Rapid communication

Nanolithography with metastable helium

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Abstract. We have used a self-assembling monolayer of dodecanethiol 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 self-assembly of alkanethiols 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 dodecanethiol 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 → 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 remaining 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
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 dodecanethiol 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$_2$S$_2$O$_3$, 0.01 M K$_3$Fe(CN)$_6$ and 0.001 M K$_4$Fe(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 $1 \times 10^{-4}$ mbar, in the experimental chamber $2 \times 10^{-6}$ 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 $\mu m$ (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 A$^2$ 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