Soft X-Ray Lithography for High-Aspect Ratio Sub-Micrometer Structures

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Abstract

Soft x-ray lithography is a promising micro-nano fabrication process for patterning ultra-precise, low and high aspect ratio micro- and nanostructures [1-5]. A new negative-tone, epoxy-based x-ray resist, mr-X, which offers comparable contrast to PMMA (> 3) at a factor of 20x higher sensitivity, is a promising candidate for this approach [6]. Using a 1 µm thick SiN membrane mask with a ~1 µm thick Au absorber, patterns were transferred into up to 10 µm thick resist using the soft exposure mode at the BESSY II WLS beamline. With typical exposure times of only a few minutes, very precise grating and filter structures have been fabricated with dimensions down to about 500 nm.

Introduction

Using x-ray lithography for patterning, sub-micrometer structures with either low aspect ratio for microelectronic applications [1,2] or with aspect ratios up to 10 for actuator [3], optic and fluidic applications have been produced. Systematic studies reported in [4,5] addressed process and limitation issues, mechanical strength of the resist material, adhesion on various substrates, and fine-tuning of the exposure source as areas that need further improvement. Nevertheless they demonstrated the potential of this technology for high aspect ratio deep sub-micrometer patterning of polymers with the smallest features of about 300 nm and resist heights up to 5 µm.

In the last years there has been an increasing interest in high aspect ratio gratings for x-ray interferometry set-ups [7-10]. For hard x-ray applications heights up to 150 µm and small grating constants in the range of 2-5 µm are needed. Another application is the transfer of high resolution gratings in photo resist layers of only a few micrometer thickness using soft x-rays. The major advantage of this approach compared to standard UV-lithography is the negligible diffraction of the shorter wavelength allowing reliable and reproducible pattern transfer from an x-ray mask into a resist-coated substrate.

Besides precision optical structures, filters with variable yet precise pore sizes for medical and environmental applications are another potential use of this technology. Thick membranes with densely packed, well-defined pores will enable applications such as the capturing of circulating tumor cells [11,12] or high throughput filtering of, for example, bacterial samples [13]. The flexibility to adjust filter pore size to the species of interest as well as the simple use of mechanically stable and supported membranes enables selective filtering of larger, representative sample volumes before injection into a dedicated microfluidic detector chip thereby reducing sample preparation efforts and enhancing sensitivity.

Our initial efforts focused on proof-of-concept experiments of test patterns transferred into 10 µm thick mr-X resist using SiN and Ni membrane masks at the BESSY II wave-length shifter beamline operated in soft mode. Further studies using the CAMD XRLM1 beamline in double-mirror mode are planned along with patterning of novel, application-specific designs.

Experimental

This chapter briefly describes the experimental set-up at HZB (BESSY II) used for initial experiments. X-ray masks used in these tests have been fabricated at Sandia National Laboratory (Albuquergue/ New Mexico) and Karlsruhe Institute of Technology, Karlsruhe as part of a DARPA funded project [14,15]. The mask pattern was generated by electron beam lithography into a ~1.5 µm thick PMMA resist coated onto a 1 µm thick SiN layer deposited onto a Si wafer, subsequent plating of ~1 µm thick gold, and release of the SiN membrane by etching the Si substrate in 70-80°C hot 30% KOH [16]. The thin gold absorber defines a fairly poor mask contrast requiring optimziation of the exposure source and process parameters.

At BESSY II two X-ray lithography beamlines are used to expose thick resist layers (https://www.helmholtz-berlin.de/forschung/grossgeraete/nanometeroptik/index_en.html). While the bending magnet beamline has a fixed spectrum, the wavelength shifter (WLS) beamline has two modes of operation: one for hard x-rays (WLS) and one for soft x-rays (WLS soft mode). For the exposures Jenoptik x-ray scanners are used. The spectral power as a function of photon energy of the bending magnet beamline and the WLS soft mode are depicted in Figure 1. Calculations are made for the same distance to the source.

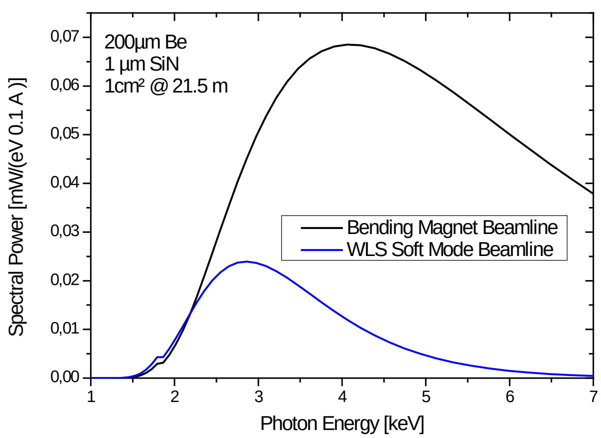


Figure 1:

Spectral power distribution after beryllium window and silicon nitride membrane at soft mode versus bending magnet lithography beamline at HZB/BESSY II.

With the effective exposure spectrum at the WLS soft mode beamline limited to photon energies between 1.5 and 6.5 keV the SiN membrane mask provides a reasonably high mask contrast, while the bending magnet with photon energies up to 15 keV are hardly blocked by the thin gold and demand a thicker gold absorber.

Mr-X resist has been developed in the BMBF-funded INNOLIGA project [6,17,18]. The main focus of this project was the improvement of the material formulation with respect to reliable and reproducible processing while at the same time ensuring excellent patterning performance with signicantly higher sensitivity than PMMA (contact micro resist technology GmbH, Berlin, Germany, http://www.microresist.de/home_en.htm, for further information about mr-X).

A gradation curve for mr-X resist samples coated onto glassy carbon mask substrates and exposed at both BESSY II beamlines through an aperture stencil mask is shown in Figure 2 [18]. The high resist contrast is indicated for both beamlines by the jump-like change from zero to maximum resist height with only a small change of exposure dose. The sensitivity and minimum exposure dose is slightly different for the two beamlines -- likely caused by additional heating at the bending magnet beamline due to its higher power output (integral of the curves shown in Figure 1). For the WLS soft mode condition a minimum exposure dose of about 60 J/cm^3 is suggested from the gradation curve, while at the bending magnet a minimum exposure dose of 40 J/cm^3 seems to be sufficient. However, adhesion tests showed that good adhesion is only achieved at exposure doses of 100 J/cm^3 at the bending magnet beamline and 80 J/cm^3 for the WLS soft mode beamline.

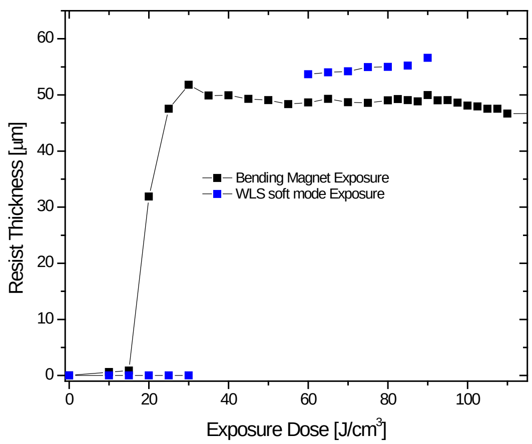


Figure 2:

Gradation curve for mr-X exposed at both HZB/BESSY II lithography beamlines using glassy carbon mask substrates of 250 µm thickness.

Combining low contrast SiN membrane x-ray masks with the new, high contrast negative photo resist allows for the use of very thin gold absorbers on the x-ray mask (see Table 1 for a comparision to SU-8 negative resist commonly used in MEMS and NEMS applications) for ‘high contrast’ imaging. The calculated data also demonstrates that the increased exposure dose for the mr-X resist is reasonable and will result in approx. 5 min exposure time for a 4” scan length and 200 mA ring current at the WLS soft mode beamline.

Table 1: Calculated exposure dose and minimum gold thickness for 10 µm SU-8 and mr-X at bending magnet / WLS soft mode beamline (beryllium window 200 µm, SiN membrane 1 µm).

Resist	Exposure dose [mA.min/cm]	Gold thickness [µm]
SU-8	1.3 / 5.7	4.75 / 1.9
mr-X	6.0 / 25.6	0.7 / 0.5

Process Parameters

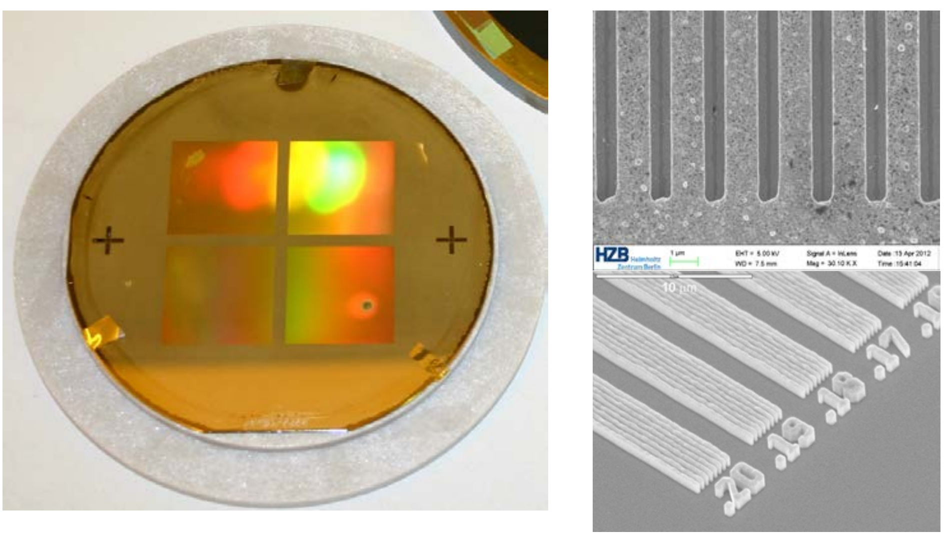
Samples were prepared by spin-coating 20 mL of mr-X 25 liquid resist onto silicon wafers at 3000 rpm and subsequently soft-baking at 95°C for 15 min. About 10 µm thick mr-X resist films with tight tolerances (± 0.3 µm) were made with these parameters. Critical for low stress is a fairly slow cool down ramp and at least 1 hr of relaxation at RT prior to exposure. Mask/substrate assembly were mounted with a ~10 µm proximity gap onto the motion stage of a Jenoptik DEX 1 scanner installed at the BESSY II WLS beamline and exposed with the soft exposure mode spectrum of Figure 1. For an exposure dose of 120 J/cm^3, exposure time was approx. 5 min for typical ring currents (200-250 mA) and an 80 mm scan range. A dose range from 60 to 120 J/cm^3 was investigated in our tests, where 90 J/cm^3 is a standard value used for tall structure patterning. Standard post exposure bake (PEB) was done on a hot plate at 80°C for 20 min with a slow cool-down ramp of 5°C/hr. Next, a brief period of relaxation of ~1hr at RT followed before the samples were developed for up to 10 min in PGMEA with a subsequent thorough rinse in IPA. Air and vacuum drying were tested with the vacuum drying showing negligible structure collapse and more repeatable results.

Results

In our first tests, two different SiN membrane masks were used to make grating structures and fine-pore filter, respectively [19].

Gratings

Figure 3 shows images of the absorber pattern of the grating mask. Line width measurements of the mask reveal that the nominal 1 µm equal lines and spaces are effectively ~1.2 µm wide gold lines and ~0.8 µm wide open spaces. Exposure through the open areas will result in patterned resist structures (lines) of ~800 nm width.



Figures 3: SiN mask – left overview showing four membrane fields containing line/space patterns; right, top: Line/Space pattern with line widths varying approx. 820±70 nm over the grating areas in ~1 µm thick gold (used for the tests), bottom shows test pattern down to 200 nm in approx. 500 nm Au from another electron beam written mask.

One of the main challenges of patterning high aspect ratio gratings is collapse of the fine, isolated, densely packed lines during the drying process as illustrated in Figure 4. For this sample standard process parameters were employed (90 J/cm^3 bottom dose, 80˚C PEB for 1hr, air drying) achieving a reasonable adhesion to the substrate but insufficient strength to prevent sticking and collapse.

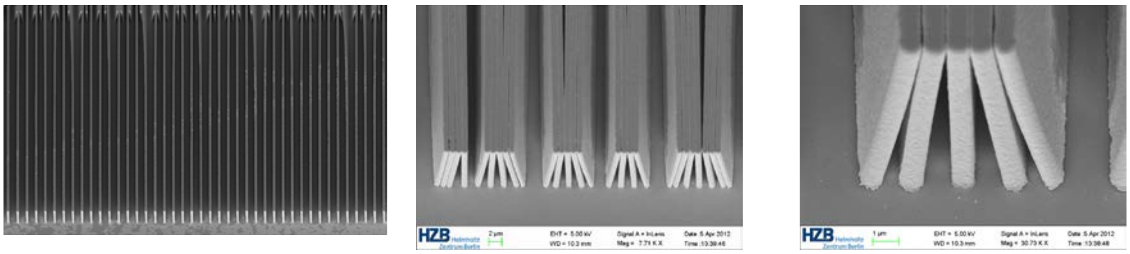
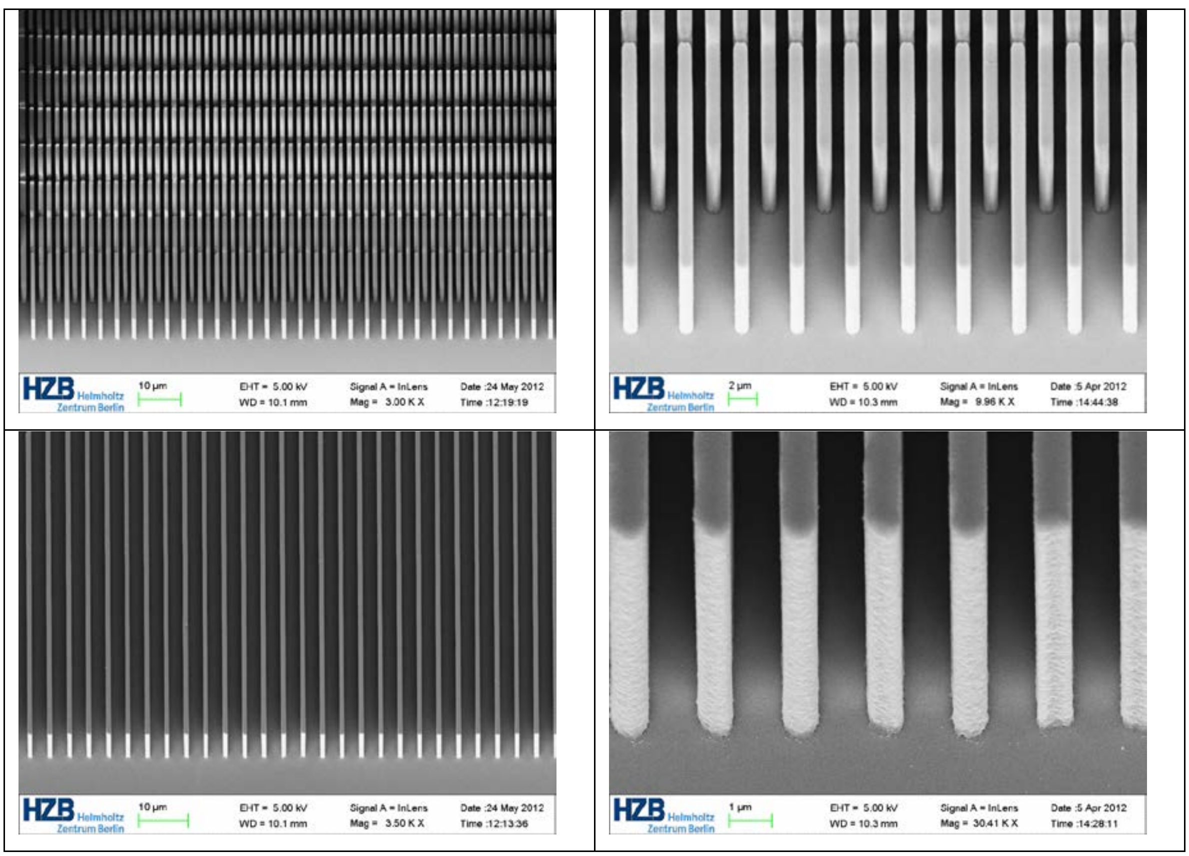


Figure 4: 10 µm tall mr-X resist structures collapsing when densely spaced during air drying caused by large surface area, capillary forces, residues and lack of material strength [4,5].

Using a higher exposure dose (120 J/cm^3), higher PEB temperature (95°C), extended development time and vacuum drying problems, collapsing structures could be resolved resulting in the highest quality structures shown in Figures 5. The line width measurements for standard and optimized processes result in lines 750 to 890nm, which is comparable to the variation of line width on the mask.



Figures 5: Examples of 10 µm tall mr-X resist structures showing no collapse due to process optimization and improved resist strength.

The width variation from top to bottom of a line structure is shown in Figure 6 and proves a very precise pattern transfer of ~880 nm at the top and ~815 nm at the bottom. The ~10% thicker structure at the top is likely caused by higher top dose and slight swelling due to extended exposure to the developer.

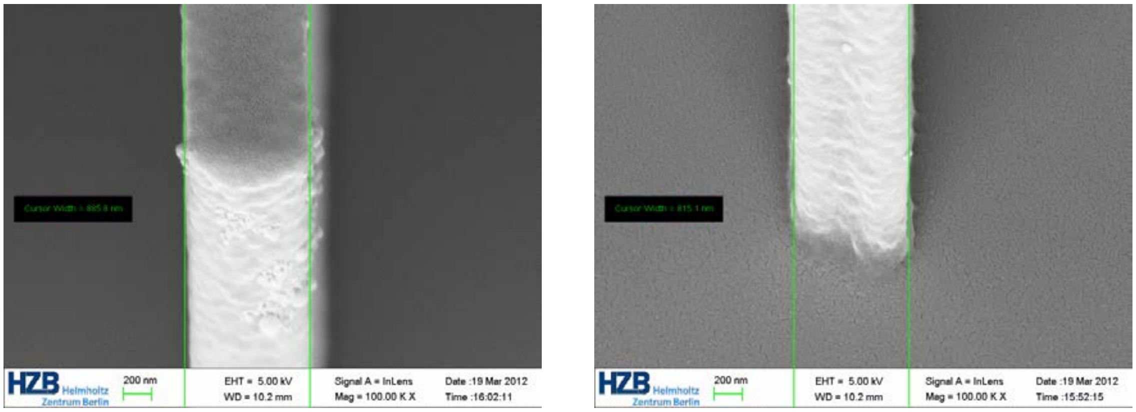
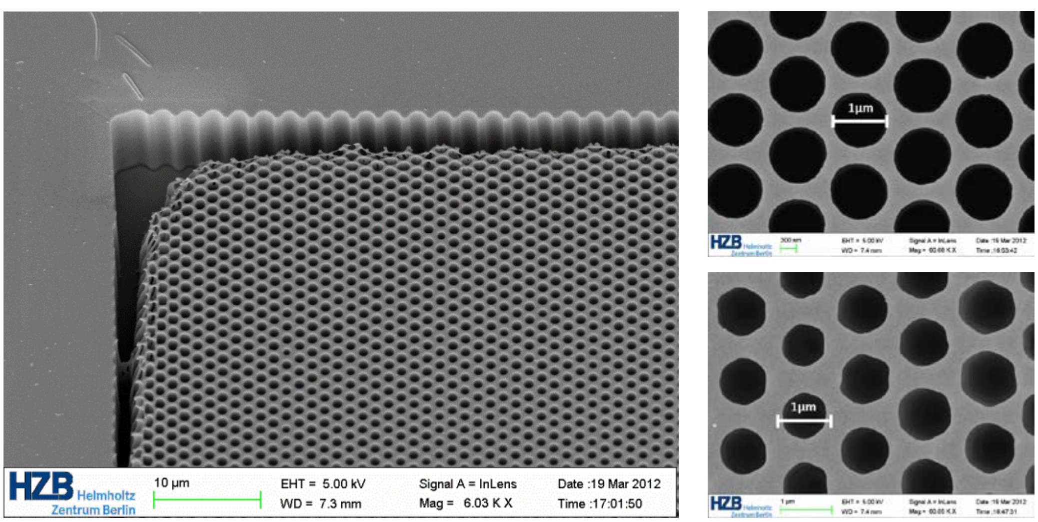


Figure 6: Measurements of line width of 10 μm tall mr-X resist structures at the top (left) and bottom (right).

Filters

Fine-pore filters were copied from another SiN mask with ~1 μm wide Au posts patterned approx. 300 nm apart. Using the standard proximity gap of ~10 μm, the posts are precisely transferred into a resist mesh of corresponding pores. Using a larger proximity gap (~100 μm) a mesh with finer pores (~ 700 nm dia.) was copied from the same mask [1]. The high stress in the cross-linked resist frame surrounding the mesh causes rupturing of the mesh in the edges indicating that it has limited strength.

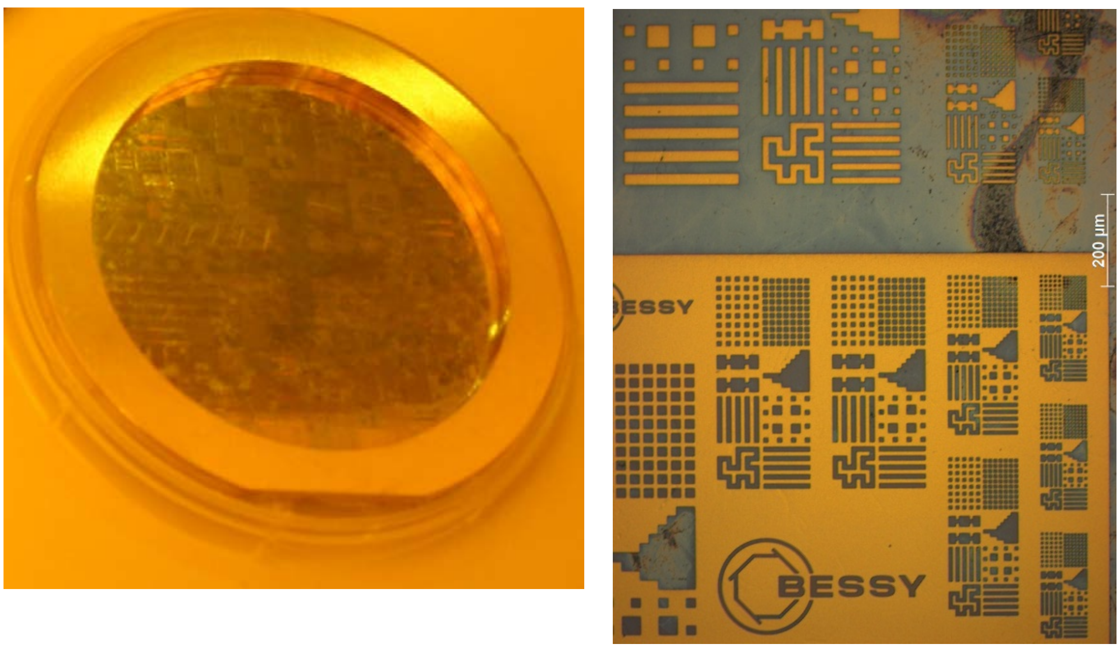


Figures 7: ~10 μm tall mr-X mesh with ~1 μm pores covering a large area of ~18 mm. The pore size was varied by changing the proximity gap between mask and resist.

Summary and future experiments

The paper introduced the readily available x-ray lithography capability at the BESSY II storage ring suitable for patterning high aspect ratio (up to 20), sub-micrometer, ~10 µm thick optical and filter structures in a new negative resist, mr-X. The SiN membrane mask technology is suitable for this process even with very thin gold absorber of ~1 µm thanks to the enhancement of the mask contrast by using a soft x-ray exposure spectrum and the high contrast of the new resist. Exposure times of only a few minutes also make this technology attractive for commercial use.

An alternative, more robust membrane material replacing the delicate SiN is Ni [20]. An example of a 2µm thick Ni membrane mask spanning a 4” steel ring is shown in Figure 8, left. The mask has been patterned by optical lithography in ~2 µm thick photo resist. The absorber patterns are about 1 µm thick with smallest features of 2 µm. In the future, this mask technique will be further optimized attempting to push the smallest feature size into the sub-micrometer range, increase gold thickness to approx. 1.2 µm, and then using these masks to conduct and optimize soft x-ray lithography processing conditions.



Figures 8: Example of a 2 µm thick Ni membrane x-ray mask patterned by optical lithography and covered with absorber structures of ~1 µm thick Au. Smallest features are 2 µm.

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