

Rapid communication

Pattern generation with cesium atomic beams at nanometer scales

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Abstract. We have demonstrated that a cesium atomic beam can be used to pattern a gold surface using a self assembling monolayer (SAM) as a resist. A $12.5\ \mu\text{m}$ period mesh was used as a proximity mask for the atomic beam. The cesium atoms locally change the wettability of the SAM, which allows a wet etching reagent to remove the underlying gold in the exposed regions. An edge resolution of better than $100\ \text{nm}$ was obtained. The experiment suggests that this method can either be used as a sensitive position detector with nanometer resolution in atom optics, or for nanostructuring in a resist technique.

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In a recent series of experiments it has been shown that a neutral atomic beam can be controlled with laser light in such a way as to grow nanoscale structures on a suitable substrate [1–4]. In this method, a standing wave light field is used as an immaterial mask. There are two constraints, which limit this method to a small number of elements: first, laser light has to be available at the resonance wavelength of the atom, and second, the atoms have to stick to the substrate and should be chemically stable once they are removed from the vacuum chamber and exposed to air. Chromium and aluminum with resonance wavelengths near $425\ \text{nm}$ and $308\ \text{nm}$, respectively, have both properties, and focusing has successfully been demonstrated.

Recently, beams of metastable helium and argon atoms have been used in a more traditional lithography technique [5, 6]. In this method, a thin layer of gold is coated with a self assembling monolayer of alkanethiols (SAM) and then exposed to the atomic beam which in these experiments was spatially modulated by a mechanical mask. After exposure to metastable atoms, etching with a standard gold etching solution transferred the mask into the gold layer. The achieved edge resolution of the transferred pattern at sub $100\ \text{nm}$ scales suggested that this technique could provide a useful lithography method. Even though all the details have not yet been clarified, it is assumed that the internal energy of the metastable atoms, which is on the order of $20\ \text{eV}$, causes damage to the SAM via a Penning ionisation

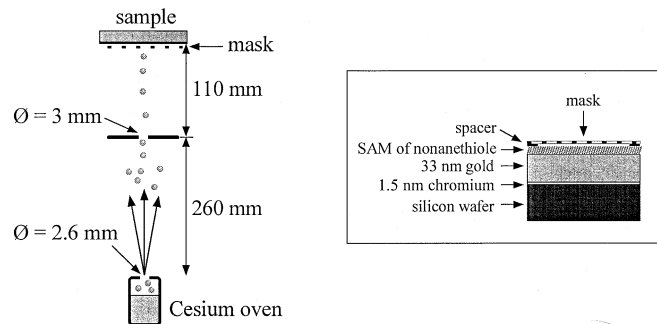


Fig. 1. Scheme of the atomic beam apparatus with an enlarged sketch of the sample

process, which makes the underlying gold layer susceptible to the gold etching solution.

Motivated by these results and discussions with colleagues [7], we have investigated the influence of a cesium atomic beam in a similar arrangement. The use of an alkali atomic beam in such a process would be desirable because light force methods have been extensively studied with alkali atomic beams, and because light sources are abundant.

We have found that a cesium atomic beam can indeed be used to transfer a given mask (a nickel mesh of $12.5\ \mu\text{m}$ periodicity) into a gold layer with a self assembling monolayer serving as a resist. In the following, we will give details of our experiment which agree well with the observations of Berggren et al. [8].

1 Experimental setup

Sample preparation was carried out with an established procedure used for metastable atomic beam printing [6]. A polished silicon wafer was first coated by evaporation with a $1.5\ \text{nm}$ chromium layer for improved sticking properties followed by a $33\ \text{nm}$ gold layer. Immediately after the evaporation, the samples were immersed into a $1\ \text{mM}$ solution of nonanethiols ($\text{CH}_3(\text{CH}_2)_8\text{SH}$) in pure ethanole, inducing the formation of a self assembling monolayer on the gold surface within 24 hours [9] (Fig. 1).

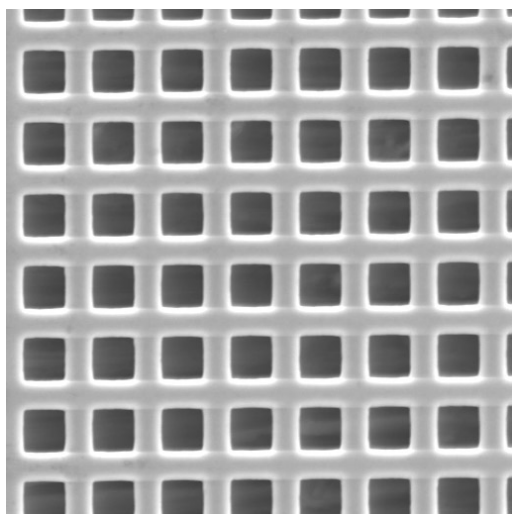


Fig. 2. SEM image of the nickel mesh (periodicity $12.5 \mu\text{m}$) used as a mask

The formation process of alkanethiole monolayers on gold has been extensively studied [12]. In our case the monolayer has a thickness of about 1 nm and consists of $4.6 \cdot 10^{14}$ molecules/cm² [13]. For diagnostic purposes the contact angle of pure water on the SAM was determined, yielding $(110 \pm 1)^\circ$ in good agreement with the values given by Bain et al. [9]. The large contact angle is a consequence of the highly hydrophobic character of the surface which very efficiently shields the underlying gold surface from a water based etching solution. The prepared samples were mounted on a holder and covered by a proximity mask made from a nickel mesh with $12.5 \mu\text{m}$ period and $8 \mu\text{m}$ square openings (Fig. 2). To avoid contact between mesh and sample, spacers of a few microns thickness were placed in between. The assembly then was inserted into a vacuum chamber within 10 minutes after taking the samples out of the solution of nonanethiole.

In the double vacuum chamber the samples were exposed to an effusive cesium atomic beam (Fig. 1). Both chambers were pumped by oil free turbomolecular pumps and could be separated by a linear gate valve which also served as a shutter for the cesium atomic beam. A base pressure of $5 \cdot 10^{-7}$ mbar was achieved within one hour after sample insertion. Cesium was evaporated from a resistively heated glass ampoule with a 2.6 mm diameter opening. A second aperture of 3 mm diameter at a distance of 260 mm was used to shape the atomic beam with a collimation ratio of 1 : 90. The atomic flux density at a typical oven temperature of 135°C was determined by absorption spectroscopy with a weak probe beam, and with a calibrated CCD camera through two dimensional fluorescence imaging, yielding in both cases a flux of $3 \cdot 10^{12}$ atoms/s·cm² at the position of the sample. This value is slightly lower than the calculated flux density of $9 \cdot 10^{12}$ atoms/s·cm² and corresponds to 0.4 monolayers/min with respect to the molecular surface density of the SAM.

We exposed the samples to the cesium beam for up to 30 minutes at room temperature. As the sample was removed from the vacuum chamber for further processing, a breath test gave a first hint of the spatial change of the wettability in the exposed region. The sample was immersed in a

gold etching solution [14] immediately after exposure and etched for 12 minutes, which is sufficient to totally remove an unprotected gold layer. For exposure times longer than 5 minutes a visible modification of the reflectivity of the surface could be observed with very high reproducibility after 3 minutes of etching.

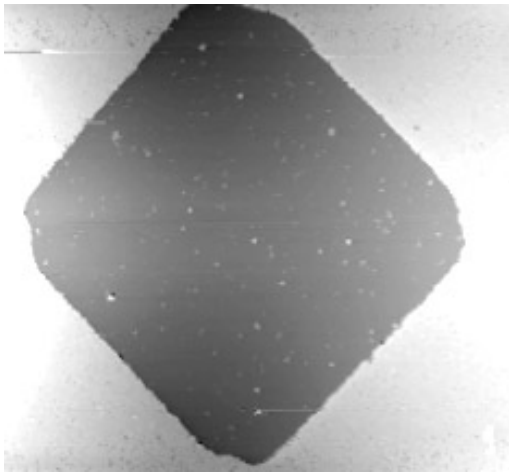
2 Results

For diagnosis of the etched gold surface, the samples were examined using a conventional light microscope, an AFM and a SEM. The light microscope images show, that the pattern of the nickel mesh is reproduced over the entire region exposed to the atomic beam. A representative AFM image (Fig. 3a) shows one $8 \times 8 \mu\text{m}^2$ square transferred into the gold surface with few remaining gold grains at the bottom. Fig. 3b is a three dimensional image of the gold step on the silicon surface. While we find edges of 40 – 50 nm width for single line scans of the AFM tip, the averaged edge resolution along $1.7 \mu\text{m}$ borderline is on the order of 60 nm (Fig. 3c), which is comparable with the deviations of our mask from a perfectly straight mesh. SEM photographs of the samples yield an edge resolution of about the same value (Fig. 3d). Both methods show an unexpected structuring of the gold surface, which we believe to be due to residual background cesium atoms. In general, as can be seen from Fig. 3e, the structure of the mask is reproduced very well. By analysing samples exposed to different doses of cesium, we have observed an optimum response with maximum contrast at doses of 3 to 5 monolayers of cesium corresponding to exposure times of 9 – 14 minutes. At a dose of 3 monolayers each nonanethiole chain is hit with 95% probability by at least one cesium atom.

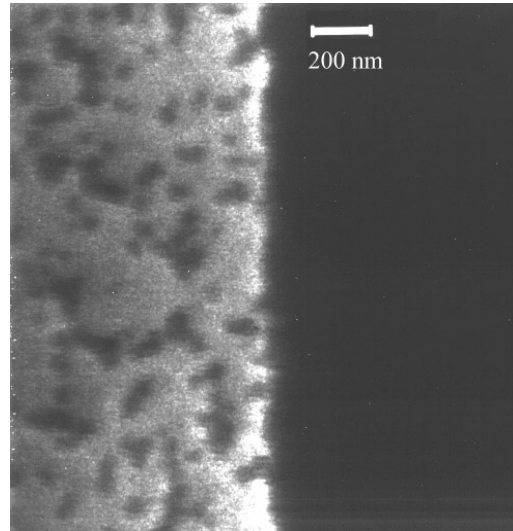
We also studied the influence of cesium atoms on the longer dodecanethiole chain, which was used for the atomic beam experiments with metastable helium [6]. We found that a structure could be patterned into this resist as well, but with large inhomogeneities across the exposed region, and with only moderate reproducibility. Furthermore, we have also replaced the cesium charge with a rubidium charge but have not found a significant modification of the wetting properties of the SAM.

3 Conclusion

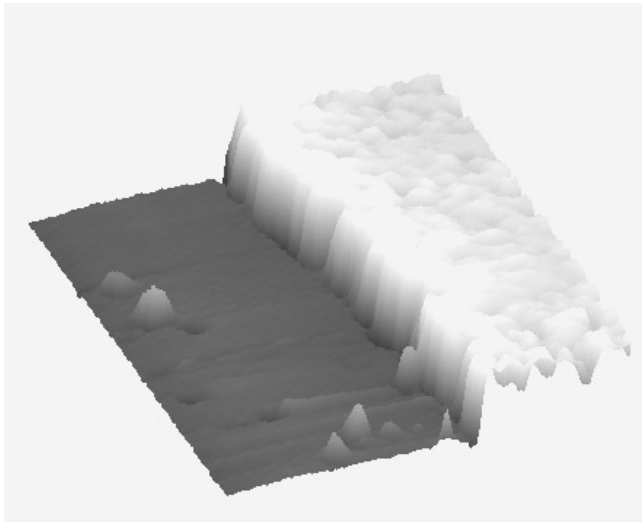
Our results demonstrate that a cesium atomic beam can be used to transfer a stencil mask into a gold layer by using a resist of self assembling monolayers. The edge resolution achieved in the process was 60 nm. An interpretation of the physical and chemical processes which change the reactivity of the inert thiole surface cannot be derived from the present work. In contrast to the metastable beam application which seems to rely on physical damage, a chemical process should be instrumental for this method. One possibility calls for open defects of the SAM to provide access to the sulfur-gold bonds at the bottom of the monolayer. This hypothesis is supported by investigations indicating that short-chain thioles seem to be more disordered and less densely packed than long-chain thioles [9, 10, 11]. This might explain why



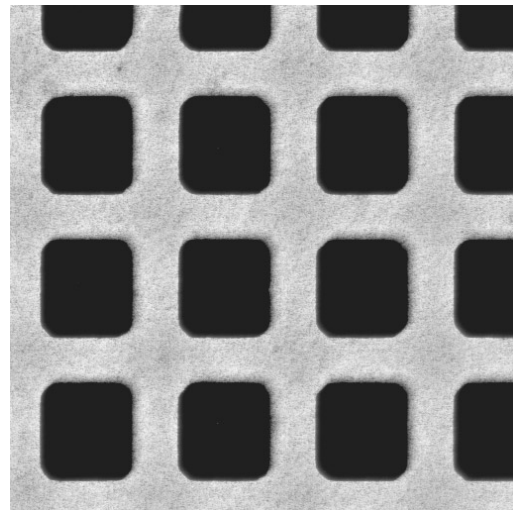
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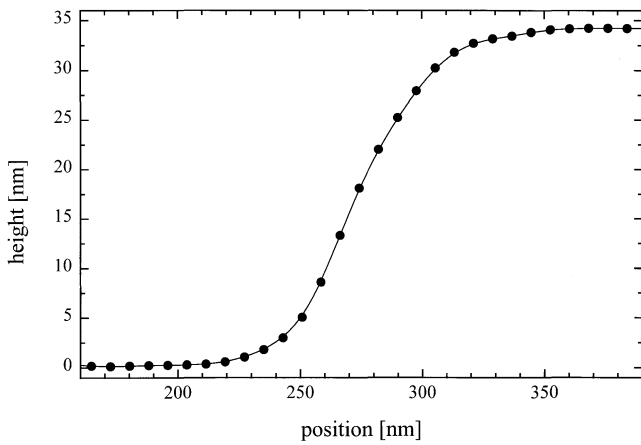
d



b



e



c

Fig. 3a–e. Images of the exposed and etched samples. Dark regions correspond to silicon whereas light regions represent remaining gold areas. **a** AFM image of one $8 \times 8 \mu\text{m}^2$ cell; **b** three dimensional AFM image of the gold step on the silicon substrate; **c** corresponding line profile averaged along $1.7 \mu\text{m}$ borderline. An edge resolution of 60 nm is determined by the 90% to 10% drop of the step height; **d** SEM image of the silicon gold border; **e** SEM overview of the sample

good results were achieved with nonanethiole, but not with the longer dodecanethiole. With the demonstrated technique alkali atomic beams could prove useful for nanostructure preparation: The physical resolution limit of atomic beams is in the Å domain, and established methods of atomic beam control and light sources are available.

Aside from the usefulness of the method described for lithographic applications, it might also fill the need for a two-dimensional detector for alkali atoms in the field of atom optics with a resolution of better than 100 nm.

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14. Gold etching solution: 1 M *KOH*, 0.1 M *K₂S₂O₃*, 0.01 M *K₃Fe(CN)₆*, and 0.001 M *K₄Fe(CN)₆* in aqua dest.