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Dense high aspect ratio hydrogen silsesquioxane nanostructures by 100 keV electron beam lithography

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Abstract
We investigated the fabrication of dense, high aspect ratio hydrogen silsesquioxane (HSQ) nanostructures by 100 keV electron beam lithography. The samples were developed using a high contrast developer and supercritically dried in carbon dioxide. Dense gratings with line widths down to 25 nm were patterned in 500 nm-thick resist layers and semi-dense gratings with line widths down to 10 nm (40 nm pitch) were patterned in 250 nm-thick resist layers. The dense HSQ nanostructures were used as molds for gold electrodeposition, and the semi-dense HSQ gratings were iridium-coated by atomic layer deposition. We used these methods to produce Fresnel zone plates with extreme aspect ratio for scanning transmission x-ray microscopy that showed excellent performance at 1.0 keV photon energy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The fabrication of sub-100 nm structures with high aspect ratio is of interest for many nanotechnological applications such as x-ray diffractive optical elements [1] or nanoelectromechanical systems [2] (NEMS). To date, hydrogen silsesquioxane (HSQ) has proven to be an excellent negative tone resist for high resolution electron beam lithography [3] (EBL). HSQ resist also exhibits a high etch resistance [4], and can be used as a mold for nanoimprinting [5] or electroplating [6–8]. Sub-10 nm features have been patterned in HSQ resist by state-of-the-art EBL tools and high contrast development processes [9–12]. However, these high resolution patterns have only been obtained in very thin HSQ resist layers, typically in thicknesses below 50 nm. When exposing thicker HSQ resist layers, it has been shown that the use of the supercritical drying benefits the fabrication of high aspect ratio structures [13], by preventing collapse caused by the surface tension of the liquid trapped in the pattern. Nevertheless, the preparation of dense high aspect ratio patterns in HSQ resist remains challenging, and has not yet been thoroughly investigated.

Here, we report on the fabrication of dense and semi-dense high aspect ratio HSQ gratings with line widths down to 10 nm in resist layer thicknesses ranging from 250 to 500 nm by combining a 100 keV EBL tool and supercritical drying. Some HSQ resist nanostructures were later used as molds for gold (Au) electrodeposition or coated with iridium (Ir) by atomic layer deposition (ALD), in order to fabricate x-ray diffractive lenses, namely Fresnel zone plates. While the Au electroplating created a negative image of the pattern by filling the empty spaces in the HSQ mold, the Ir-coating by ALD was used as a top-down approach to reduce the pattern dimensions by a conformal deposition onto the sidewalls of the HSQ template [14, 15]. The focusing properties of these optical elements were tested in a scanning transmission x-ray microscope at 1.0 keV photon energy and they demonstrated an excellent performance in terms of spatial resolution by resolving 15 nm-wide features.

2. Experimental methods

The resist layers were prepared from a commercial HSQ solution (FOx-14 Flowable Oxide, Dow Corning). Prior to the EBL exposure, the silicon (Si) chips and the 200 nm-thick silicon nitride (Si_3N_4) membranes were baked for 5 min at

180 °C, to remove any residual moisture. Then, the samples were spin-coated at 1000 and 4000 rpm for 60 s, to obtain resist layer thicknesses of 500 and 250 nm, respectively. The HSQ layers were not baked to get the highest contrast during the EBL exposure and development[3]. The substrates intended for Au electrodeposition were coated with a plating seed layer consisting of 5 nm chromium (Cr) and 20 nm of Au before the spin-coating step. While developed HSQ nanostructures have good adhesion on bare Si and Si_3N_4 substrates, their adhesion to Au is poor [16]. The exposed HSQ patterns on Au were often washed away during immersion in the developer. To regain good adhesion of HSQ on the metallized substrates, a 5 nm layer of Cr was deposited on the Au layer.

The EBL exposures were performed with a Vistec EBPG5000 plus tool at 100 keV electron energy, a 400 μm aperture, a beam current of 500 pA and an estimated Gaussian spot size of 10 nm. Patterns consisting of gratings with periods ranging from 200 down to 40 nm were exposed. We prepared ordinary gratings with equal line widths and spaces (duty cycle of 0.5) and semi-dense gratings in which the line width was one quarter of the period (duty cycle of 0.25). In addition, Fresnel zone plate patterns with diameters of 100 and 240 μm were also exposed. They consisted of circular diffractive transmission gratings with a radially increasing line density. The optimal dose was empirically determined for every line width and period. A dose of approximately 5000 $\mu C\ cm^{-2}$ was necessary for the exposure on bulk Si, whereas the value had to be increased by almost a factor of two (to roughly 9000 $\mu C\ cm^{-2}$) when exposing HSQ layers on the 200 nm-thick Si_3N_4 membranes, due to the lack of the backscattered electron dose.

The samples were developed for 4 min in a NaOH buffered solution made of 1:3 of MICROPOSIT™ 351 developer (Rohm and Hass) and water. They were rinsed in water and kept immersed in isopropyl alcohol (IPA). To prevent the collapse of the high aspect ratio structures during drying due to the capillarity forces, the samples were supercritically dried [13] in carbon dioxide (CO_2). They were immersed in IPA into the critical point dryer chamber that was then closed and sealed at an initial temperature of 10 °C. The chamber was filled with liquid CO_2 at high pressure (50 atm). Using the exhaust outlet, the chamber was cyclically purged and refilled with CO_2 until there was no IPA left. Then, the temperature and pressure were raised to 35 °C and 100 atm; well above the critical point of the CO_2 (72.8 atm at 31.1 °C). During the final step, the chamber was slowly depressurized keeping the temperature constant at 35 °C. As a result, the HSQ structures were dried in a liquid–gas interface free environment.

After the drying step, the high aspect ratio HSQ structures were used as molds to fabricate the functional metallic x-ray diffractive optical elements. The metal structures were either grown by Au electrodeposition or coated by ALD of Ir. The Au electroplating was performed in a cyanide-based plating bath at a current density of 2.5 $mA\ cm^{-2}$. After the electrodeposition step, the HSQ mold was removed by hydrofluoric acid (HF). The ALD was used to create a highly conformal iridium thin film using the high aspect ratio HSQ structures as a template. The ALD was performed with a F120 reactor (ASM Microchemistry Ltd, Finland) using $Ir(acac)_3$ (acac=2,4-pentanedione) and O_2 as precursors at 300 °C. The pressure in the reactor was below 10 mbar, the evaporation temperature of iridium precursor was 155 °C and the O_2 flow was around 10 sccm. Further details of the iridium ALD technique are described elsewhere [17].

3. Results and discussion

For the preparation of high aspect ratio HSQ nanostructures, the use of a 100 keV EBL tool was crucial. The very small electron beam spot size of about 10 nm had to be combined with the ability of high energy electrons to penetrate deep into resist layers with very little forward scattering. The benefits of 100 keV EBL for high aspect ratio structures have already been investigated for PMMA resist [18], where gratings with periods down to 110 nm were successfully patterned in 1.1 μm-thick layers. Here, we had the goal of creating high aspect ratio structures with periods well below 100 nm. HSQ resist was a favorable candidate due to its higher stiffness, thermal stability and higher EBL resolution capabilities compared to PMMA.

Figure 1 shows scanning electron microscopy (SEM) pictures of 50 nm lines and spaces (L/S) in a 350 nm-thick HSQ layer. Figure 1(a) illustrates a major problem that occurs after the development, if the resist is dried by a conventional N_2 blow on high aspect ratio structures. The surface tension of the liquid trapped between adjacent lines causes their collapse. Whenever compatible with the final application of the structures, the collapse can be avoided by inserting connecting links or 'buttresses' into the original pattern [19]. The stabilizing effect of buttressing on the lines is demonstrated in figure 1(b). In both cases, the exposure was performed on bulk Si with an electron dose of 5500 $\mu C\ cm^{-2}$.

A further improvement to prevent the collapse of the high aspect ratio HSQ structures is the use of supercritical drying after the development [13]. The advantages of using supercritical drying are illustrated in figure 2. Low magnification SEM images of two exposures performed with identical EBL exposure and development parameters are shown. Patterns with L/S of 50, 40, 30, 25 nm were exposed in a 380 nm-thick resist layer. Whereas the sample in figure 2(a) was blow-dried in N_2, the sample in figure 2(b) was supercritically dried in CO_2. The HSQ lines in the latter case did not collapse and the profit of supercritical drying for dense high aspect ratio structures is evident.

We also explored the feasibility of patterning high aspect ratio structures with sub-100 nm periods in 550 nm-thick HSQ layers. In this case, we investigated the actual resulting line width as a function of the line width in the designed EBL pattern. Following a similar approach described in [18], we estimated a line width broadening during the EBL exposure of about 10 nm compared to the line width intended in the pattern design. To compensate this effect, 10 nm-thinner lines were exposed to obtain the appropriate final line width, at the expense of a higher exposure dose. Figure 3 shows gratings

[3] Thermal treatment of the HSQ resist favors the same transition at the molecular level occurring during the EBL exposure from cage to network structure [3].

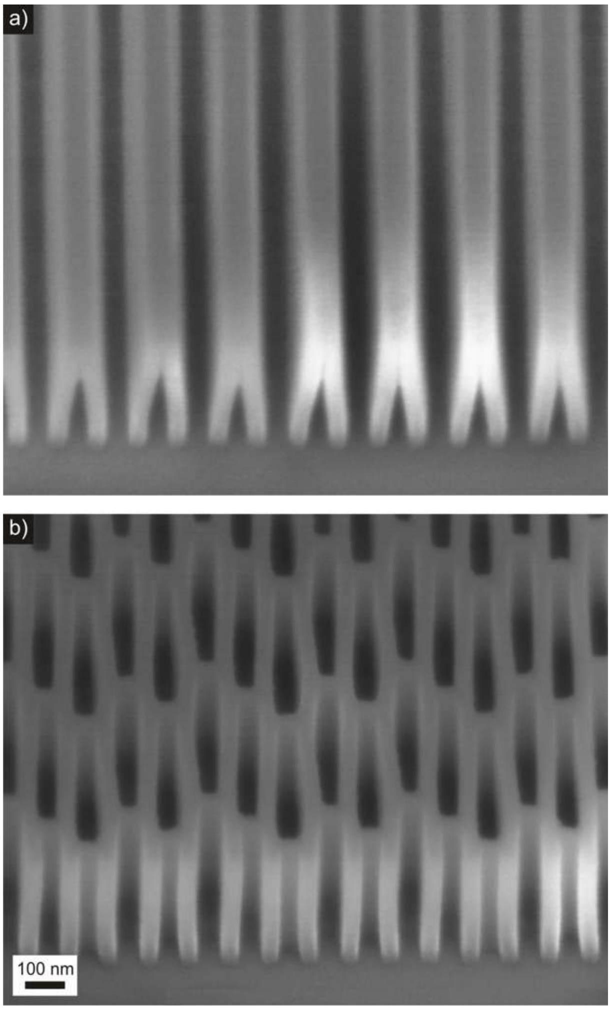

Figure 1. Gratings consisting of 50 nm L/S in a 350 nm-thick HSQ layer exposed by 100 keV EBL. (a) Collapse of dense high aspect ratio structures due to surface tension of liquid trapped in contiguous lines during the development drying process by ordinary N_2 blow. (b) By buttressing adjacent lines the collapse of the pattern can be prevented. The SEM images were acquired at a tilt angle of 45°.

with periods of 80, 60 and 50 nm. All the structures were patterned with buttresses and the samples were supercritically dried in CO_2. While dense gratings in figure 3 exhibit duty cycles close to 0.5, semi-dense gratings have duty cycles closer to 0.25. The aspect ratio of the 25 nm L/S is clearly above 20 and it demonstrates the outstanding benefits of combining high energy EBL, structure buttressing and the supercritical drying for HSQ resist.

Figure 4 shows top view SEM images of semi-dense gratings of periods of 60, 50 and 40 nm with a duty cycle of about 0.25. These patterns were exposed in 250 nm-thick resist layers. The separation of the buttresses was optimized to avoid the collapse of adjacent lines. An optimum buttress spacing was found to be roughly ten times the line width. The 10 nm-wide lines in figure 4(c) have an aspect ratio of 25, and can be used as a template for Ir-coating by ALD to achieve 20 nm period (duty cycle of 0.5) in the metallic structures. According to our experience, lines thinner than 10 nm are not stiff enough to be patterned in 250 nm-thick resist layers with this approach.

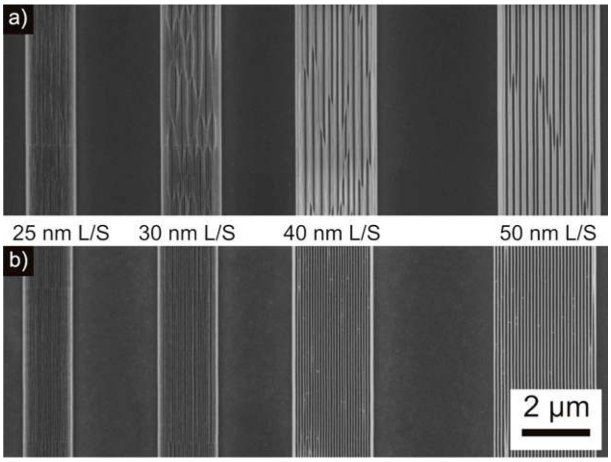

Figure 2. Top view at low magnification images of HSQ gratings with L/S of 50, 40, 30 and 25 nm in a 380 nm-thick HSQ layer. Samples in (a) and (b) were processed identically except for sample (b) which was supercritically dried. Clearly, structures in (b) did not collapse as structures in (a).

In particular, we used the high aspect ratio HSQ nanostructures to prepare x-ray diffractive optical elements. In a Fresnel zone plate, the outermost zone width determines the ultimate resolution that can be reached by the x-ray microscope, and it should therefore be as small as possible. Its diffraction efficiency depends on the material and height of the structures. As Au is a suitable material we used the HSQ structures as Au electrodeposition molds in a first approach. In the soft x-ray energy range, between 0.3 and 1.0 keV, an optimal diffraction efficiency is obtained by Au thicknesses between 120 and 180 nm. Thus, HSQ molds with a thickness of 150 nm were patterned, and a thickness of 140 nm of Au was grown by electroplating. Figure 5(a) shows a resulting 240 μm diameter Au Fresnel zone plate with an outermost zone width of 30 nm. Figures 5(b) and (c) show the 30 nm L/S before and after the removal of the HSQ mold in HF. The cracks observed in (b) are due to electron beam damage and appeared only during the SEM inspection.

In order to realize Fresnel zone plates with even smaller outermost zone widths (<20 nm), we used a second approach, similar to that introduced in our previous works [14, 15]. This method resembles the so-called iterated spacer lithography [20, 21] and relies on the deposition of the Fresnel zone plate material onto the sidewalls of a prepatterned template structure by ALD. This results in a doubling of the effective line density. The template consist of only half the final line structure, and the patterning of semi-dense gratings is specially interesting for this purpose. In the past, we have used templates made of Si [14, 15], but here we have directly used the high aspect ratio HSQ molds. Figure 6 illustrates the fabrication method of the zone-doubling approach. After the 100 keV EBL on a 300 nm-thick layer of HSQ resist and development with supercritical drying, the HSQ template structures were Ir-coated by ALD.

Figure 7 shows a 100 μm diameter Fresnel zone plate with an outermost zone width of 15 nm pattern fabricated by the zone-doubling technique. Figures 7(b) and (c) demonstrate the

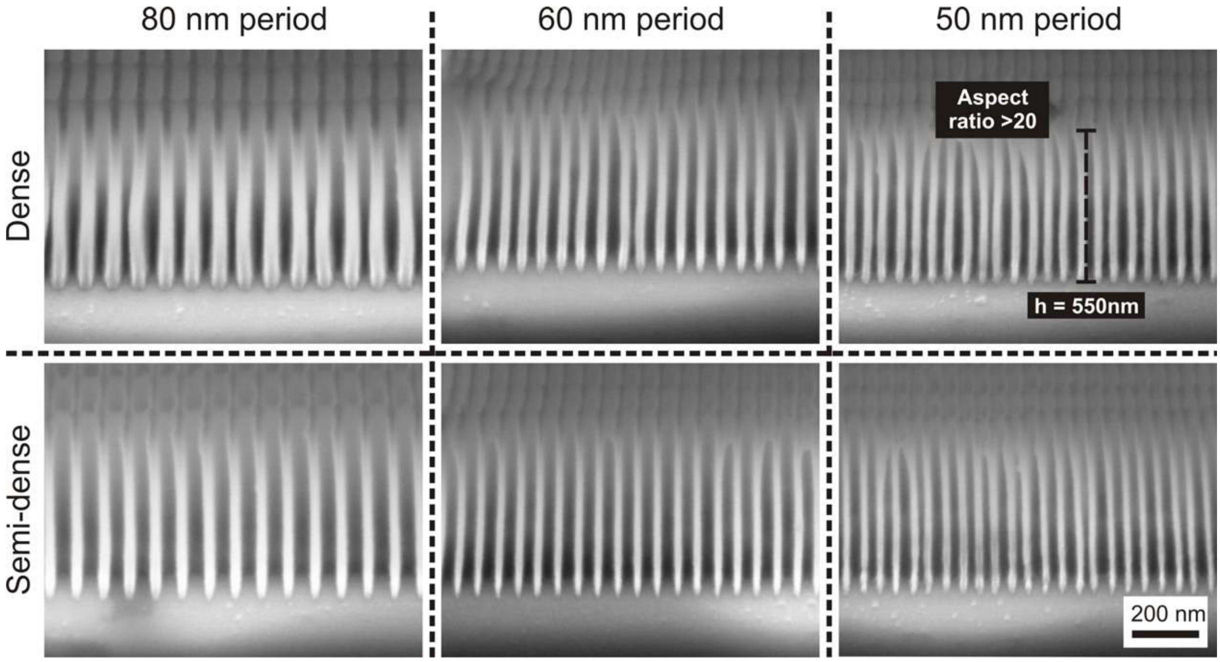

Figure 3. Dense and semi-dense high aspect ratio HSQ gratings in a 550 nm-thick layer of resist with periods of 80, 60 and 50 nm. The aspect ratio is above 20 for the 25 nm L/S. The SEM images were acquired at a tilt angle of 50°.

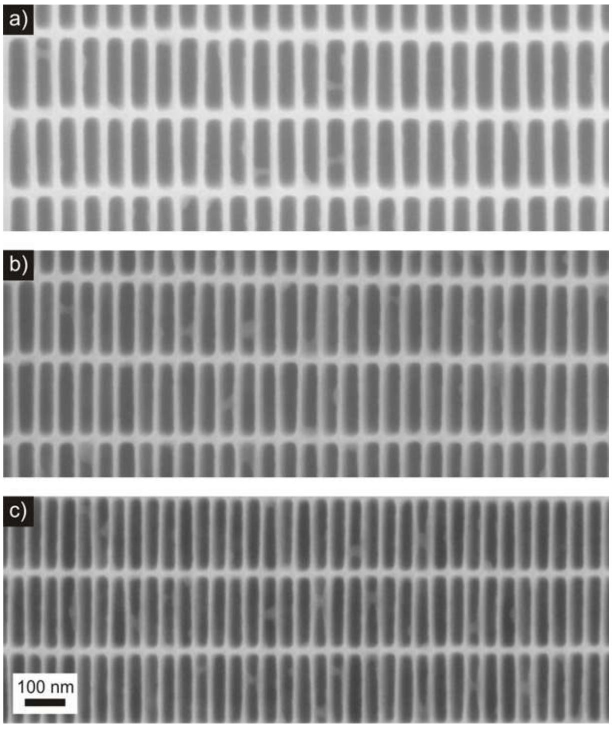

Figure 4. Top view of semi-dense HSQ gratings in a 250 nm-thick resist layer. (a) 15 nm-wide lines in a 60 nm period, (b) 12 nm-wide lines in a 50 nm period and (c) 10 nm-wide lines in a 40 nm period.

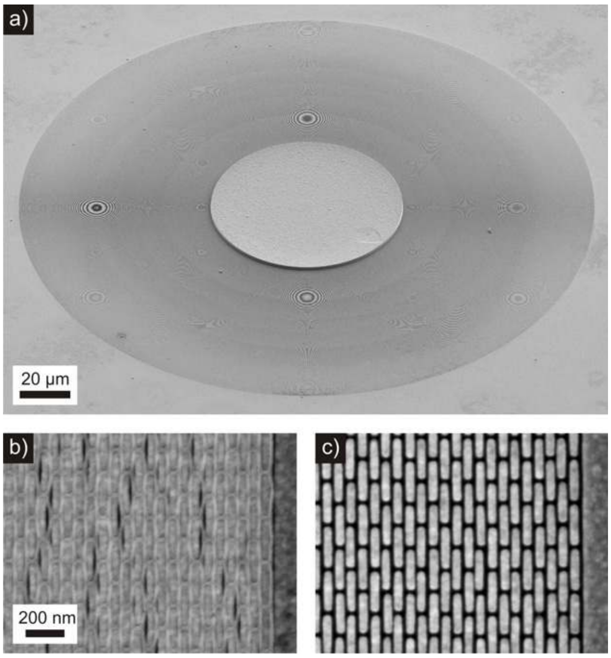

Figure 5. Fresnel zone plate made of Au using a 150 nm-thick HSQ patterned layer as electroplating mold. (a) SEM overview of the element that has a diameter of 240 μm and an outermost zone width of 30 nm. (b) and (c) are showing high magnification of the outermost area of the Fresnel zone plate with 30 nm L/S before and after the removal of the HSQ mold in HF.

excellent accuracy of the Ir thin film deposited by ALD. The images show exactly the same area at the outermost region of the Fresnel zone plate with 15 nm lines and a period of 60 nm in the HSQ template, before and after the Ir-coating. The ALD step was conformally covering the sidewalls of the HSQ template with a metallic thin film, producing a zone-doubled Ir structure of 15 nm L/S. To preserve the mechanical stability of the HSQ lines in a circular pattern such as a Fresnel zone plate, the density of the buttressing was discretely increased as

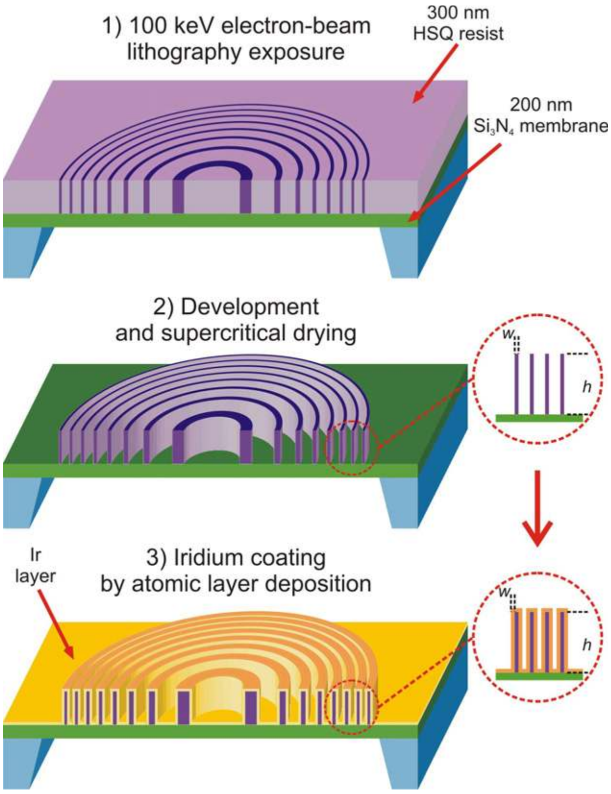

Figure 6. Steps in the fabrication of the zone-double Fresnel zone plate using an HSQ template: (1) the 100 keV EBL on 300 nm-thick HSQ layer, (2) development and supercritical drying and (3) Ir-coating by ALD. Note that line density is doubled between steps (2) and (3) at the outer regions of the Fresnel zone plate pattern.

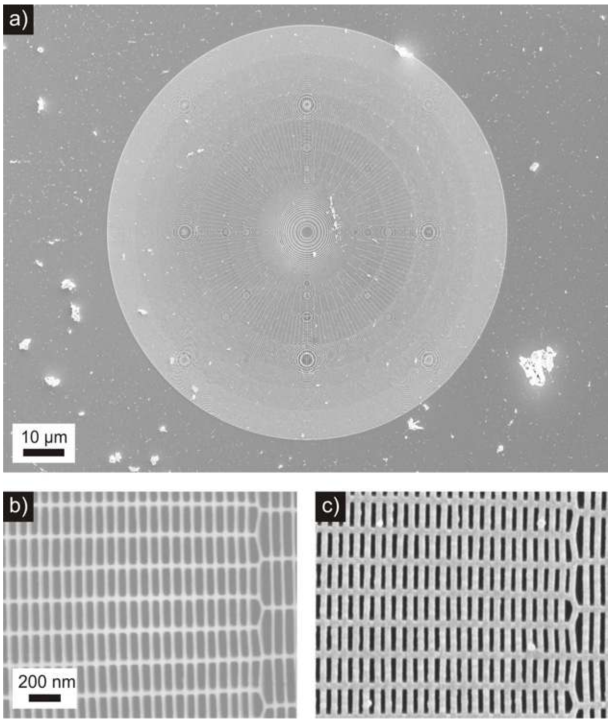

Figure 7. Zone-doubled Fresnel zone plate made of Ir by coating an HSQ resist template. (a) SEM overview of the structure that has a diameter of 100 μm and an outermost zone width of 15 nm. (b) and (c) show high magnification SEM pictures of the outermost region before and after the coating of Ir by ALD. The resulting structure contains an effective Ir grating made of 15 nm L/S.

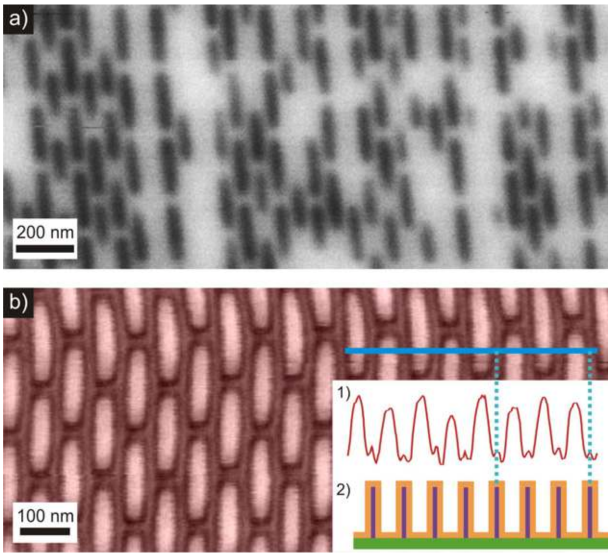

Figure 8. STXM images using the Fresnel zone plates shown in figures 5 and 7. (a) STXM of the Au test sample with 30 nm L/S by using an Au Fresnel zone plate with 30 nm outermost zone width at 1.0 keV photon energy. (b) STXM of an Ir/HSQ zone-doubled grating with 15 nm L/S. The image was acquired while focusing the Ir/HSQ Fresnel zone plate with a 15 nm outermost zone width at 1.0 keV photon energy. The thin Ir layer (dark) can be seen at the edges of the HSQ line.

a function of the radius. The defective wavy line on the right side of figures 7(b) and (c) is a consequence of the change in the buttressing density and the pulling force exerted by contiguous lines. A few defective lines, however, do not impair the overall quality of the Fresnel zone plate.

To evaluate the performance of the fabricated optics, the Fresnel zone plates were tested by scanning transmission x-ray microscopy (STXM) at the PolLux beamline [22] of the Swiss Light Source (Villigen, Switzerland). In such an experimental station, the Fresnel zone plates are used to focus the x-ray radiation to a tiny spot on the sample. Then, the sample is raster scanned while the transmitted radiation is recorded by a photodiode detector. Thus, our fabricated elements were mounted as the focusing optics of the experimental setup. The energy of the x-rays was set to 1.0 keV. The first inspected sample consisted of structures made of Au with a period of 60 nm. Figure 8(a) shows an STXM image obtained by using the Au Fresnel zone plate with a diameter of 240 μm and an outermost zone width of 30 nm from figure 5. The Au lines and the gaps are resolved, demonstrating the good performance of the fabricated lens. The image was acquired by scanning the sample with a step size of 5 nm and a dwell time of 20 ms.

Finally, figure 8(b) exhibits an STXM image acquired using the zone-doubled Fresnel zone plate made of Ir/HSQ with a diameter of 100 μm and an outermost zone width of 15 nm from figure 7. In this case, a zone-doubled grating with a template period of 60 nm and Ir-coating of about 15 nm was used as the test sample, as depicted in the inset (2). Step size in the STXM image was set to 3 nm, with a dwell time of 60 ms. The HSQ template structures in the sample were indeed slightly thinner than 15 nm in width. As demonstrated in the inset (1), showing the corresponding intensity profile along the light blue segment, the buried HSQ lines are visible[4]. Hence, we were able to resolve the sub-15 nm lines using the Ir/HSQ Fresnel zone plate. Further and throughout characterization of the spatial resolution and diffraction efficiency of these lenses will be published elsewhere.

The zone-doubling technique using the high aspect ratio HSQ templates is specially significant in terms of reproducibility and the high fabrication yield. To date and due to limitations on the nanofabrication of Fresnel zone plates with the outermost zone smaller than 25 nm, soft x-ray microscopes are currently operating at a spatial resolution of 30–25 nm. Sub-20 nm features have been resolved in a reduced number of cases [15, 23, 24]. We believe that the approach introduced here using the high aspect ratio HSQ structures in combination with ALD represents a significant step forward for soft x-ray microscopy as it allows for 15 nm spatial resolution to become standard operation.

4. Conclusions

HSQ resist is a very promising material for the fabrication of a large variety of nanostructures by EBL. The fabrication of sub-100 nm structures with high aspect ratio is of interest for many nanotechnological applications. Here, we have investigated the feasibility of using 100 keV EBL to directly expose high aspect ratio structures in thick HSQ resist. We combined the high energy EBL with supercritical point drying to successfully prevent the collapse of the structures during development. We have produced extremely high aspect ratio structures ($>$20) in HSQ resist layers, in particular, 25 nm L/S have been patterned in 550 nm-thick layers. We applied this method to produce high quality x-ray diffractive optics, which demonstrated an excellent performance in a scanning transmission x-ray microscope, by resolving structures of 15 nm line width.

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[4] The shallow peaks arise due to higher transmission through the buried HSQ lines in comparison to the highly absorbing Ir-coating.