Negative Resists for Ultra-Tall, High Aspect Ratio Microstructures

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Abstract

In this joint research project, collaborators at HZB and CAMD investigated the fabrication of ultra-tall, high-aspect ratio microstructures patterned into two new negative resists using deep X-ray lithography (DXRL). Focus of the research efforts was on sensitivity, contrast, and dimensional accuracy, all compared to PMMA -- the well-established standard resist in DXRL. Both resists showed very good dimensional accuracy with diameter variations less than 1µm over a process area of 80mm for 1mm high structures. A broad process window was demonstrated, which can be used to fine-tune the sidewall verticality as well as structure dimensions. Both resists showed overall results rivaling the structure quality of PMMA resist with a factor of 20 and higher sensitivity, making them attractive also for commercial use.

Introduction

X-ray lithography in Polymethylmethacrylate (PMMA) resist allows patterning of high resolution, high aspect ratio micro-optical and micromechanical components with extreme precision and tight tolerances [1]. While PMMA resist process and material meets the requirements for these applications, lack of sensitivity and long processing times have been an obstacle for successful commercialization. SU-8 negative resist has been researched for X-ray lithography applications since early 2000. Despite promising results it could not meet processing, repeatability and tolerance demands. In an effort to resolve these issues, new negative tone resist materials, namely mr-X from MRT GmbH, Berlin, Germany, and SUEX, from DJDevCorp, Inc., Sudbury, MA, USA have been developed and are currently being introduced into the market [2,3,4,[5]]. First results comparing the new negative resists with PMMA for the fabrication of ultra-tall high aspect ratio microstructures will be discussed.

Mr-X has been developed in the BMBF-funded INNOLIGA project [6,7,8,9]. 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 significantly higher sensitivity than PMMA. SUEX epoxy Thick Dry Film Sheets (TDFS) are made of high quality solvent-free epoxy-based resist material offering a competitive solution over liquid resist formulations. SUEX resist is utilizing an antimony-free photo acid generator (PAG) in very low concentration. The sheets are prepared under a highly controlled extrusion process, which provides uniform resist coatings between two throw-away layers of protective polyester film. Resist application is done in a simple lamination process and samples are ready for exposure within minutes as no time-consuming soft-bake is necessary [5].

Figures 1 show some typical high-aspect ratio microstructures patterned by DXRL in both resists. Vertical, straight sidewalls and good dimensional control indicate that up to 2 mm tall

structures with features down to 10µm are possible. Research efforts described in the following text provide more quantitative information on dimensions and sidewall verticality as well as sensitivity.

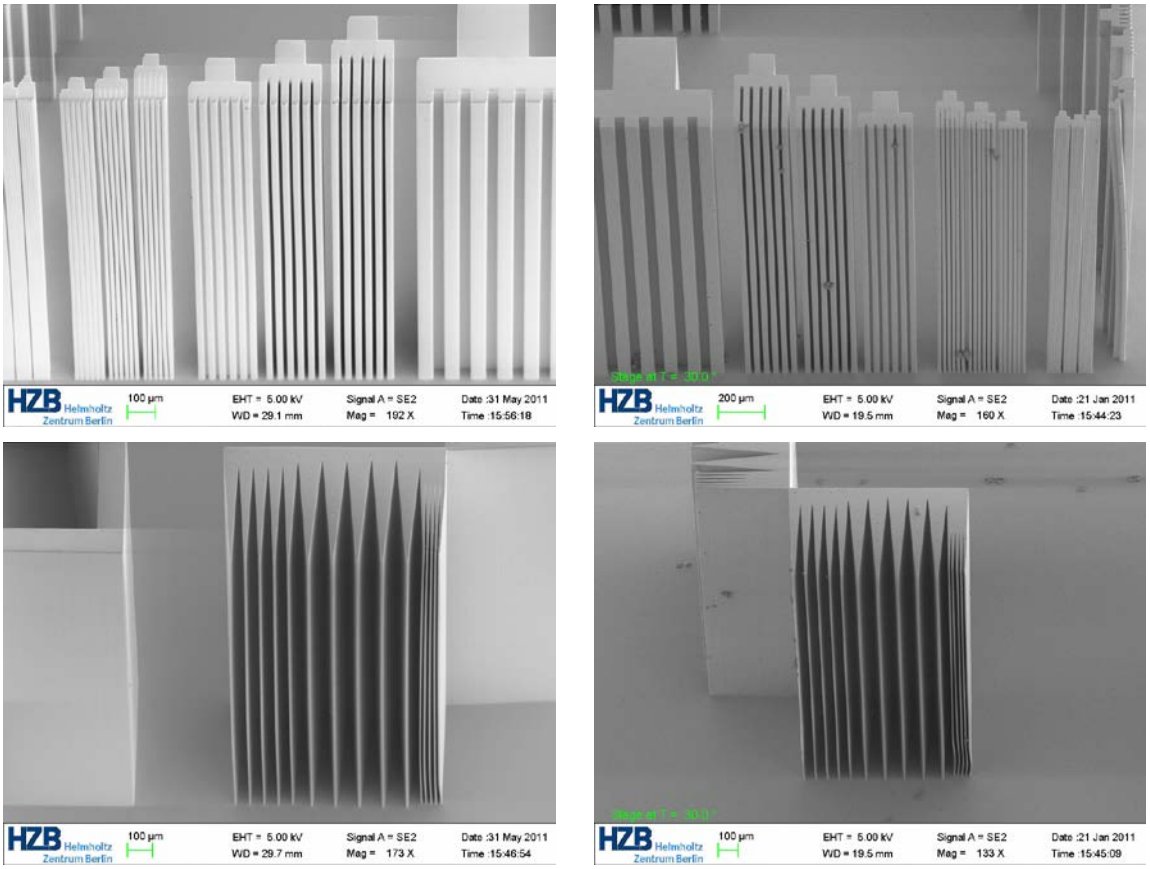

Figure 1: Finger structures (top) and jag structures (bottom) made of mr-X (left) and SUEX (right) in ~2 mm height. The exposures were performed at the BESSY II LIGA wavelength shifter beamline with a bottom dose of about 90 J/cm³ for mr-X and 180 J/cm³ for SUEX resist, respectively and exposure times of less than 10 mins for a 100 mm substrate.

Sensitivity and contrast

Sensitivity and contrast of both resists were determined by backside exposures at the BESSY II LIGA bending magnet beamline and compared to SU-8 [10,11,12]. Figure 2 shows the set-up of the exposure along with the measured height of post structures as a function of the exposure dose directly at the interface of substrate and resist.

While the sensitivity of mr-X is lowered by a buffer additive, SUEX's low sensitivity is explained by its very low PAG concentration. Both, mr-X and SUEX, have a sensitivity of 20 ± 4 and 22 ± 4 J/cm^3, respectively compared to only 2.2 ± 0.2 J/cm^3 for SU-8. While SU-8 is patterned with a typical bottom dose of 15 J/cm^3 the new resists are still a factor ~10 more sensitive than PMMA with a sensitivity of 250 J/cm^3 and typical bottom dose values of 3000 J/cm^3 [13]. SU-8 has a lower contrast of 1.7 than mr-X and SUEX with contrast values of 3.3 ± 0:1 and 3.2 ± 0.5, respectively, and both match the contrast of PMMA with a value of 3. Both resists are less sensitive to dose leakage through the X-ray mask absorber pattern and promise more stable and repeatable lithography results as process parameters can be adjusted in a fairly

wide range. The chemical composition of the mr-X and SUEX resist material is carefully controlled to ensure repeatable process performance. In case of mr-X, fluctuations in resin lots are controlled by fine-tuning the molecular weight distribution. Additionally, the use of buffer highly increases the crosslinking density and contrast. The low absorption of the antimony-free SUEX leads to a low dose gradient and, because of this, to an equally controlled crosslinking reaction of the epoxy resin over structure height.

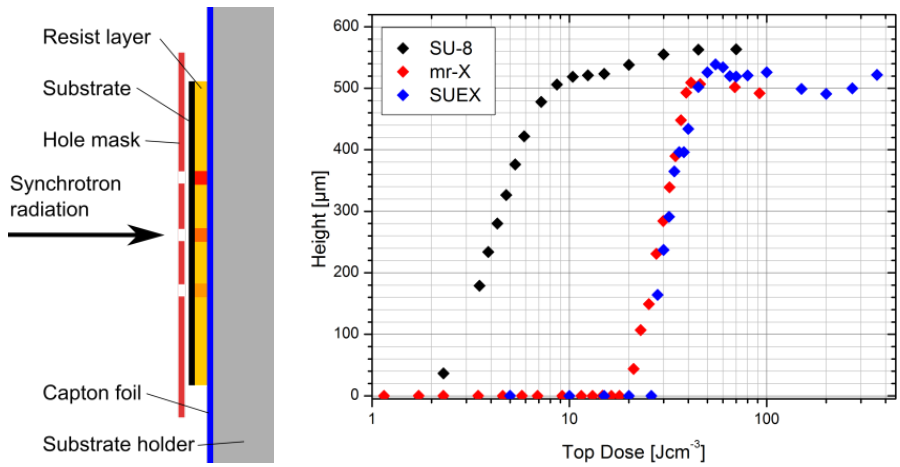

Figure 2: Set-up for gradation experiments by backside exposures (left) and gradation curves of SU-8, mr-X and SUEX obtained by exposures at the bending magnet beamline at BESSY II (right).

Dimensional accuracy

The measurement of the dimensional accuracy of high aspect ratio microstructures includes the control of absolute dimension as well as sidewall verticality. Large posts of 1 mm height were patterned in PMMA with a bottom dose of 3500 J/cm^3, in mr-X with 90 J/cm^3 and post exposure baked at 65ºC for 60 min, and in SUEX with 180 J/cm^3 and post exposure baked at 110ºC for 60 min. The post diameters were measured with a Werth fiber probe and coordinate measurement machine [14] in heights of 50, 125 and 200 µm beneath the resist surface. The nominal post diameter was measured to 1495.6 ± 0.4 µm by optical measurements of a 30 µm thin resist layer. Table 1 lists the measurement results. Within the error margin the three resists show nearly the same results.

Resist	Post diameter [µm]
PMMA	1500.2 ± 0.8
mr-X	1501.3 ± 0.9
SUEX	1501.7 ± 0.5

Table 1: Average measured post diameter compared for PMMA, mr-X and SUEX.

Both negative resists show negligible crosslinking shrinkage compared to SU-8 posts [9] with ± 0.5 %. The values across the patterned substrate area of 80 mm are comparable and well inside customer's tolerance of ± 1 µm.

The diameter of the structures can be fine-tuned by changing the process conditions. For example, three dose variations (80, 120 and 160 J/cm^3) were exposed into mr-X resist layers of

500 and 1000 µm height at the 4T wavelength shifter beamline of BESSY II. The results are shown left in Figure 3. The post diameter measurements show the expected increase with exposure dose but also a higher increase of the higher resist layer, even though the top to bottom dose ratios are comparable with 1:5 and 1:7, respectively. One explanation could be a difference in the solvent distribution over the resist height as both samples had the same overall solvent content [8]. The right graph in Figure 3 shows results of the solvent free SUEX exposures (120, 180 and 240 J/cm^3) at the bending magnet beamline. It shows a different dependence of the SUEX post diameters, where the post exposure bake (PEB) temperature determines the offset from the mask diameter. At 180 J/cm^3 the post diameter and their deviation across the substrate are minimal. Also PEB temperature has an effect on the absolute dimensions with a higher PEB temperature resulting in wider structures [8]. It should be emphasized that these are first results and that more studies are needed to determine critical parameters, such as process design bias, in order to guarantee tight absolute dimensions.

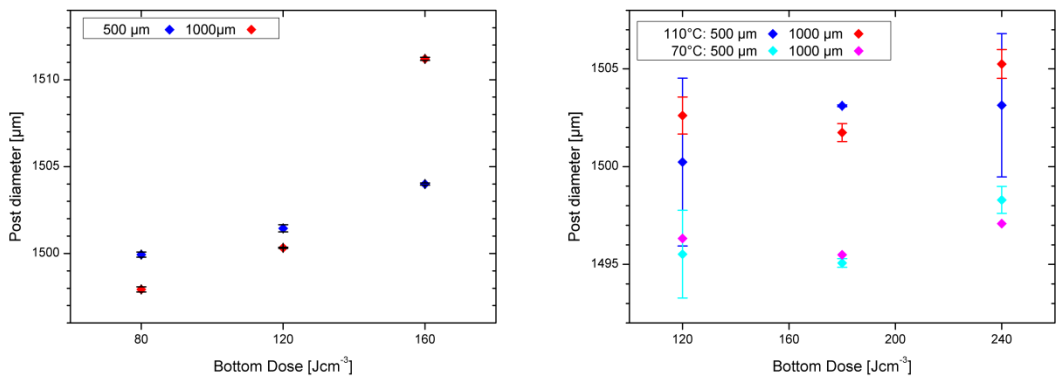

Figure 3: Change in diameter of mr-X posts with exposure dose for two layer thicknesses (left) and of SUEX posts with exposure dose for two layer thicknesses and varying post exposure bake temperatures.

Sidewall deformation

For both resists the sidewall deformation of microstructures was measured using a WYKO NT3300 white light interferometer from Veeco Instruments with a magnification of 40x [15]. The deviation from an optimal linear profile is depicted as a function of exposure dose in Figure 4 (left). In the graph on the right profiles of mr-X and SUEX are shown, which demonstrate that the sidewall bow can be adjusted with exposure dose for fixed PEB conditions [16].

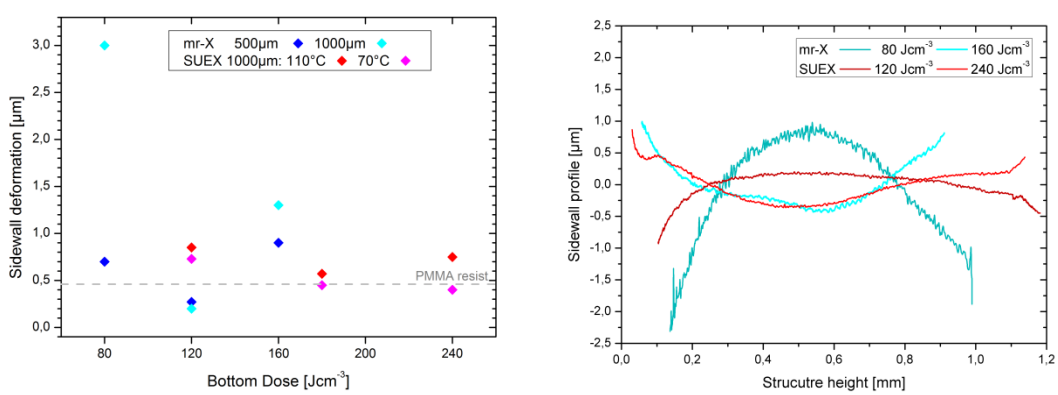

Figure 4: Sidewall deformation of mr-X and SUEX as function of exposure dose (left) and exemplary sidewall profiles for low and high exposure doses at 65ºC and 110ºC respectively (right).

The mr-X structures show a greater deviation from a linear profile than the SUEX structures. For the middle dose both resists show a sidewall verticality of 0.6 µm for 1000 µm tall structures comparable to PMMA structures of the same height. Also here more studies are needed to optimize dose, dose ratio, and PEB temperature in an effort to fabricate almost perfectly vertical sidewalls.

Summary and future potential

Both new negative resists show very good dimensional accuracy rivaling the structure quality of PMMA resist. In addition, they offer a broad process window that allows for fine-tuning of structure dimensions and sidewall profiles. Furthermore, by more carefully controlling the cross-linking reaction either with buffer or low PAG concentration, a reliable and repeatable process is guaranteed with advantages over SU-8. Despite a lower sensitivity than SU-8 both resists offer higher sensitivity than PMMA (> factor 10). Process parameter optimization will also allow making very tall structures of up to 4 mm as illustrated for mr-X in Figure 5. Posts with 120 µm diameter and 1500 µm length are shown in Figure 5, left, made by a three step exposure with a bottom dose of 90 J/cm^3. Even smaller posts with sides of 40 and 50 µm in almost 4 mm height are shown in Figure 5, right, illustrating the future potential. In this case, a higher bottom dose of 105 J/cm^3 ensured a higher degree of cross-linking and consequently a higher Young's modulus.

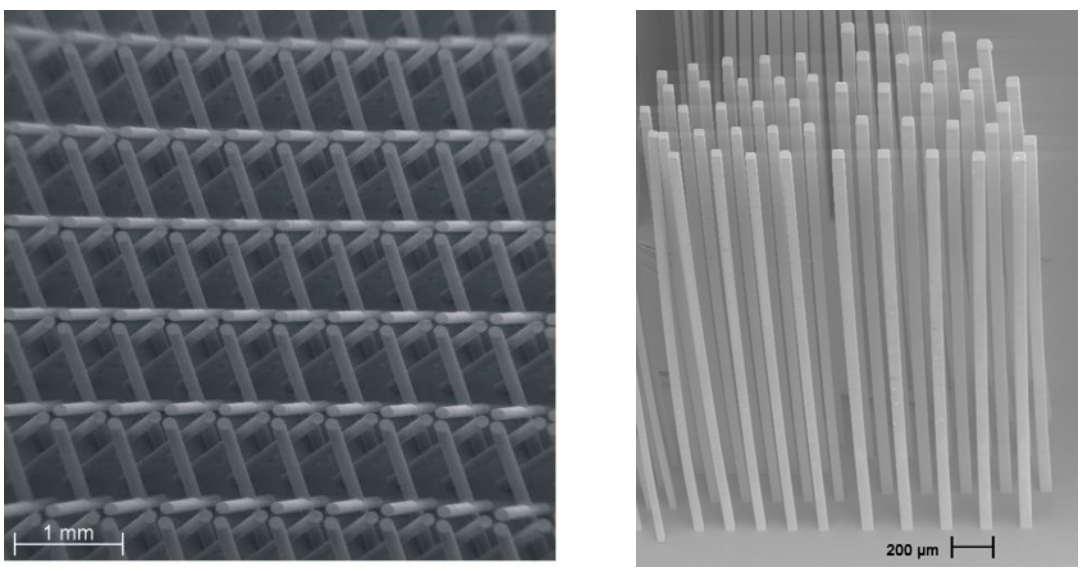

Figure 4: Three dimensional structures with 1500 µm length (left) and pillar structures with aspect ratios of 100 at a height of 3900 µm (right) made of mr-X [4].

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