

HSQ Double Patterning Process for 12 nm Resolution X-Ray Zone Plates

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Abstract

Soft x-ray zone plate microscopy is a powerful nano-analytic technique used for a wide variety of scientific and technological studies. Pushing its spatial resolution to 10 nm and below is highly desired and feasible due to the short wavelength of soft x-rays. Instruments using Fresnel zone plate lenses achieve a spatial resolution approximately equal to the smallest, outer most zone width. We developed a double patterning zone plate fabrication process based on a high-resolution resist, hydrogen silsesquioxane (HSQ), to bypass the limitations of conventional single exposure fabrication to pattern density, such as finite beam size, scattering in resist and modest intrinsic resist contrast. To fabricate HSQ structures with zone widths in the order of 10 nm on gold plating base, a surface conditioning process with (3-mercaptopropyl) trimethoxysilane, 3-MPT, is used, which forms a homogeneous hydroxylation surface on gold surface and provides good anchoring for the desired HSQ structures. Using the new HSQ double patterning process, coupled with an internally developed, sub-pixel alignment algorithm, we have successfully fabricated in-house gold zone plates of 12 nm outer zones. Promising results for 10 nm zone plates have also been obtained. With the 12 nm zone plates, we have achieved a resolution of 12 nm using the full-field soft x-ray microscope, XM-1.

Keywords: double patterning, Fresnel zone plates, hydrogen silsesquioxane, hot development, 3-MPT, adhesion, x-ray microscopy, imaging resolution, multilayer grating samples, condenser zone plates.

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I. INTRODUCTION

In the burgeoning quest of nanoscience and nanotechnology, soft x-ray zone plate microscopy^{1,2} has become a very attractive and powerful technique that complements other analytic microscopies. With the operating wavelength between 5 nm ($h\nu = 250\text{eV}$) to slightly below 1 nm (2000eV), soft x-ray microscopy can identify trace element of low-Z materials and 3d transition metals, such as C, N, O, Al, Ti, Fe, Co, Ni and Cu. Particularly for ferromagnetic 3d elements, usage of x-ray magnetic circular dichroism as absorption contrast has enabled direct imaging of magnetic domain structures. Since its inception, invaluable knowledge in life science³⁻⁵, nanomagnetism⁶⁻⁸, and material sciences^{9,10} have been gained through the use of soft x-ray microscopy. To probe the fundamental behaviors in these sciences, imaging resolution in the order of 10 nm is strongly needed.

The resolution of the x-ray microscopy is largely determined by the imaging zone plate. For diffraction-limited zone plate lenses, the resolution is approximately equal to the outermost (smallest) zone width of the zone plate¹. Conventional electron beam lithography^{11,12}, the most successful technique for fabricating high quality zone plates, has limited success in fabrication of 15 nm and below zones, due to electron beam sizes comparable to the zone width, scattering in resist, intrinsic resist contrast, and development issues such as resist swelling and collapse. To circumvent these obstacles, we previously developed a double patterning technique¹³ in which a dense zone plate pattern is sub-divided into two semi-isolated, complementary zone set patterns [Fig. 1]. These patterns are fabricated separately and then overlaid with high accuracy to yield the desired pattern. The key to success with this process is the accuracy of the overlay. For diffraction-limited zone plates, accuracy better than one-third of the smallest zone width is needed. In our previous work, we had realized the technique using PMMA¹⁴ and zone plates with 15 nm outer zone width had been successfully fabricated for the first time. The PMMA process, however, did not scale down reliably. Specifically, modest resist contrast, combined with 8-10 nm electron beam size of our exposure tool, could not clear the PMMA pattern with high yield. In this work, we developed a new variation of double patterning process using HSQ, which has enabled us to fabricate zone plates of 12 nm outer zones, with promising results of the 10 nm zone plates.

II. NEW DOUBLE PATTERNING PROCESS WITH HSQ

A. *Using HSQ in the double patterning process*

Hydrogen silsesquioxane (HSQ), a spin-on glass material, was found to be a high resolution, negative tone, electron beam resist^{15,16}. It has good mechanical strength and planarization property, as well as high etch resistance to oxygen plasma. Dense lines of 14 nm period have been demonstrated in HSQ using the “salty” base development¹⁷. To adopt this resist to the double patterning zone plate process, we explored various high contrast development systems¹⁷⁻¹⁹, as well as soft bake conditions. Vacuum drying of the HSQ’s solvent at room temperature after resist coating, combined with development in 0.26N tetramethyl ammonium hydroxide (Microposit LDD26W, Rohm and Haas) at 45°C, yielded smooth, sub-10 nm semi-isolated lines with good reproducibility. Lines narrower than 25 nm, however, experience poor adhesion to the gold plating base, which is used here for electroplating the metal zones. To improve the HSQ adhesion, we followed Thompson *et al.*²⁰ and developed a surface priming procedure using (3-mercaptopropyl) trimethoxysilane, or 3-MPT (Acros Organics N.V.), which are long chain polymers that have affinity to gold on one end, and to hydroxyl on the other end. Soaking a gold substrate in this chemical followed by hydrolysis in diluted hydrochloric acid forms a self-assembled monolayer of 3-MPT molecules on the surface. This monolayer can withstand high electron dosage and the “hot” LDD26W development, and it can be removed by UV-ozone exposure. Using this priming process before HSQ coating, semi-isolated patterns of zone width as narrow as 8 nm can be fabricated without collapse or detachment from the gold substrate. Dense zones with half-pitch less than 15 nm, however, exhibit collapse after the base development and the subsequent drying step. The dense zones, as described below, are reinforced by addition of short lateral supports, or buttresses, across adjacent zones. The placement of such buttresses is pseudo-random, minimizing constructive interference from these structures at the focal plane of the zone plates.

B. *The HSQ double patterning process*

The complete HSQ double patterning process is rather different from the PMMA process used before. The new process not only addresses the challenges discussed above,

but also accommodates the negative tonality nature of HSQ. The differences result in a single electroplating step to form all absorptive metal zones, in comparison to two separate steps in the PMMA process. This simplification eliminates the possibility of two different plating thickness for the two zone sets. Fig. 2 illustrates the process flow of the HSQ double patterning process. First, alignment marks are fabricated on a 100 nm thick low stress membrane window wafer [Fig. 2(I.1)]. The wafer, consisted of an array of 0.5 mm membrane windows, is pre-coated with a 5 nm thick chromium adhesion layer and a 7 nm thick gold plating base using electron beam evaporation. Alignment marks are fabricated at the four corners of a major field (114 μ m field size, 1.75 nm pixels) on each membrane window, using a standard positive resist process. The marks, as seen in Fig. 3, are variants of four two-dimensional Barker alignment mark series²¹, each of which is a rotated copy of the other, and a similar set of marks closer to the center. The smallest elements in the Barker marks are 60 nm squares. The marks are electroplated with gold to about 90 nm thick and form a high contrast transmitted electron signal.

Next, the resist plating mold is removed [Fig 2(I.2)]. This is a crucial step to forming a high-quality, continuous 3-MPT adhesion layer on the wafer surface in the following procedure. We strip the resist by flood exposing the wafer with ultraviolet light and developing the resist. This recipe removes the resist rather effectively without damaging the plating base. In the case where resist residue is still present, a fresh gold layer of 5 nm is evaporated onto the wafer surface.

Once a clean gold substrate is prepared, the wafer surface is primed by soaking in 0.02M 3-MPT in ethanol for 2 hours [Fig. 2(II.1)]. Excessive 3-MPT is then washed off with ethanol, and the wafer is blow dried with N₂. To complete the priming procedure, the wafer is soaked in 0.01N hydrochloric acid at 30°C for 5 hours, and the residue acid after soaking is removed by rinsing the wafer with ethanol and drying in N₂. The wafer is now ready for the first zone set patterning with HSQ.

To start the fabrication, a 50 nm thick HSQ film is spin-coated on the wafer, which is then placed in a vacuum chamber of 10⁻⁶ torr at 25°C [Fig. 2(III.1)] to evaporate the solvents. Before zone set I is exposed, the orthogonality, scaling, rotation and offset of the electron beam deflection are calibrated with the inner set of the alignment marks

using an internally developed algorithm [Fig. 2(III.2)]. Electrons of 100keV are then used to expose zone set I at the major field center. With the typical current of 0.5pA, the exposure time of each pattern is below a minute. The wafer is then developed in LDD26W at 45°C for 2 minutes, and chilled in 1:10 LDD26W:water mixture at 30°C for 40 seconds before rinsing in de-ionized water. After the fabrication, zone set I is further crosslinked with electrons, at a dose four times of that used in the patterning exposure, to avoid additional attack of the structure by the developer in subsequent steps [Fig. 2(IV.1)]. No fresh resist is coated on the wafer in this step.

Next, buttresses are fabricated in the outer region of the zone pattern [Fig. 2(V)]. For this, a fresh layer of HSQ is spin-coated on the wafer and dried in vacuum. Following the same steps for fabricating zone set I, the electron beam deflection is calibrated to the inner set of alignment marks, and buttresses are exposed. The wafer is subsequently developed, chilled and rinsed in the same manner as described above. With the buttresses fabricated, the wafer is ready for zone set II fabrication [Fig. 2(VI)]. The same steps for fabricating zone set I are again used here. To achieve high overlay accuracy, the outer set of alignment marks, covered only by fresh, uncrosslinked resist, is used for the deflection calibration. Zone set II is exposed at 100keV, and the wafer is then developed, immersed in dilute LDD26W solution, and rinsed in water thoroughly [Fig. 2(VI.2)]. As a precaution to collapse of the dense HSQ structures, we subsequently rinse the wafer with ethanol to displace the water on the surface, and blow dry it gently. Next, we use the HSQ structure as a mask and remove the 3-MPT in the clear areas by UV-ozone. An exposure of 7 minutes is chosen for sufficient cleaning and moderate heating of the silicon nitride membrane window and the HSQ structure. The wafer is then carefully plated with gold (Enthone BDT-510) using pulse currents to form the absorptive metal zones [Fig. 2(VI.3)]. Finally, the HSQ structure is removed using buffered hydrofluoric acid, leaving the desired zone plate structure.

The key to the success of the double patterning process is the overlay accuracy of the two zone sets. We use an internally developed mark registration and alignment algorithm²² to achieve high overlay accuracy. In this algorithm, the position of each alignment mark is first estimated by calculating the cross-correlation of the mark's scanned image and its template. To acquire the mark location to beyond the pixel

resolution, the autocorrelation of the template is fitted to the cross-correlation, and the residue value is in turn fitted with a second order polynomial. The minimum of the polynomial is then calculated to analytically determine the mark location. Once the locations of the four marks are obtained, the orthogonality, scale, rotation and offset of the deflection field are determined using the least square method. Since this algorithm uses the whole marks, the deflection calibration is resistant to mark defects, and sub-pixel alignment accuracy to the marks is achieved routinely. In the double patterning process above, both zone sets are aligned to the marks in the “zero level”. Systematic alignment errors stemming from the fabrication inaccuracy of the alignment marks are thus eliminated.

In addition to the overlay accuracy, reproducibility of the HSQ fabrication processes for both zone sets and buttresses is also essential. The “hot” development, combined with usage of relatively fresh resist and consistent time delay in air before development, provides a robust process for the double patterning. One may note that the fabrication of zone set I and the buttresses are not combined. The reason is that the combination compromises the zonal quality near the buttresses, where the buttresses are widened due to the proximity effects from the zones, and the zones are slightly pulled towards the buttresses as HSQ contracts during development.

III. RESULTS AND DISCUSSIONS

Using the HSQ double patterning process, we successfully fabricated zone plates of 12nm outer zones. The fabrication was performed in the Center for X-ray Optics’s Nanofabrication Laboratory and the Nanowriter electron beam lithographic tool²³, a modified 100keV Leica VB6 system optimized for curvilinear shapes²⁴. Fig. 4 shows the scanning electron micrograph of the outer region of a 12 nm zone plate. The zone plate has 250 gold zones, a diameter of 24 μm , and a gold thickness of 30 nm. The zones resemble ones fabricated with a single exposure. Measurements indicate that 1.6 nm overlay accuracy (1σ) was achieved with this zone plate. Breaks in the gold zones left by the buttresses can be seen in various areas. This micrograph as well as in the magnified view of the outermost region in the figure inset, show that at this scale the gold grain

sizes were not perfectly controlled, and large grains occasionally push the resist zones sideway.

We are extending the double patterning process to narrower zones. Complete zone plates of 10.4 nm outer zones have been fabricated. A scanning electron micrograph of part of such a zone plate is shown Fig. 5. The zone plate has 250 gold zones, 20.8 μm diameter, and 30 nm thick gold plating. The overlay is less accurate than that of the 12 nm zone plates. This may be caused by unequal zone widths from zone set I and the complementary set II. Wider zones shift the gold zones closer to the narrower adjacent zones, reducing the placement accuracy of the gold zones. For these zone plates, buttresses were placed closer to minimize zonal collapse during zone set II development and electroplating. Gold grains similar to those in the 12 nm zone plate were formed by the plating.

The 12 nm zone plates were tested using the soft x-ray full-field transmission XM-1 microscope²⁵ at LBNL’s Advanced Light Source (ALS) [Fig. 6]. Analogous to a simple optical microscope, the x-ray microscope collects and focuses the bending magnet synchrotron radiation to the sample, which is imaged by a high-resolution “micro” zone plate, and full-field images are recorded by a CCD detector. A high numerical aperture condenser zone plate (CZP) of 30 nm outer zones was fabricated to provide better matched, less coherent, annular illumination for the testing. The condenser has 40820 zones and a diameter of 9.8 mm. The central area of 7 mm diameter is left unexposed due to the usage of an external central stop. Fabricated on quadruple 5 mm silicon nitride membrane windows, the condenser was exposed using the Nanowriter e-beam system, at a current of 1 nA. With the resist of PMMA, the exposure took three and a half days. Fig. 7 shows a scanning electron micrograph of the outer region of a gold plated CZP, as well as a photograph of the whole condenser. While the outer zones have varying widths, they do not significantly impact the CZP’s focusing performance.

Various types of test objects, including star patterns, pseudo-random arrays, and periodic lines and spaces, were imaged with the 12 nm zone plates. Fig 8(a) shows an x-ray image of a 40 nm thick gold star pattern obtained with a 12 nm zone plate, at the wavelength of 1.75 nm ($h\nu=707\text{eV}$). Numerous pattern details can be seen clearly in the

image. The image is compared favorably to the scanning transmission electron micrograph of the test pattern [Fig. 8(b)]. As shown in Fig. 8(c), the zone plate reproduced the small details in the pattern with high fidelity. To quantify the resolution performance of the zone plate, we fabricated high quality grating patterns with precise periods. For this, we used magnetron sputtering to deposit uniform, low-stress periodic molybdenum and silicon multilayer coatings on silicon substrates, with half-periods from 20 nm down to 7 nm. Thin cross sections of the multilayer coatings (100 nm thick) are made and attached to TEM grids using the FIB in-situ lift-out process²⁶. Fig. 9 shows a transmission electron micrograph of a multilayer test sample after processing, containing twenty periods of 12 nm molybdenum and silicon layers and thirty periods of 9 nm Mo and Si layers. The perfectly straight molybdenum and silicon layers in cross section are used as dense line patterns for the resolution testing.

Fig. 10 shows the x-ray images of 20 nm, 15 nm, 12 nm and 10 nm half-period Mo/Si gratings obtained at 1.75 nm wavelength using the 12 nm zone plate. Gratings down to 12 nm half-period were resolved by the zone plate. At the next smaller half-period, 10 nm, image contrast drops to zero. While 10 nm line and space resolution is theoretically possible for the imaging setup and parameters used here, the actual experimental resolution of 12 nm has been achieved with the new 12 nm zone plate. The resulted discrepancy may be due to the environmental factors such as vibrations, system drift, and the optical alignments. Improvement of the microscope engineering design is underway to test the ultimate resolution of the zone plate.

IV. CONCLUSIONS

We successfully developed a double patterning zone plate process using the high resolution resist HSQ. Adhesion of narrow HSQ structures to gold substrate is significantly improved using the 3-MPT surface preparation process. With particular attentions to the stringent requirements and characteristics of narrow dense zones, we realized high quality zone plates of 12 nm outer zone width using the double patterning process. Promising results have been obtained for 10 nm zone plates, and we anticipate to reach 10 nm resolution and below in not so distant future.

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Figure Caption

Fig. 1. An illustration of the double patterning zone plate fabrication technique. The Fresnel zone plate pattern (right) is composed of odd-numbered opaque zones (black) and even-numbered transparent zones (white). Set I (left pattern), containing zones 1, 5, 9 ..., and its complement, set II (center pattern), are fabricated sequentially and overlaid with high accuracy to form the desired zone plate.

Fig. 2. Illustration of the HSQ double patterning zone plate process. It is made up of six parts: (I) alignment mark fabrication, (II) surface priming, (III) zone set I fabrication, (IV) blanket exposure of zone set I, (V) buttresses fabrication, and (VI) zone set II fabrication.

Fig. 3. The layout of the alignment marks and zone plates. Two sets of Barker alignment marks are fabricated at the corner of a major field, and the zone plate at the field center. A field size of 114 μm with a pixel size of 1.75 nm is used in the fabrication here.

Fig. 4. A scanning electron micrograph of the outer region of a 12 nm zone plate fabricated using the double patterning process. Sub-pixel overlay accuracy of 1.6 nm was achieved. The gold zones have a thickness of 30 nm.

Fig. 5. A scanning electron micrograph of the outer region of a 10.4 nm zone plate fabricated using the double patterning process.

Fig. 6. A schematic of the soft x-ray full-field transmission XM-1 microscope, at the Advanced Light Source (ALS) of LBNL. X-ray from a bending magnet synchrotron source is focused by a condenser zone plate (CZP) onto the sample, and a “micro” zone plate (MZP) projects a full-field image onto a CCD detector. The 12 nm zone plate was installed as a MZP for imaging testing.

Fig. 7. (a) A scanning electron micrograph of the outer region of a 30 nm gold condenser zone plate (CZP). The condenser has 40820 zones and a diameter of 9.8 mm. The central area of 7 mm diameter is left unexposed due to the use of an external central stop. (b) A photograph of the whole condenser, which was fabricated on

four 5mm silicon nitride membrane square windows. The membrane thickness is 100 nm.

Fig. 8. (a) A x-ray image of a 40 nm thick gold star pattern taken with the new 12 nm zone plate at the wavelength of 1.75 nm (707eV). (b) A scanning transmission electron micrograph of the same pattern. Numerous sample defects in the micrograph can be seen clearly in the x-ray image. (c) The top left areas of the x-ray image and the micrograph are shown for comparison.

Fig. 9. A transmission electron micrograph of one of the multilayer test sample used for resolution testing. Twenty periods of 12 nm molybdenum and silicon layers, on top of thirty periods of 9 nm Mo and Si layers, are shown after the magnetron sputtering and the FIB in-situ lift-out process.

Fig. 10. The x-ray images of 100 nm thick Mo/Si multilayer cross-section samples at half-periods of (a) 20 nm, (b) 15 nm, (c) 12 nm and (d) 10 nm, obtained with the 12 nm zone plate at 1.75 nm wavelength (707eV). The dark lines are molybdenum, and the light ones are silicon. Lines and spaces down to 12 nm can be observed with the zone plate. At 10 nm half-period, image contrast reaches zero.

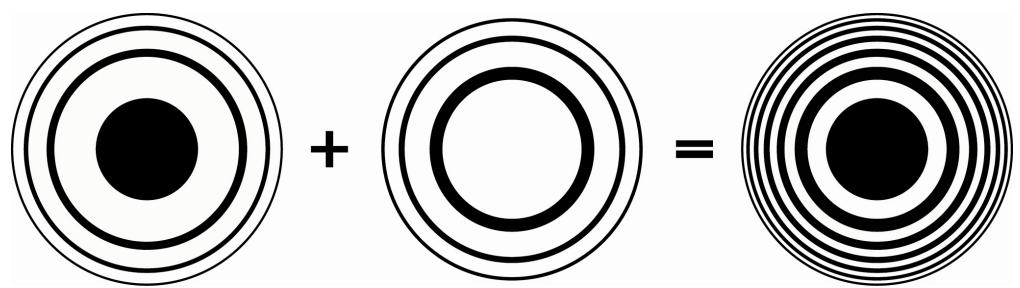


Fig. 1.

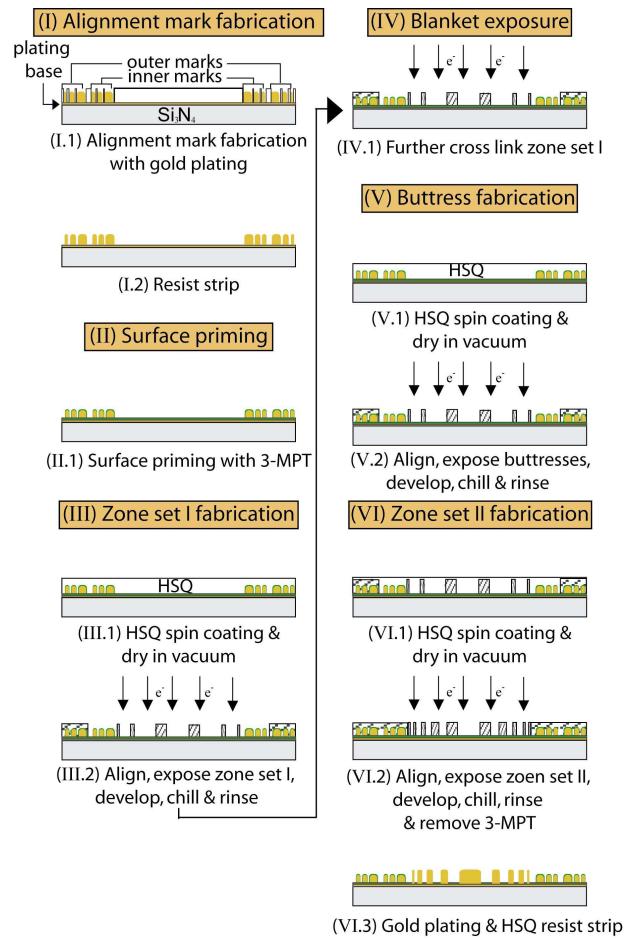


Fig. 2.

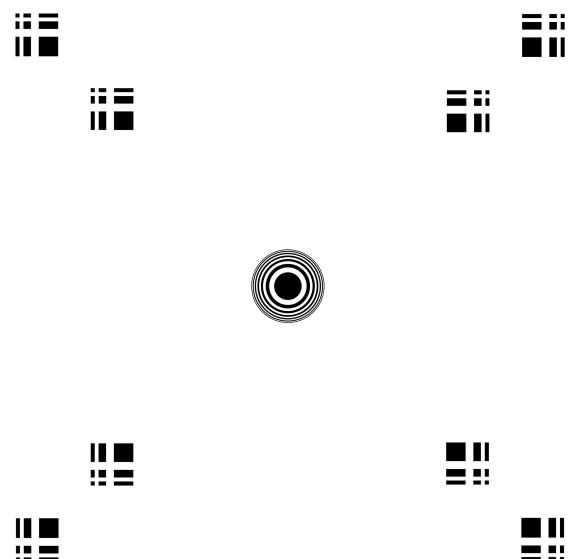


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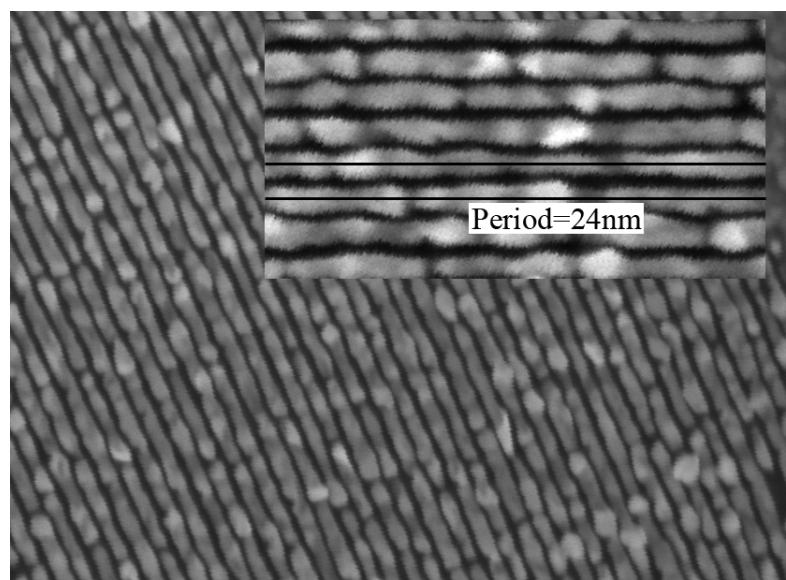


Fig. 4.

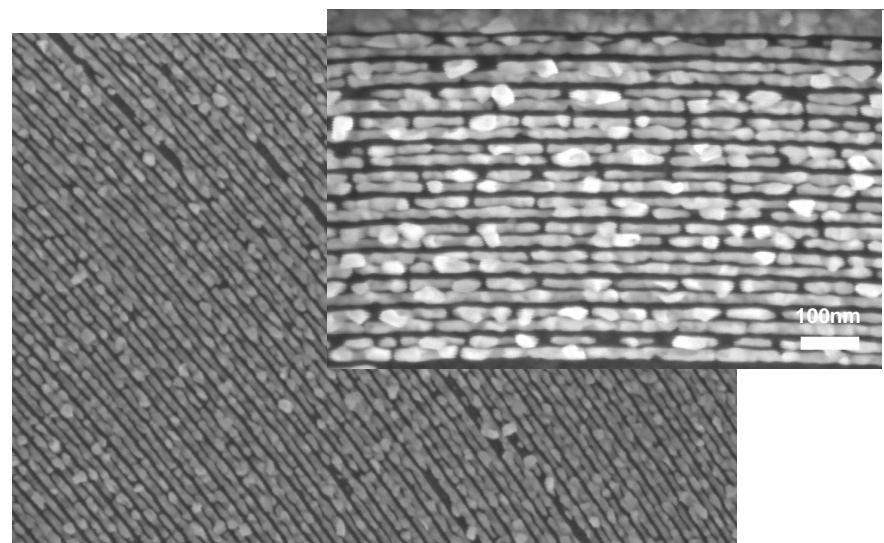


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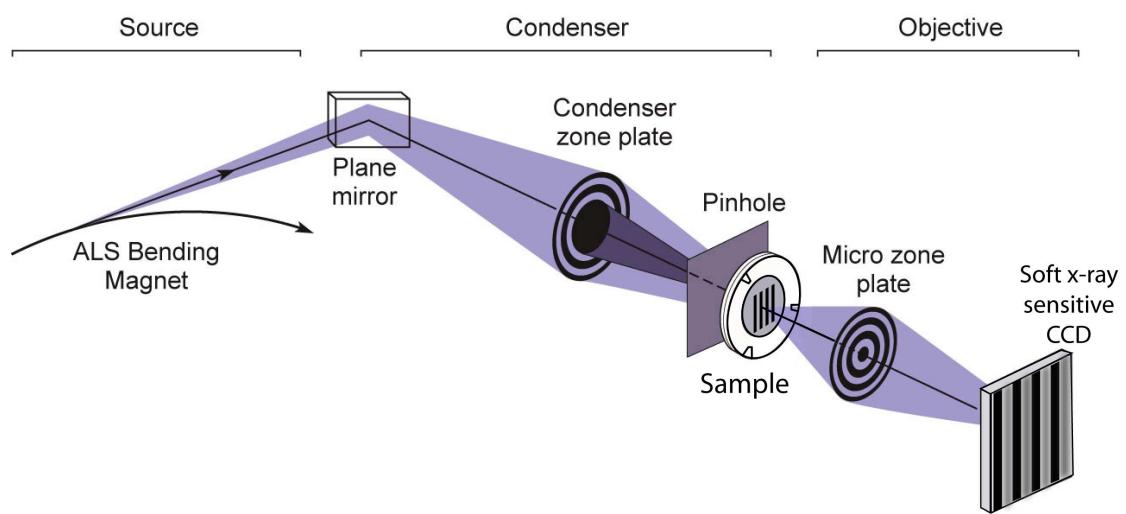


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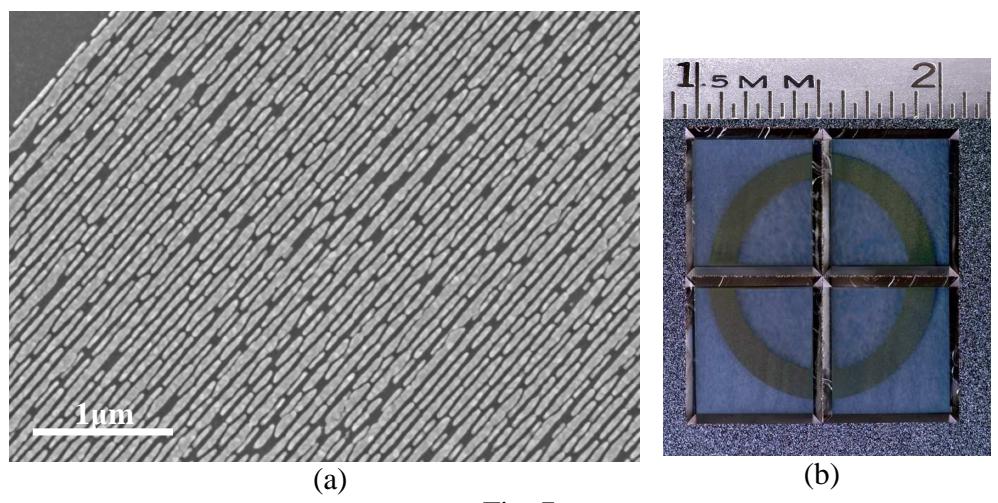


Fig. 7.

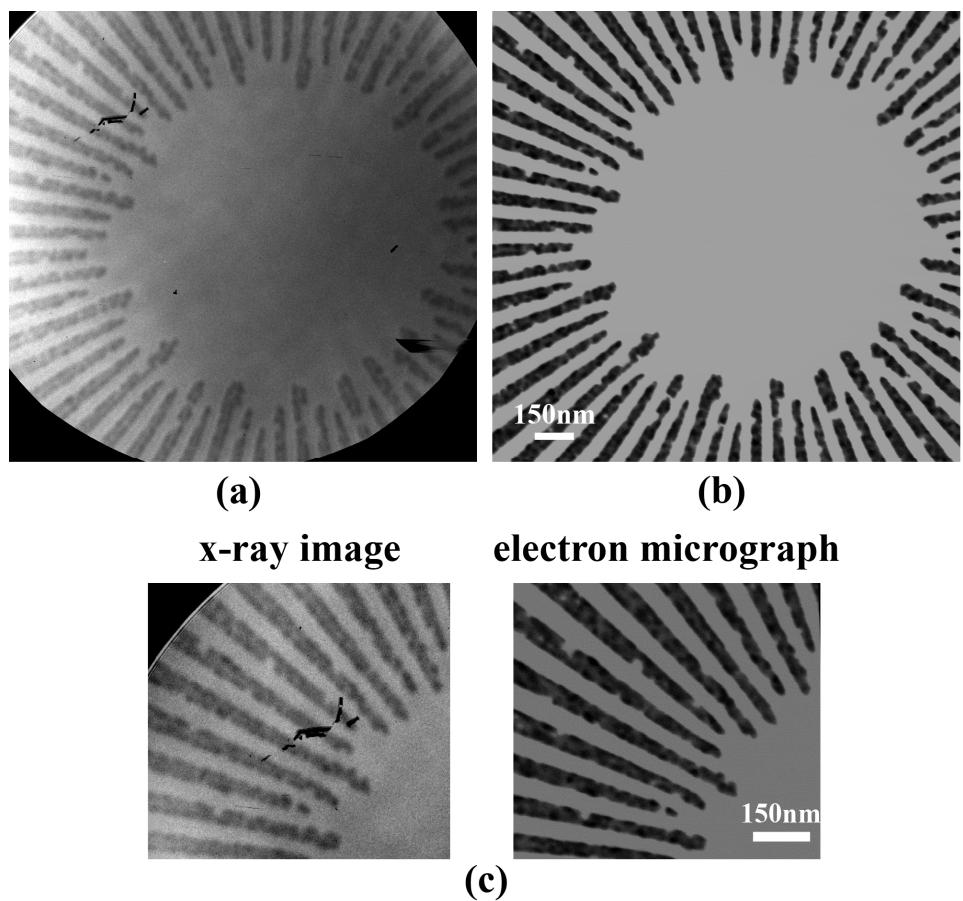


Fig. 8.

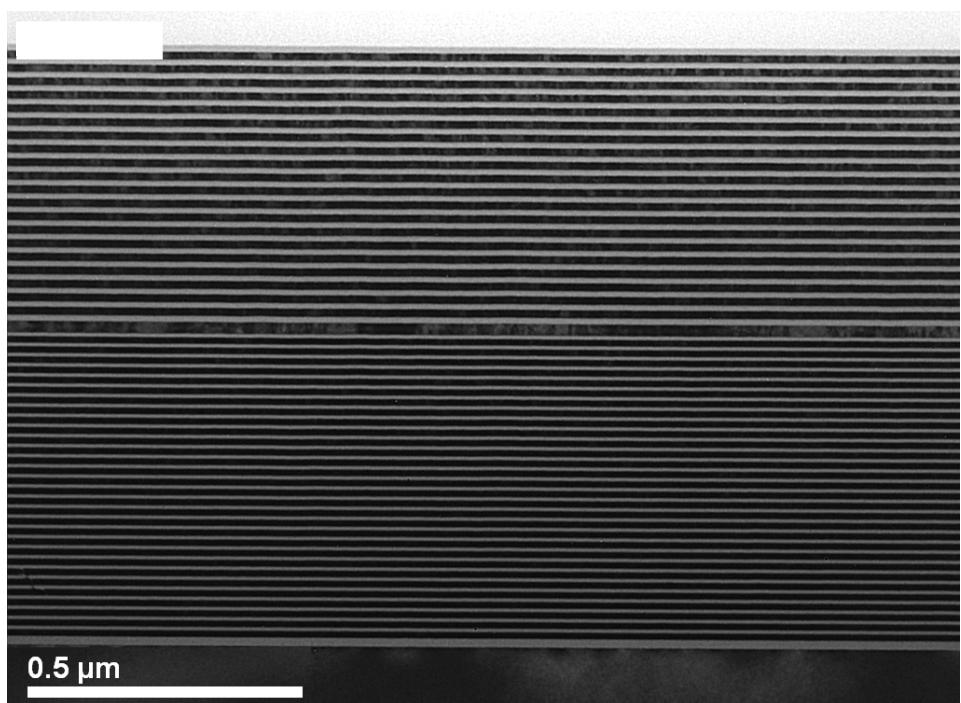


Fig. 9.

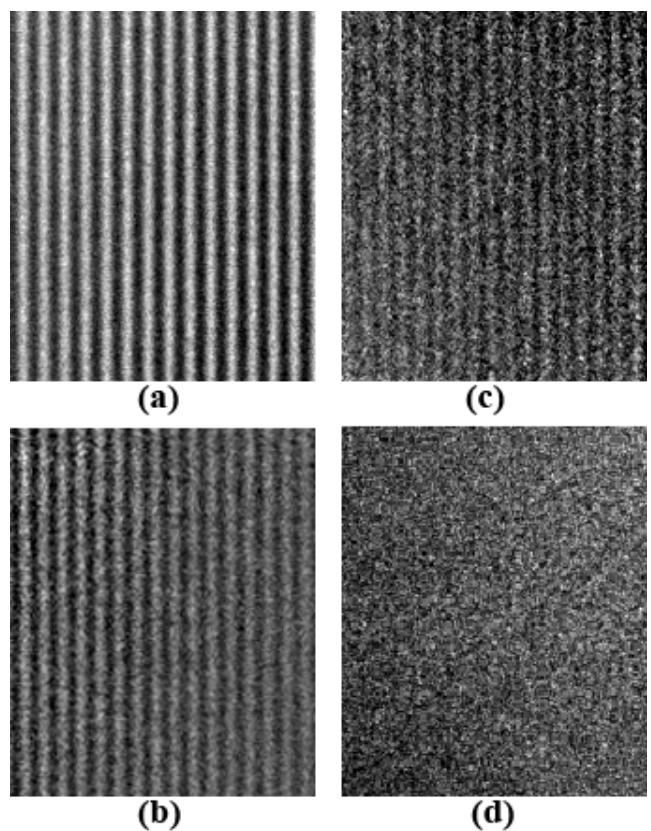


Fig. 10.