Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

High-resolution and large-area nanoparticle arrays using EUV interference lithography

Waiz Karim [1, 2], *Simon Andreas Tschupp* [3], *Mehtap Oezaslan* [3, 4], *Thomas Justus Schmidt* [3, 5], *Jens Gobrecht* [1], *Jeroen Anton van Bokhoven* [2, 6, **], *Yasin Ekinci* [1, *]

[1] Laboratory for Micro and Nanotechnology, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland,

[2] Institute for Chemical and Bioengineering, ETH Zurich, Switzerland

[3] Electrochemistry Laboratory, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland

[4] Department of Chemistry, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg Germany

[5] Laboratory of Physical Chemistry, ETH Zurich, Switzerland

[6] Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland

Corresponding authors:

[*] yasin.ekinci@psi.ch, [**] jeroen.vanbokhoven@chem.ethz.ch

S1: Multiple-beam EUV interference lithography using HSQ gratings with footing

Mask fabricated using the footing strategy and employing interference of four beams have a set four gratings arranged in a manner so that an interference pattern of their first-order diffraction is obtained between the gratings. The interference pattern produces patterns with hole and dot arrays on EUV exposure at different dosage. This mask fabrication strategy requires only a single EBL step and simplifies the mask making process. Fabrication of transmission mask using the footing strategy was done on the Si_3N_4 membranes with a thermally evaporated Cr/Au/Cr layer multilayer. A 250-nm-thick HSQ resist was spin-coated on this membrane. This targeted resist thickness leads to the highest diffraction efficiency of HSQ material according to our calculations (see Fig. 2). Linear gratings were written on the resist using EBL which was followed by development of the resist using the method described earlier. Reactive ion etching using chlorine gas was then performed to remove the last Cr layer, which is followed by electroplating a 120-nm-thick nickel layer as photon stop on the base Au layer. In order to prevent electroplating of nickel in between the gratings, a much thinner HSQ footing layer was also written between the HSQ gratings during the EBL process. Fig. S1 (a) shows the SEM image of the resulting large-area transmission mask with four linear gratings. The SEM image in Fig. S1 (b), at higher magnification, shows the HSQ gratings with a period of 400 nm along with the HSQ footing layer. This strategy avoids patterns collapse and increases the yield of fabrication substantially.

EUV exposure was performed with this mask and the patterns were recorded on silicon wafers spin-coated with HSQ resist. Fig. S1 (c) to Fig. S1 (f) show the SEM images of the obtained patterns at a low dose which results in dot arrays and the exposure at high dose gives hole arrays. The generated patterns were uniform over an area of 1-2 μm^2 but suffered from substantial inhomogeneity over larger area. The shape and size of the dots in Fig. S1 (c) and hole in Fig. S1 (e) vary substantially across the exposed field. We attribute this inhomogeneity to the fact that the HSQ gratings are vulnerable to thickness variations which arise during HSQ spin coating. In addition, even minor errors in the alignment of the membranes during EBL writing of HSQ grating and HSQ footing changes the thickness of HSQ layers, each with a 400×400 μm^2 area. Since the diffraction efficiency is not constant in the vicinity of 250 nm thickness (as seen in Fig. 2), these small variations in the thickness of HSQ gratings results in substantial inhomogeneity on EUV exposures which is much more dominant for large exposure area. Uneven attenuation and diffraction from the gratings in the mask can also be validated in the zeroth order diffraction patterns (i.e. non-interfering transmitted light through the gratings) as seen in Fig. S1 (d) and Fig. S1 (f).

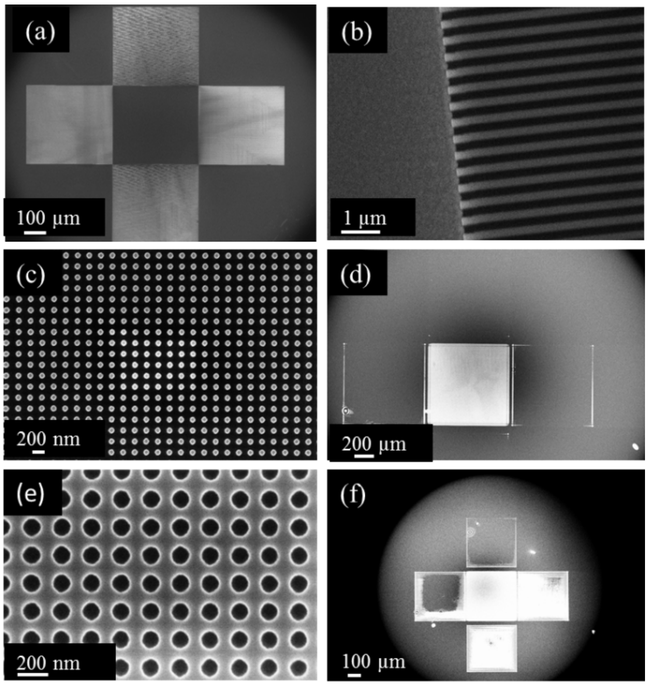

Fig. S1. (a) SEM image, at low magnification, of a 4-beam mask on a 100-nm-thick Si_3N_4 membranes fabricated using EBL and footing strategy. Each of the four gratings are spread over 400 × 400 μm^2. (b) SEM image, at high magnification, shows the HSQ grating with 400 nm period. HSQ lines are 250 nm thick and has a thin HSQ footing layer in between the lines while the area outside the gratings has electroplated nickel as photon stop. (c)-(f) shows SEM results of EUV exposure using this mask. (c) and (e) shows SEM image of the EUV exposure results at low and high dose respectively . Patterning is uniform for an area of 1-2 μm^2 area but non-uniformity over large area. (d) and (f) shows the corresponding zeroth order diffraction patterns at low and high dose. Inhomogenity of exposure patterns is clearly seen over a 400 × 400 μm^2 which results in disparity of particle sizes.

S2: EUV-IL using ATL with HSQ gratings

2D gratings such as holes arrays are required in transmission masks for ATL to produce dot arrays for a negative resist such as HSQ. We first employed a strategy to write hole-arrays over an area of 500 × 500 μm^2 in HSQ resist and use this directly as masks. Since HSQ is a negative tone resist, this involves large EBL writing time and is a low throughput process for mask fabrication but, on the other hand, involves no further fabrication step which increases the yield of fabrication. The periodicity of hole-arrays in the transmission mask was 300 nm which resulted in EUV exposure results seen in Fig. S2. The substrate was placed in the achromatic Talbot regime at a distance of 1.5 mm away from the mask and we observed 40 nm dot arrays with a periodicity of 212 nm at a low exposure dose. The resulting patterns were extremely non-uniform and this is attributed to the inhomogeneous thickness of spin-coated HSQ and thereby varying thickness of gratings, which leads to fluctuations in diffraction efficiency over such large area (Fig. 2). This observation is in accordance with the EUV exposure results obtained by using the four-beam masks with HSQ footing (Fig. S1).

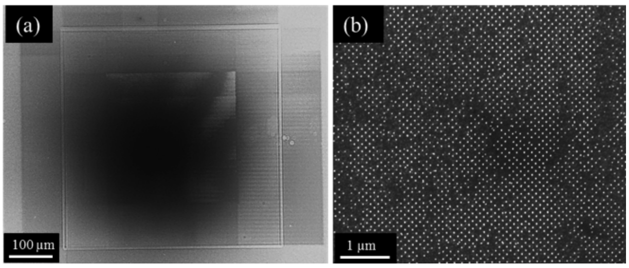

Fig. S2. (a) SEM image of EUV exposure results using transmission masks with hole-arrays in HSQ for patterning 500 × 500 μm^2 large area. (b) SEM image at higher magnification shows 40 nm dots arrays but high non-uniformity in the patterns is clearly visible in both images.