Monte Carlo simulation of surface etching with colloidal mask

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This work reports a study of oxygen plasma etching process used for fabrication by colloidal lithography technique of nanopatterns of functionalized thiol molecules on gold substrate. Patterns consisting in arrays of mercaptohexadecanoic acid spots on gold are fabricated by plasma etching with a colloidal mask (polystyrene beads with diameter of 500 nm) of a mercaptohexadecanoic acid molecular monolayer on a gold substrate. The structure of the fabricated patterns is investigated by atomic force microscopy and the results are compared with a Monte Carlo 3D simulation of the anisotropic etching process.

1. Introduction

Colloidal lithography (CL) is a promising inexpensive fabrication tool for producing regular and homogenous surface patterns over large area [1]. The main fabrication step in CL is deposition of a monolayer of nanoparticles (nanobeads or nanospheres) packed in a crystal with hexagonal geometry over a relatively large area of a substrate surface. A variety of nanofabrication techniques, such as self-assembly, spin coating, electric-field-induced electro kinetic flowing, and Langmuir Blodgett deposition, have been developed to deposit large-area 2D colloidal masks [2]. Nanolithography techniques based on these colloidal masks have been used in fabrication of large-area surface patterns for applications in technological fields such as biosensors, data storage, photonic materials and optoelectronic devices.

Another key fabrication step in CL involves the use of low-pressure plasma technology for unisotropic deposition or etching of thin films on the substrates with colloidal masks. In this work we study reactive ion etching (RIE) in oxygen plasma as a method to fabricate patterned surfaces with functional thiol molecules on gold. RIE is a very efficient plasma technique used in microelectronics. While for etching silicon substrate, RIE uses CF_4 or SF_6 plasmas, etching of organic molecules uses O_2 plasma. In the case of polystyrene (PS) colloidal masks, O_2 plasma etches not only the substrate, but also the mask reducing the bead size and widening the interstitial spaces in the initially close-packed 2D colloidal mask[3].

In this paper, we study the oxygen plasma etching step of CL technique used to generate patterns of functionalized thiol molecules on gold substrate. The first part of the work gives results of 3D Monte Carlo simulation of the anisotropic etching process. The plasma etching is considered perfectly anisotropic, the mask and substrate being subjected to a parallel flux of etching particles (oxygen positive ions) perpendicularly to the substrate. The etching rate in simulation is determined by the density of reactive ions arrived on the etched surface. The height profiles of the etched surfaces obtained in simulation is compared with the height profiles of the atomic force microscopy topography images of the nanopatterns obtained in CL experiments.

2. Numerical simulation

The simulation of anisotropic etching process with colloidal mask was made with a 3D Monte Carlo code. The plasma is considered as a reservoir of etching particles (oxygen positive ions) and separated by the sample surface (a substrate with a monolayer of PS beads) through a positive plasma sheath, the sample surface being biased at a negative potential against the plasma potential (see Fig. 1). Thus, the plasma sends a parallel flux of etching particles perpendicularly to the substrate surface. The substrate is covered by a perfectly close-packed monolayer of PS beads (500 nm in diameter) forming a 2D crystal with hexagonal symmetry. Each PS sphere is tangent to its first order six neighbours, thus leaving etching spaces between any three adjacent spheres. A sphere is surrounded by 6 first-order neighbours and 12 second-order neighbours. Thus, the colloidal mask can be regarded as a multiplication of a ‘unit cell’ composed of 7 spheres (a central one and the first 6 neighbours). For an accurate description of the etching process over a ‘unit cell’, the simulation was extended to the 12 neighbours of a ‘unit cell’. The trajectory of each etching particle in the plasma sheath is considered collisionless. The only collisions are with the colloidal mask (which in this simulation were considered elastic) and the substrate. The substrate, with a surface of 2.5×2.5 μm^2, is etched by the arriving particles, the etching depth being proportional to their surface density. In the simulation is considered also the etching of the PS beads of the mask, although this etching is unrealistic because the shape of the beads is maintained spherical, their radius being decreased with a constant rate. In the experiments, the spherical shape of the beads is not maintained because etching anisotropy and dependence of the etching effect on the incident angle of the incident etching particle on the bead surface. However, although the simulation at this stage looks simple, a remarkable agreement with the experiment, as regards the shape of the fabricated nanopatterns, is obtained.

3. Comparison with the experiment

Fabrication of the nanopatterned surface was performed by etching with a PS colloidal mask of a layer of mercaptohexadecanoic acid (MHD) molecules deposited on gold. Briefly, the gold surface is functionalized by self assembled monolayer deposition of MHD molecules, then the colloidal mask of polystyrene beads (ϕ = 500 nm) is deposited by spin coating and, finally, the obtained sample is etched by oxygen plasma for 30 seconds. Finally the PS beads are lift-off by sonication in water, thus leaving a pattern formed by an array of MHD circular spots (ϕ = 430 nm) on gold substrate.

Oxygen plasma etching was carried out in reactor with a magnetic-field-enhanced inductively-coupled radio frequency discharge in oxygen at low pressure (0.6 Pa), which generated a high-density plasma as a source of etching particles (oxygen ions) [4]. The sample was loaded on an electrode (8 cm apart of the inductive coil) that was powered by a radio frequency power supply to bias the sample surface at a negative potential of -100 V (Fig. 1). A positive charge sheath is created between the self-biased sample surface and plasma, the plasma ions being accelerated in this sheath towards the surface. Thus, the sample surface is subjected to an intense and anisotropic flux of positive ions of oxygen that break bonds in the MHD molecules. At the working gas pressure, the sheath is collisionless, thus the etching being unisotropic. Due to the very dense plasma, the etching is very fast, the MHD molecules being removed completely from the unshadowed gold surface in less than 30 seconds. However, the oxygen plasma etching has reduced also the size of the PS beads, thus some regions of the sample surface being exposed to the etching particles for a shorter time [5].

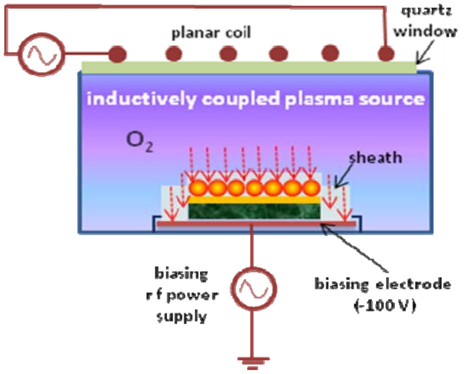

Fig.1. Schematic of the experimental set-up used to generate oxygen plasma for the etching process.

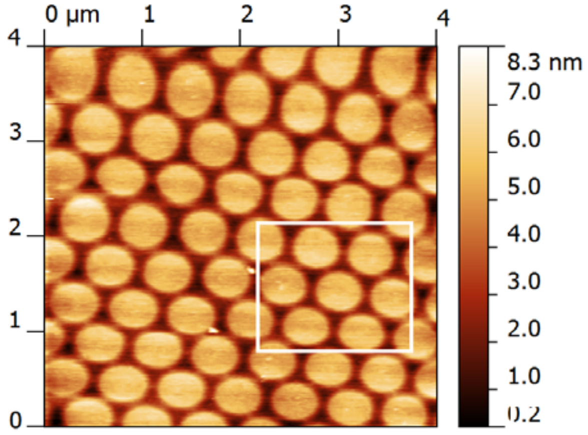

Fig.2. AFM image of the nanopattern obtained by etching with a colloidal mask of a monolayer of mercaptohexadecanoic acid molecules on gold.

This generates a transition region between clean gold surface and un-etched MHD spots. Figure 2 shows a topography AFM image of the pattern of MHD spots on gold. Firstly, we notice that the diameter of spots (around 430 nm in this image) is smaller than the diameter of the PS beads. This is an effect of mask etching. Etching of the mask generated areas of incompletely etched MHD layer.The etching pattern of a ‘unit cell’ (represented in the white rectangle in Fig. 2 and in detail in Fig. 3a) is compared to the pattern of a “unit cell” resulted from the simulation (Fig. 3b). For comparison reasons, the experimental image was plotted in the same colour code used for the simulation results. The red colour indicates the non-etched zones while the blue colour corresponds to the most etched zones (bare gold). A good match of the two images in Fig. 3 can be observed.

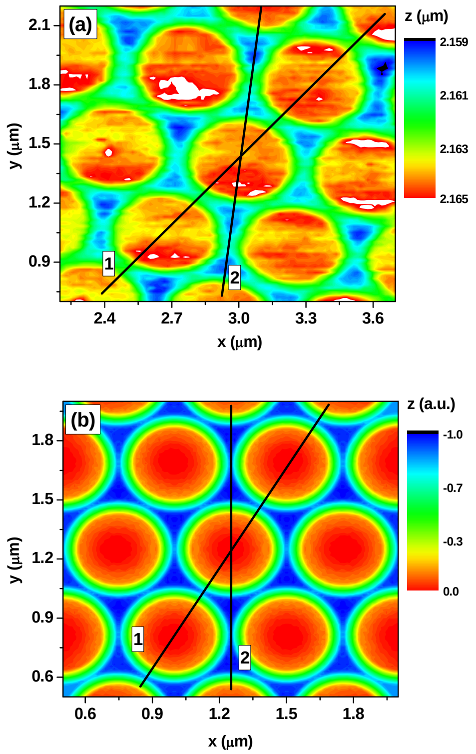

Fig.3. Experimental (a) and simulated (b) patterns obtained by plasma etching

This is a proof that the assumptions made in simulation are correct. For a detailed comparison, we have analysed the height profiles along the lines (1) and (2) in the experimental and simulated patterns (Fig. 4). The line (1) goes along the points of initial contact between the PS beads while the line (2) goes through the middle of mask-non-protected areas. Thus, the positions along the line (1) correspond to regions exposed to etching for variable time duration, which results in regions of incomplete etching of the MHD layer. On the other hand, the height profile along line (2) shows regions of complete etching of the MHD layer (regions unmasked at the beginning of the etching process). Regions of partial etching are visible also in this profile. The experimental and simulated height profiles in the regions of completely non-etched regions do not perfectly match. This is probably an effect of re-deposition of the etched material in the shadow of the beads. The re-deposition process can also explain why the margins of the MHD spots are higher than the centres of the spots (see the experimental height profiles in Fig. 4).

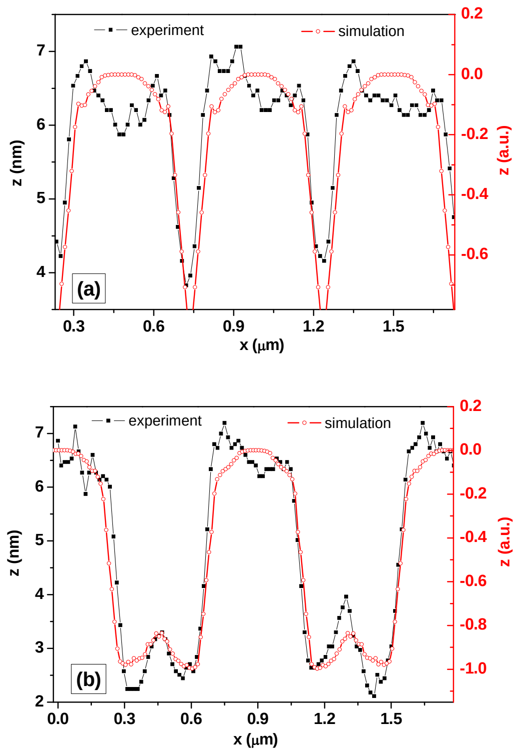

Fig.4. Comparison between the experimental (black) and simulated (red) height profiles along (a) line (1) and (b) line (2).

4. Conclusion

Colloidal lithography is a promising inexpensive technique used to obtain regular and homogeneous surface patterns over large areas. This technique comprises different fabrication steps, each of them being critical for the successful fabrication of the patterns. In this study, we have investigated plasma etching with colloidal masks as a main step in fabrication of patterns consisting of arrays of spots of a self assembled molecular monolayer on a gold substrate. The fabricated patterns were investigated by atomic force microscopy and the results were compared with the patterns obtained by Monte Carlo simulation of the etching process. The simulation considered the effect of a homogeneous and anisotropic flux of etching particles (oxygen positive ions) on the colloidal mask and molecular monolayer of MHD molecules on gold substrate. The oxygen plasma etched also the mask, thus reducing the dimension of the polystyrene beads and enlarging the distance between the non-etched spots of the pattern. The effects of mask etching are visible on topography images of the patterns as regions of incomplete etching. Comparison between experimental and simulated patterns reveals also a effect of re-deposition of the etched material in the in the regions shadowed by the beads

5. Acknowledgement

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