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 of ultra-precise, low and high aspect ratio micro- and nanostructures [1-5]. Research presented in this paper builds upon 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 [6]. Using a 1µm thick SiN membrane mask with a ~1µm thick Au absorber, patterns were transferred into 10µm thick resist using the soft exposure mode at the BESSY II WLS beamline. With typical exposure times of a few minutes very precise grating and filter structures can be fabricated with dimensions down to about 500nm.

Keywords: soft x-ray lithography, high aspect ratio micro and nanostructures, optical gratings, fluid filters

1 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 demonstrated. Systematic studies reported in [4,5] addressed process and limitation issues, mechanical strenght of the resist material, adhesion on various substrates, and fine-tuning of the exposure source as areas needing further improvement. Nevertheless they demonstrated the potential of this technology for high aspect ratio deep sub micron patterning of polymers with smallest features of about 300nm and resist heights up to 5µm.

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 150µm and small grating constants in the range of 2-5µm are needed. Another application is the tranfer of gratings in photo resist layers of only a few micrometer thickness using soft x-rays. The major advantage here compared to standard UV-lithography is the neglectable diffraction effect and therefore a high reproducibility of copying the original grating pattern from an x-ray mask into a resist-coated substrate.

Another interesting applications are filters for medical and environmental use. Here a combination of mechanical stability requiring thicker membrane materials and densely packed, well-defined pore sizes utilizing the imaging quality of X-ray lithography will enable applications such as capturing of circulating tumor cells [11,12] or high throughput filtering for example of bacterial samples [13]. The flexibility to adjust filter pore size to the species of interest as well as the simple use of mechanically stable, possibly 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.

This paper will primarily discuss the fabrication of HAR sub-micrometer structures into mr-X negative resist of 10µm thickness and demonstrate some first results.

2 EXPERIMENTAL

This chapter briefly describes the experimental setup at HZB/BESSY 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 ~1.5µm thick PMMA resist coated onto a 1µm thick SiN deposited onto a Si wafer, subsequent plating of ~1µm 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.

2.1 Exposure Spectra

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

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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.

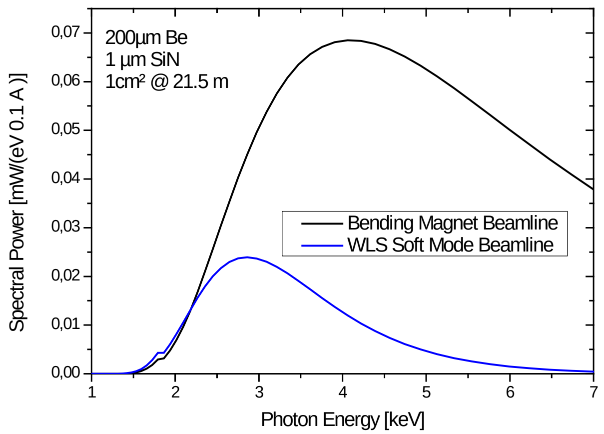


Figure 1: Spectral power distribution after beryllium window and silicon nitride membrane at soft mode versus bending magnet lithography beamline at HZB/BESSY II.

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 sufficient for the patterning task while the bending magnet with photon energies up to 15 KeV are hardly blocked by the thin gold and demand a thicker gold.

2.2 Negative mr-X Resist

Mr-X 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, for further information about mr-X). A critical sensitivity and contrast measure for negative resists is the gradation curce shown in Figure 2 for mr-X resist samples coated onto glassy carbon mask substrates and exposed at both BESSY II beamlines through an aperture stencil mask [18]. The high resist contrast is indicated for both beamlines by the jump-like change from zero to maximum resist height with 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.

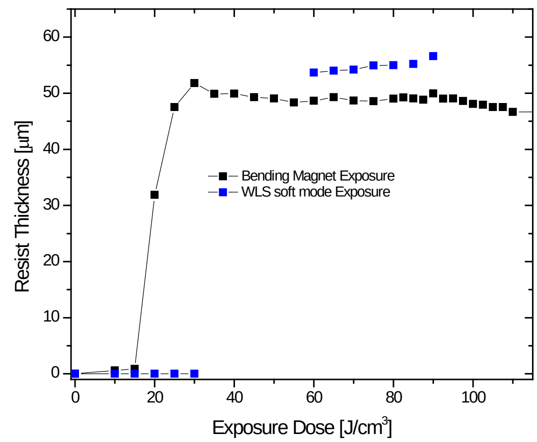


Figure 2: Gradation curve for mr-X exposed at both HZB/BESSY II lithography beamlines using glassy carbon mask substrates of 250µm thickness.

Combining low contrast SiN membrane x-ray masks with the new, high contrast negative photo resist allows 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).

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

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

3 PROCESS PARAMETERS

Samples were prepared by spin-coating 20mL of mr-X liquid resist onto silicon wafers and subsequently soft-baking at 95°C for 15min. About 10µm thick mr-X resist films with tight tolerances (± 0.3µm) 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 ~10µm 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. 5min for typical ring currents (200-250mA) and an 8cm scan range. A dose range from 60 to 120 J/cm^3 was investigated in our tests, where 90 J/cm³ is standard. Standard post exposure bake was done on a hot plate at 80°C for 20min and a slow cooling down ramp of 5°C/hr.

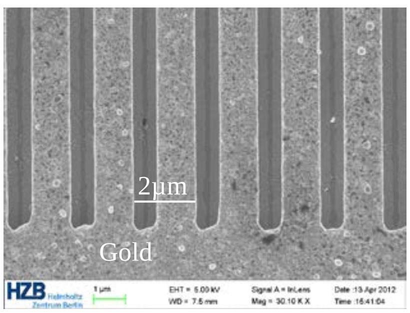
After another brief period of relaxation (~1hr) samples were developed for up to 10min in PGMEA with subsequent thorough rinse in IPA. Air and vacuum drying were tested with the vacuum drying showing negligible structure collapse and more repeatable results.

4 RESULTS

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

4.1 Gratings

Figure 3 shows an SEM image of the absorber pattern of the grating mask. The SEM pictures were taken with a LEO 1560 from Carl Zeiss SMT AG. The line width measurements on the mask reveals that the nominal 1µm equal lines and spaces are effectively ~ 1.2µm wide gold lines and ~0.8µm wide open spaces. Exposure through the open areas will result in patterned resist structure.



Figures 3: SiN mask surface. The line width varies approx. 820±70nm over the grating areas.

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.

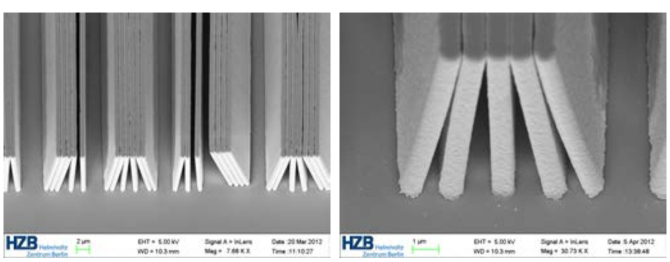


Figure 4: 10µm tall mr-X resist structures collapsing during air drying caused by large surface area, capillary forces, residues and lack of material strength [4,5].

Using a higher exposure dose (120 J/cm³), higher PEB temperature (95°C), extended development time and vacuum drying these initial problems could be resolved resulting in highest quality structures shown in Figure 5. The line width measurements for standard and optimized processes result in lines 750 to 890nm wide which is comparable to the variation of line width on the mask.

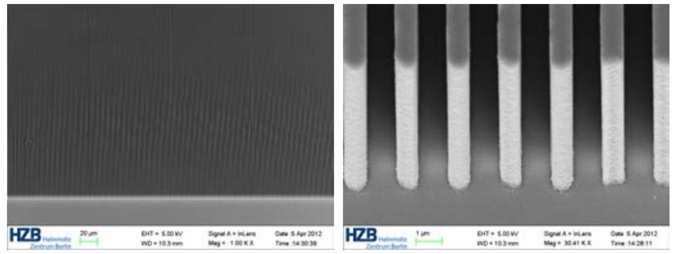


Figure 5: 10µm tall mr-X resist structures showing no collapse due to improved resist strength and process optimization.

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

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

Besides long lines and spaces also slotted lines suitable as an in-plane flow filter have been successfully patterned as illustrated in Figure 7. The indivdual wall segments demonstrate excellent adhesion, sufficient material strength, and very precise dimensional control of the X-ray lithography process..

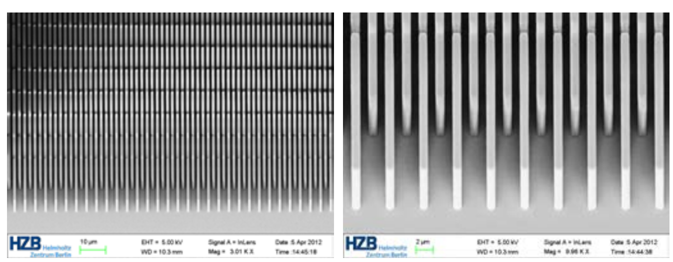
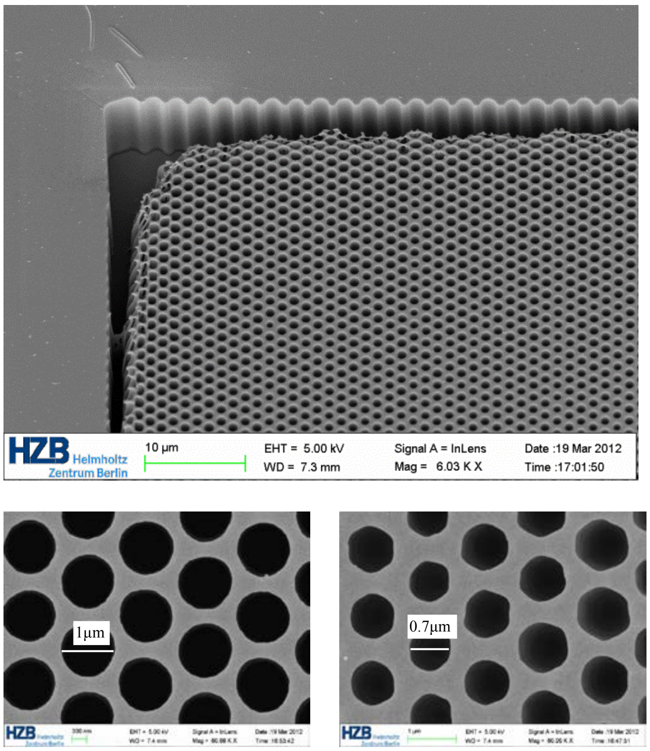


Figure 7: 10µm tall mr-X isolated structures.

4.2 Filter

Fine-pore filters were copied from another SiN mask with ~1µm wide Au posts patterned approx. 300nm apart. Using the standard proximity gap of ~10µm the posts are precisely transferred into a resist mesh of corresponding pores. Using a larger proximity gap (~100 µm) a mesh with finer pores (~ 700nm 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 only limited strength.



Figures 8: ~10µm tall mr-X mesh with ~1µm pores covering a large area of ~18mm. The pore size was varied by changing the proximity gap between mask and resist.

5 SUMMARY AND CONCLUSION

The paper introduced a readily available X-ray lithography capability at the BESSY II storage ring suitable for patterning high aspect ratio (up to 20), sub-micrometer, ~10µm 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 ~1µm thanks to the enhanced mask contrast of a soft x-ray exposure spectrum and the high contrast of the new resist. Exposure times of only a few minutes make this technology also attractive for commercial use.

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