMMA drying temperature), $(\Delta h) = 70$ nm; *c* — the same mask with three new grooves cut in dried PMMA, $(\Delta h) = 140$ nm. *d* — Height profiles along lines *1* and *2* (solid and dashed curves, respectively). The scale bar is 1.5 μm.

not return to the initial point, and figures are left open. This is due primarily to the piezo scanner motion creep and incorrect operation of the mathematical algorithm developed to compensate the scanner nonlinearity. With capacitance sensors switched on, the probe motion trajectory ceases to change appreciably between passes in the process of vector lithography, and the polymer is squeezed out at one and the same point (Fig. 4, *b*). The probe returns to the initial point at the end of a pass, and closed figures are thus obtained.

Thus, owing primarily to an increased mask formation rate, the vector lithography mode may turn out to be more promising than raster lithography. This method has its limitations in the necessity of application of a fairly advanced system for compensation of nonlinear distortion in the process of piezo scanner motion (in the present case, such a system was based on capacitance sensors) and the need for a mask template to be available in the SPM software. The use of several probe passes in the process of formation of a mask for microparticles allows one too reduce the SPM probe—sample interaction force. A weak interaction force is needed when a polymer gets squeezed out completely from a certain area and an SPM probe starts interacting with a solid substrate that may damage its tip.

2. External factors and their influence on the mask formation process

2.1. Influence of the sample temperature on the mask formation process

The process of preparation of a PMMA film to mask formation includes the procedure of film drying at a temperature of 90°C. Since the hardness of a dried PMMA film increases, it was decided to perform drying after the formation of a mask by probe lithography. This was supposed to reduce the SPM probe—sample interaction force needed to pierce through the PMMA layer down to the substrate. It was found experimentally that an interaction force of 100 nN was sufficient for an undried film. This value is approximately three times lower than the force used to pierce through the standard PMMA film (300 nN). Although the quality of a mask formed in an undried PMMA film was fairly high (Fig. 5, *a*), its shape and size changed after film drying at 90°C, and the

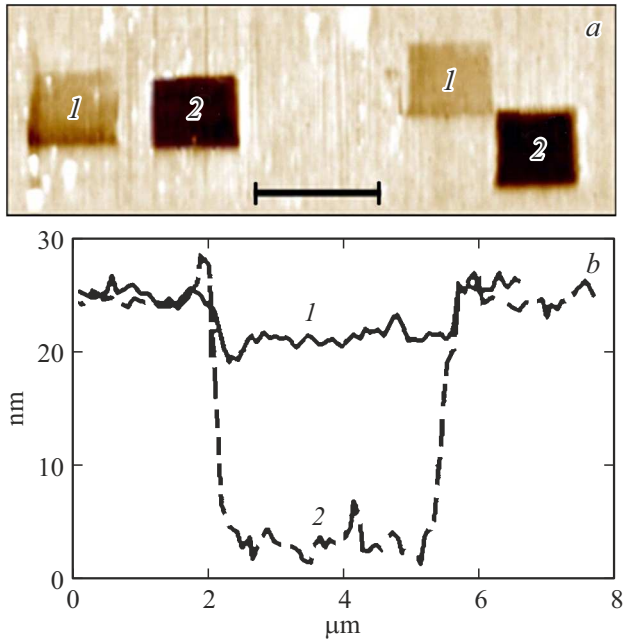

Figure 6. *a* — AFM image of the PMMA surface with certain regions of it subjected to one and the same pressing force at a sample temperature of 27°C (squares with number *1*) and 55°C (squares with number *2*). *b* — Height profiles for squares *1* (solid curve) and *2* (dashed curve). Squares were formed one after another at the corresponding temperatures. The scale bar is 5 μm.

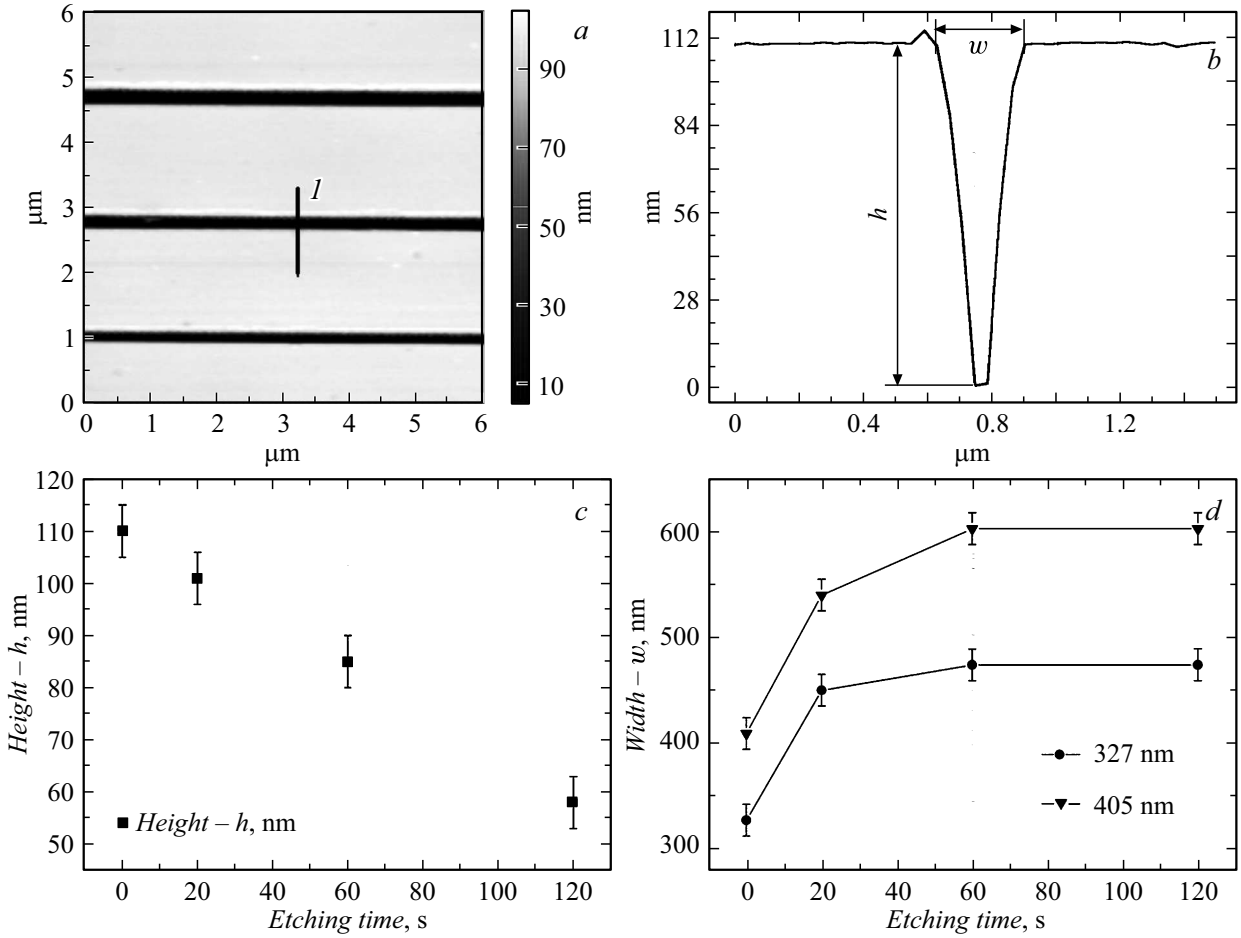

Figure 7. AFM image of a mask in PMMA (*a*) and profile along line *1* (*b*) that illustrates the parameters characterizing PMMA dissolution (width w of the formed groove and PMMA film thickness h). Dependence of the PMMA thickness (*c*) and the width of two grooves in PMMA with initial widths of 405 and 327 nm (*d*) on the time of etching with a developing solution.

quality deteriorated (Figs. 5, *b, c*). A reduction in quality is understood here as a change in the sidewall angle of a formed mask. Side walls are prone to dulling in the process of drying. For the lift-off procedure to be successful, the angle between the substrate surface within a mask and its walls should not exceed 90°. Owing to this, isolated islands of metal within a mask and a metal film on the PMMA surface form during sputtering. At angles greater than 90, a metal film deposited onto a sample with a mask may become continuous and, consequently, hard to remove by lift-off. In order to make sure that a change in the mask quality (dulling of edges) occurred in the course of drying and is not related to, e.g., a change in the SPM probe tip radius, an additional mask for the production of microparticles was formed in the polymer using the same probe after drying, and its AFM image was obtained (Fig. 5, *c*). This provided evidence that the sidewall angle changes exactly during polymer drying at a high temperature (Fig. 5, *d*). Thus, it is impractical to alter the procedure of preparation of a polymer film for mask formation.

A change in the procedure of preparation of a film is not the only way to reduce its hardness. It is known that PMMA also softens under heating [1]. Therefore, an increase in temperature of a sample should translate into a reduction in the force needed to pierce through a PMMA film with an SPM probe. The following experiment was carried out to verify this assumption. A mask in the form of a continuous square was formed by vector lithography. The probe pressing force was kept constant at 45 nN. A square was first formed at room temperature (27°C), the sample was heated to 55°C, and a second square was formed next to the first one. The temperature was not raised further, since, according to the manufacturers data for D300 probes, a diamond crystal is secured to a cantilever with glue that has a maximum heating temperature of 70°C. The sample was then cooled to room temperature, and a new square was formed. After that, the sample was again heated to 55°C, and another square was formed. The AFM image of the obtained sample is shown in Fig. 6. According to the obtained data, a 28°C increase in sample temperature during lithography leads to a roughly four-fold enhancement of the depth of SPM probe penetration into PMMA under

the same pressing force (Fig. 6, *b*). Therefore, heating of the sample during lithography provides an opportunity to reduce significantly the SPM probe–surface interaction force while preserving the same mask formation rate. This helps extend the time to failure of an SPM probe and, consequently, enhance the reproducibility of shape of a mask.

2.2. Effect of chemical etching on the process of mask formation

A polymer is squeezed out from certain regions of the surface during SPL. This should lead to rupture of its chains and, presumably, affect its structure in these regions. Therefore, standard procedures of chemical etching of PMMA may theoretically be used to improve the quality of a mask. A 1 : 3 solution of methyl isobutyl ketone in isopropyl alcohol [1], which is the standart developing agent for PMMA, was used in our experiments. The influence of etching time on the size of a mask formed by SPL in PMMA was examined. The geometric size of the formed mask was determined by AFM, and the mask was then etched by immersing it into the developing solution for 20 s. After that, the mask was rinsed with isopropyl alcohol, dried at room temperature, and examined by AFM. The procedure was then repeated.

It was found that the PMMA film thickness decreases monotonically (Fig. 7, *c*). At the same time, the width of a groove increases rapidly within the first 20 s of etching in the developing solution, but subsequent widening proceeds at a significantly lower rate that is comparable to the thickness reduction rate (Fig. 7, *d*). The obtained data suggest that the PMMA dissolution is accelerated due to the rupture of polymer chains under the influence of an SPM probe during lithography. Owing to this, the polymer material squeezed out from the mask formation region is also removed quickly. A certain fraction of squeezed-out polymer may also be washed away mechanically when a sample is immersed into the developing solution. Thus, chemical etching may help improve the quality of the obtained mask. However, one should take into account the fact that the lateral dimensions of regions with PMMA removed from them increase.

Conclusion

The obtained results revealed that scanning probe lithography may be used efficiently to fabricate structures with lateral dimensions in the micrometer range (e.g., microparticles with configuration anisotropy).

A properly functioning system for compensation of the nonlinear piezo scanner motion distortion (in the present case, this system was based on built-in capacitance sensors) provides an opportunity to achieve a significantly better reproducibility of the obtained structures. This system also allows one to produce masks in several passes with a reduced force of interaction between an SPM probe and a polymer material in which the mask is formed. The lifetime of an SPM probe increases in this case.

It was established that raster lithography is the optimum mode for production of masks of a complex geometric shape, although this approach does raise the mask formation time. Vector lithography is the mode of choice for production of masks for simple microparticles. It was demonstrated that the SPM probe pressure may be reduced if a sample is heated slightly in the process of mask formation in PMMA. This helps extend the time to failure of an SPM probe. Alternatively, the mask formation time may be shortened significantly due to a reduction in the number of passes, since the depth of probe penetration into PMMA increases approximately by a factor of 4 if the pressure is kept the same as in room-temperature experiments.

It was demonstrated that chemical etching helps remove squeezed-out polymer from a formed mask and, consequently, improves the quality of this mask. However, one should take into account the fact that etching induces an increase in the size of a formed mask.

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Conflict of interest

The authors declare that they have no conflict of interest.

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