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Nanolithography with metastabile helium

S. Nowak, T. Pfau, J. Mlynek

Fakultät für Physik, Universität Konstanz, 78434 Konstanz, Germany
(Fax: +49-7531/883072, E-mail: Stephan.Nowak@uni-konstanz.de)

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Abstract. We have used a self-assembling monolayer of dodecanethiole molecules as the resist for a lithography technique based on a beam of metastable helium atoms. Doses as low as 3 metastable helium atoms per 10 molecules are enough to write patterns into this resist. An edge resolution of 30 nanometers is demonstrated. The writing mechanism is based on the damage of the resist due to Penning ionization.

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Standard optical lithography techniques are believed to be limited in principle to resolutions above 100 nm. Therefore various possibilities are discussed to complement them. Requirements for such alternative techniques are high spatial resolution, the possibility to form arbitrary structures, and short duty-cycle-times. Simplicity of the setup and the possibility of parallel writing are advantageous. Recent developments in this context in electron and ion beam lithography as well as in X-ray-lithography are discussed in [1].

Recently different atom beam techniques with thermal beams have been investigated for lithography. As atoms are electrically neutral, no space charge effects occur that make the beam divergent; therefore no high kinetic energy of the particles is required. Diffraction is no severe limit for the resolution because the de Broglie wavelength of thermal atoms is less than 1 Å. These atom beam techniques rely either on direct patterning with atoms that stick on the surface [2], or on patterning of a special resist with metastable rare gas atoms [3]. The resist used in the latter approach is based on the selfassembly of alcanethiols on coinage metals [4] and the change of the wetting properties of this self-assembling monolayer (SAM) for an etch solution after exposure. It was demonstrated, that with an exposure dose of 10 metastable argon atoms per molecule of the SAM the resist could be altered such that in an etching procedure an edge resolution of 100 nm could be achieved [3]. It has also been shown, that a very similar resist could be used for low energy electron lithography reaching a similar resolution [5].

Here we present the use of self-assembling monolayers as a resist for a high resolution lithography technique using a beam of metastable helium. We achieve an edge resolution of 30 nm with an exposure dose of only 0.3 metastable helium atoms per molecule of the SAM. The low kinetic energy of the particles, which is in the order of 100 meV, does not alter or damage the substrate surface. To pattern the resist the internal energy of the metastable atoms is used instead, which is about 20 eV for metastable helium.

The process is shown in Fig. 1. We prepare silicon substrates with an evaporated gold film of a typical thickness of 30 nm. On the gold film we deposit a self-assembling monolayer (SAM) of dodecanethiole as resist, which makes the sample surface highly hydrophobic.

A measure for the quality of the SAM is the contact angle of pure water, which is $> 110°$ in our case [4, 6]. This sample is then exposed to a beam of metastable helium. Metastable helium atoms hitting the surface release a secondary electron with an energy of ≈ 10 eV in a Penning process with a de-excitation efficiency close to 1. This process can be described with the equation $He^* + M \rightarrow He + M^+ + e^-$, where M stands for one molecule of the SAM, which gets ionized. As the ionization threshold of these molecules is about 10 eV, the escaping electrons can have kinetic energies of more than 10 eV [7]. In organic layers electrons of this energy have an inelastic mean free path of about 8 Å[8], so that with a high probability another inelastic scattering event can take place, and another molecule of the SAM may be ionized. This damage of the SAM changes locally its wetting properties in a way that a chemical reagent dissolved in water can penetrate the remainings of the SAM and get in contact with the gold layer. Therefore the local changes in the SAM can be transferred to the gold layer in a final wet chemical etching step.

The internal energies of metastable helium, which are 19.82 eV for the $He^*(2_3S)$ state (predominant in our beam, $> 95\%$) and 20.61 eV for the $He^*(2_1S)$ state [7], are about twice as large than the internal energy of metastable argon [3]. This means, that in this process with helium in principle two molecules of the SAM can be ionized, whereas only one ionization is possible with argon. Furthermore, the Penning ionization efficiency is about a factor of 10 larger for helium than for argon [9]. This may explain, why the exposure dose is so much smaller for metastable helium, compared to argon.

For the sample preparation we evaporate a 30 nm thick film of gold (99.999 %) onto a Si[100] surface with a thin adhesion layer of chromium (5 Å) on it. This is done in a

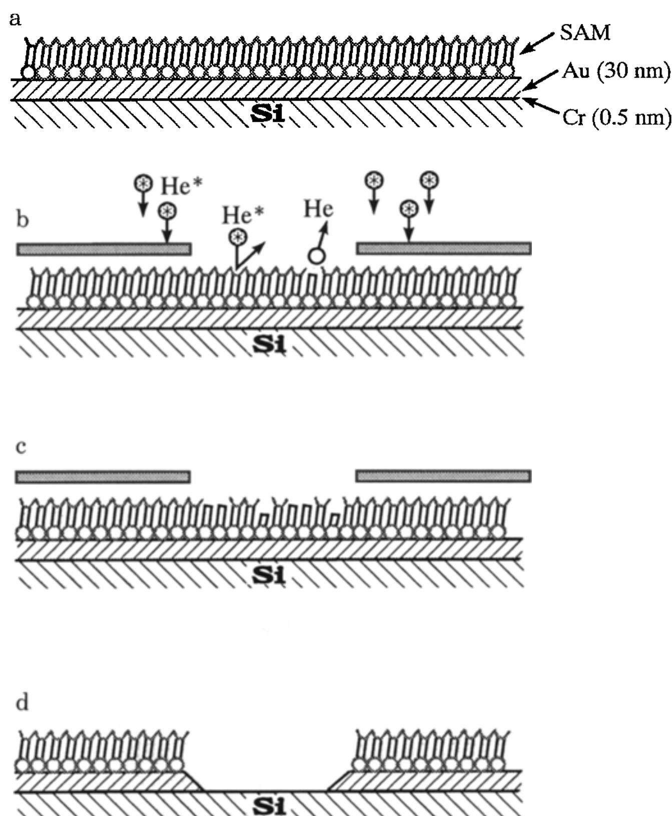

Fig. 1. The patterning process. **a** Deposition of the SAM on a gold sample. **b** Exposure to a beam of metastable helium atoms through a free standing transmission mask. **c** De-excitation of metastable atoms causes local alterations of the SAM. **d** The pattern in the SAM is copied to the underlying gold layer in a wet chemical etching step

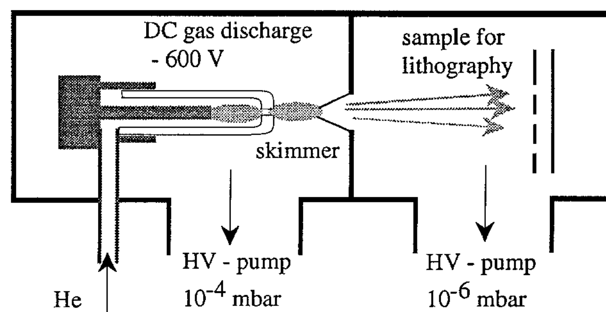

Fig. 2. The experimental setup (schematic). The distance from the glass nozzle to the skimmer is typically a few millimeters, the distance from the skimmer to the sample was 12 cm in our experiments

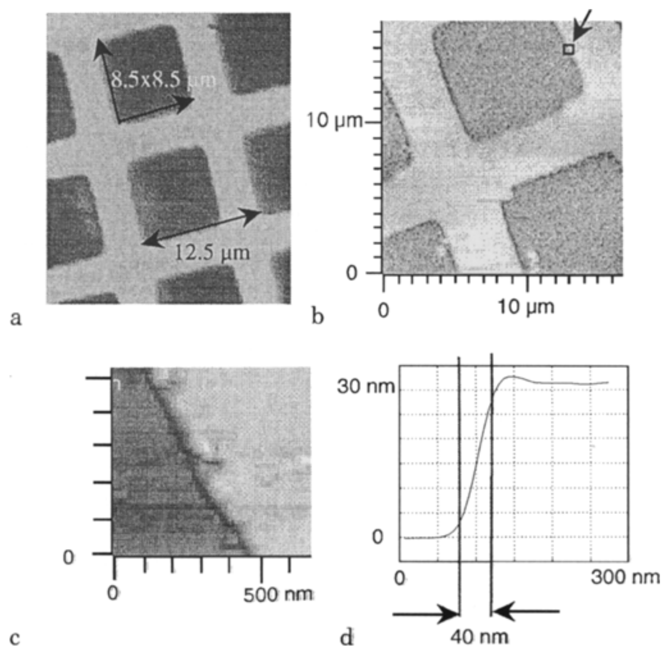

Fig. 3. Experimental results: **a** is a light microscopic picture of the mask, **b** shows the topography of a sample prepared by lithography, recorded with an AFM. Regions in darker grey are lower lying. A magnification of an area on the sample indicated by the small frame (at the tip of the arrow) in **b** is shown in **c**. The picture shows smooth surfaces on top of the gold layer as well as on the substrate surface (*left side*). An integrated topography profile of this area is shown in **d**, as explained in the text

commercial UNIVEX 450 evaporator, the thickness of the layers is controlled with an Inficon XTC deposition controller to a relative precision of 3%. The RMS roughness of the surface is < 2 nm. We then deposit the SAM by dipping the sample into a 2 mM solution of dodecanethiole in ethanol for at least 24 h.

The etching was performed immediately after exposure in a gold etching solution [10] consisting of 1 M KOH, 0.1 M $K_2S_2O_3$, 0.01 M $K_3Fe(CN)_6$ and 0.001 M $K_4Fe(CN)_6$. The process was performed at room temperature where the etch rate is about 2.5 nm/min. The samples were investigated with an atom force microscope (AFM, Park Scientific Instruments).

The experimental setup is shown in Fig. 2. We work in a high-vacuum apparatus with two chambers, in the first of which the beam is generated in a simple DC-gas discharge scheme which is described elsewhere [11]. After passing through a skimmer of 500 microns diameter where we have a beam brightness of about $10^6\ s^{-1}\ sr^{-1}\ cm^{-2}$ the beam travels on in the second chamber, where the lithography sample is mounted. The background pressure, which is mainly due to helium, is in the source chamber typically $1 \cdot 10^{-4}$ mbar, in the experimental chamber $2 \cdot 10^{-6}$ mbar.

To demonstrate the resolution we did proximity printing experiments, where we mounted a mask in contact with the lithographic sample. This mask was a commercially available nickel mesh with square apertures of $(8.5\ \mu m)^2$ and a periodicity of 12.5 μm (see Fig. 3). Systematic investigations showed that the dose with which we achieved the best contrast was as low as 0.3 metastable helium atoms per molecule of the SAM, where we assumed an effective area of $10\ Å^2$ for each molecule of the SAM [12]. We reached this dose in an exposure time of 6 min, where the sample was mounted 12 cm downstream from the skimmer. This dose was determined with a detector based on Penning ionization, which is described elsewhere [11].

Transverse electrical fields were applied to the atom beam to rule out ions or electrons as cause of the damages to the SAM in several experimental runs. We found no influence of such a field, therefore we believe that residual charged particles are not responsible for the damage of the resist. The UV photons which come out of the beam source and could also give rise to lithographic patterning have a wavelength of 54 and 59 nm. To rule out an effect of these, we put a

spacer of 10 μm thickness in between the lithographic sample and the mask, and we achieved edges sharper than 150 nm in these runs. However, the shadow of the photons behind the mask gets smeared out by diffraction to a width of 500 nm. Therefore the observed sharpness of the edge cannot be due to exposure with photons and we assign the dominant damage of the resist to the metastable atoms. This result is supported by experimental runs, where we mounted membranes of glassy carbon in front of the sample. These are partly transparent for UV photons, but shield the sample from metastable atoms. We found no lithographic patterning in these runs.

Results of our experiments are shown in Fig. 3. In Fig. 3 a we show a picture of the mask taken with an optical microscope. Fig. 3 b shows the topography of a sample prepared by our lithography technique and recorded with the AFM. Brighter areas are higher on the sample. The mask is reproduced with high exactness. Figure 3 c is a detailed view of one step on the sample in an area marked by the frame at the tip of the arrow in b). The grey scale coding is the same as in b). The curve in Fig. 3 d was obtained from this set of data by taking the average of the height values along straight lines parallel to the edge. There are three main features clearly visible: (i) The height of the step is 30 nm, which is the full thickness of the gold layer. (ii) The integrated cross section on top of the gold layer as well as the surface of the underlying substrate is very smooth, which means that there are no major spots of roughness on top as well as on the bottom. There are no remaining gold islands in the etched area and no holes deeper than the mean roughness of the gold surface. (iii) The width of the step integrated in the manner explained above is 40 nm (the criterion for the determination of this number is the width, where the step descends from 90 % to 10 % of the total height). Individual cuts through the topography show a step width of 30 nm. This width corresponds to the thickness of the gold layer. We believe that this is the achievable limit in our case, because the layer and the etching process are isotropic.

We observed also patterning of a bare gold layer without using the SAM when the dose is at least one order of magnitude larger. The edge resolution is similar, however the contrast is reversed. We assign this effect to the protection of the gold against the etch solution at the exposed areas due to formation of crosslinked hydrocarbon layers. These hydrocarbon chains contaminate our beam and background gas due to the use of oil diffusion pumps.

In conclusion we demonstrated a new lithographic technique based on a neutral metastable helium beam. The process is technically simple and can be extended to parallel operation of several sources or to larger source areas. The principal resolution limit of 30 nm was achieved. On the one hand the process can be used in a proximity process with free standing masks. The masks are not damaged as the involved energies are small compared to other techniques. On the other hand atom optical methods like laser focusing can be used to produce structures with sub 100 nm resolution with this technique as well as with deposition techniques [2].

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