Diffractive x-ray optics using production fabrication methods

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Zone plates are the key focusing element for many x-ray (7–20 keV) and soft x-ray (200–500 eV) applications, yet, production with electron-beam lithography poses obstacles to their widespread availability. In addition, fabrication processes to date have limited the studies of amplitude Bragg–Fresnel-type elements in the hard x-ray regime. We report new processes that couple 100 keV electron-beam lithography with established production methods to achieve two goals: (1) improving the overall yield and volume of ultrahigh-resolution soft x-ray zone plates and (2) applying deep silicon etching techniques to extend the state of the art in high aspect ratio Bragg–Fresnel optics required to create high efficiency focusing of high-energy x rays. [DOI: 10.1116/1.1537232]

I. INTRODUCTION

X-ray probes have long been established as useful tools in a variety of applications. With soft x rays in the energy range of 250–800 eV, one can obtain 20–50 nm resolution images of micrometer thick hydrated specimens with a sensitivity to the chemical state of many low-*Z* elements.[1] Higher-energy x rays in the 5–15 keV range can be focused to ~100 nm spot sizes, and used for trace element mapping in fluorescent microprobes,[2] or the mapping of strain in crystalline solids.[3]

Fresnel zone plates are used to obtain the highest-resolution x-ray images for imaging, spectroscopy, microdiffraction, and trace element analysis in materials, environmental, and biological sciences. In general, the resolution of a zone plate is governed by the width of the outermost zones while the efficiency is determined by the thickness and material of the zones. Because this optic works in transmission, it is also necessary that soft x-ray Fresnel zone plates be fabricated on fragile silicon nitride windows. To date, high efficiency zone plates for soft x rays have been fabricated with electron-beam lithography in electroplated nickel with outermost zones of 20 nm over a diameter of 80–160 μm resulting in a spot size of less than 30 nm.[4]

While the demand for zone plates is widespread, their immediate availability is rather small. Generating a large supply of soft x-ray zone plates is challenging because of the low yield per electron beam (e-beam) write and the fragility of the silicon nitride windows on which the zone plates must be fabricated. Extremely careful handling during each step in the fabrication process as well as during subsequent use is necessary in order not to break these windows and lose the zone plate altogether. An additional factor affecting the overall supply of zone plates is the general availability of access to e-beam lithography tools, which does not nearly match the number of zone plate users. While a small number of these optics with desired characteristics can be made,[4,5] creating an inventory and fulfilling the needs of users worldwide is an ongoing problem. Therefore, a solution was sought that would allow for the replication of soft x-ray zone plates as well as circumvent the need for repeated e-beam access. Replication methods could greatly increase their availability, just as was done a century ago with replicas of mechanically ruled gratings for spectroscopy. Early results using step and flash imprint lithography (S-FIL) for replicating zone plate patterns are reported in Sec. III.

Alternatively, in the hard x-ray range, the choice of optical elements is limited, due to the small refractive index differences between materials, particularly at large (10 keV) photon energies. For this range, transmission zone plates have been shown to provide focusing with spots as small as 100 nm.[6] These are an extension of the type used successfully in the soft x-ray energy ranges.[5]

In the hard x-ray regime, Bragg diffraction from the crystal planes is possible, which opens up an alternative to the transmission zone plate: Bragg–Fresnel zone plates.[7–9] The process of standard Bragg diffraction can be viewed as the reflection from weakly reflecting layers of atoms which interfere constructively for specific choices of energy and angle, resulting in perfect reflectivity in the dynamical limit, even though individual layers only reflect weakly. A Bragg–Fresnel zone plate imposes the Fresnel zone structure on the Bragg crystal to achieve focusing in reflection. In particular, the analog of the phase zone plate has been studied, and the depth of the etched grating has been chosen to give a π phase shift. With this approach, zone plates with outermost

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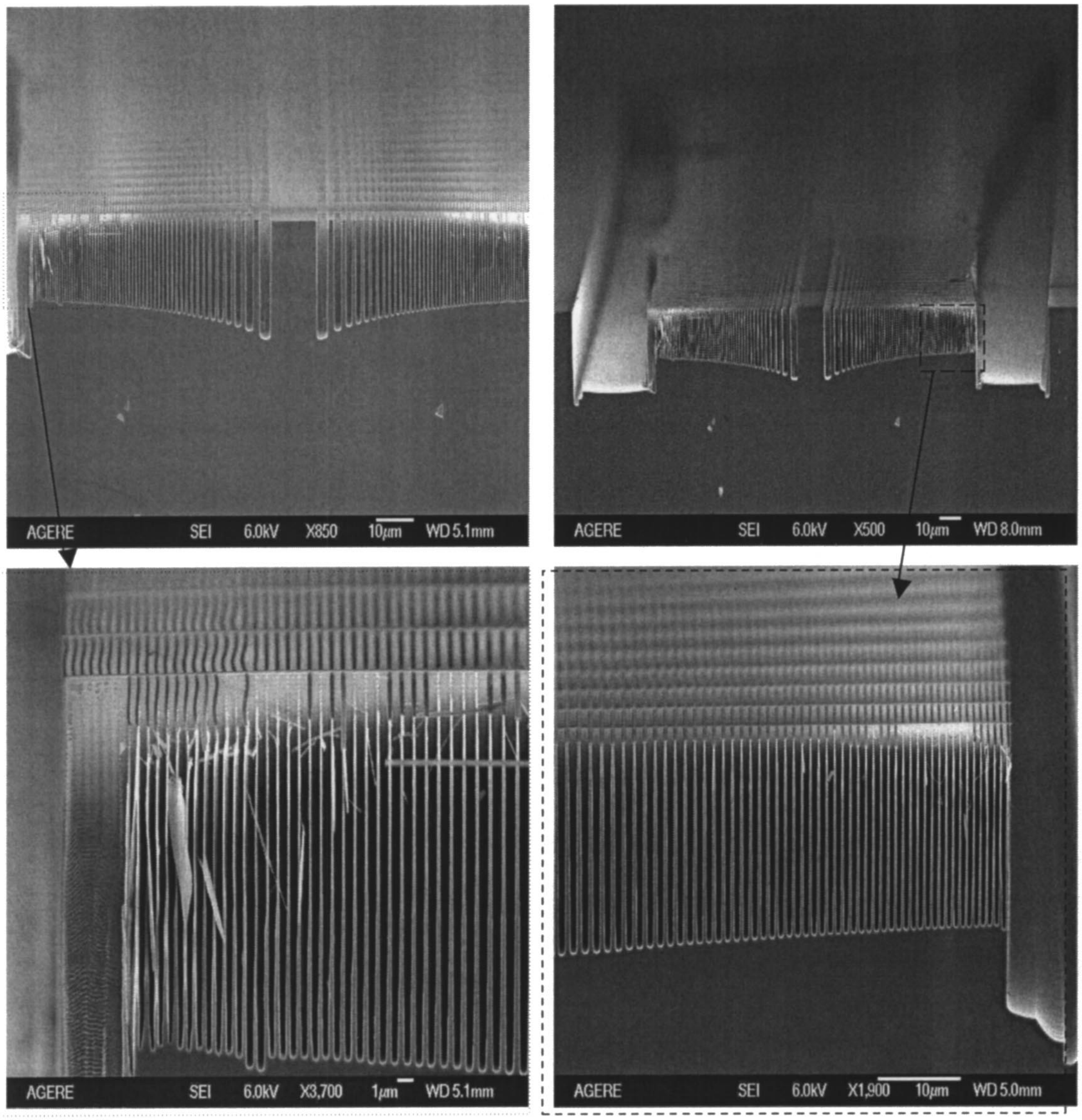

FIG. 1. SEM's of cross sections of deep etched Bragg–Fresnel zone plates. The patterns were defined with e-beam lithography on a JEOL JBX-9300FS and deep etched using a modified BOSCH process. On the left-hand side are (nominal) 250 nm outermost zones and on the right-hand side are (nominal) 400 nm outermost zones. The actual smallest zone width is <200 nm. The etch depth is 15–20 μm with aspect ratios 25–100.

zones of 100 nm have been fabricated by etching 1.5 μm in silicon.[10] In the typical transmission amplitude zone plate, alternate Fresnel zones are blocked or open resulting in constructive interference at the focal point. In the Bragg–Fresnel amplitude zone plate, one etches the standard zone plate pattern into the single crystal. One way to view the resulting structure is that of a stack of partially reflecting zone plates, with each layer of the crystal being a separate zone plate.

In these structures, incident x rays on a Bragg–Fresnel zone plate are reflected both from the patterned silicon zones as well as the unpatterned bulk silicon below the etch depth. The light reflected from the unpatterned silicon contributes to a background signal. This background has, to this point, hindered the fabrication and investigation of amplitude-type reflective x-ray optics. Two methods were sought to achieve background elimination while maintaining good focusing properties. First, a process was sought that would allow for very deep etching of the zones, beyond the extinction depth of x rays in silicon. The second method was an attempt to etch the zones on a silicon-on-insulator (SOI) substrate where the SOI layer acts as an absolute absorber allowing reflection only from the Fresnel zones. Details of this work are described in Sec. II.

The eventual solutions to the problems of zone plate replication and hard x-ray Bragg–Fresnel zone plate manufacture involved linking the lithographic ability of the e-beam tool (in our case a JEOL JBX-9300FS) with other pre-existing fabrication methods. This writer operates at 100 kV and can deliver a spot size down to 4 nm. By combining the exposure tool capabilities to previously established and tested processes, we were able to simplify the overall proce-

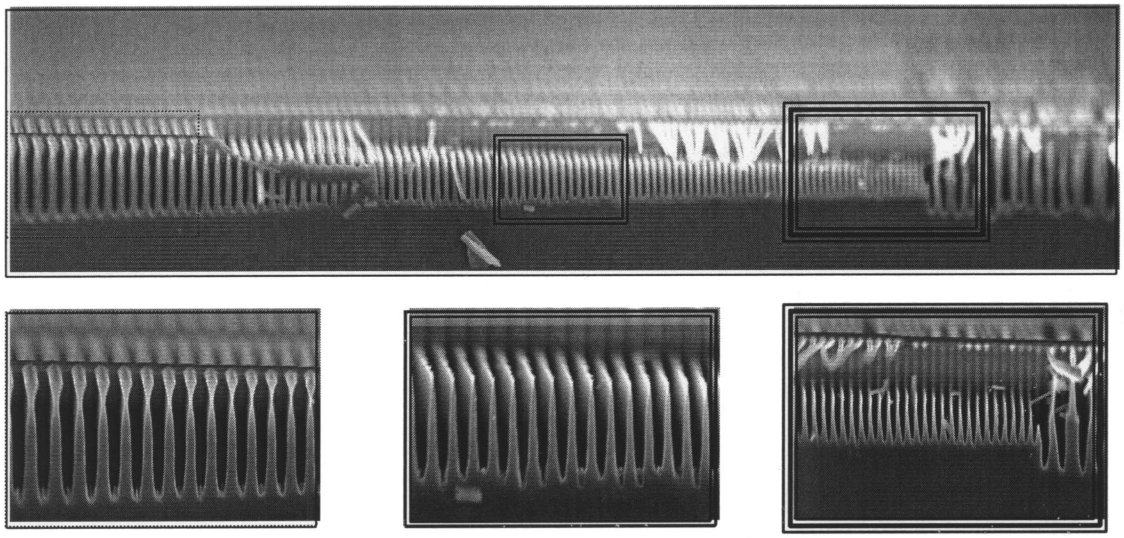

FIG. 2. First attempts for zone plates on SOI written on bulk silicon (no oxide). SEM's show cross-sectional view of Bragg–Fresnel zone plate etched in ~2 μm of silicon. Close up views: left-hand side shows larger (200 nm) zones, center 100 nm zones, and right-hand side ~80 nm zones. Initial tests of these optics at a synchrotron beamline show good focusing properties that is inhibited by background light. Present work is underway to transfer the process to SOI substrates.

dures and cut down on iterative fine tuning while reaching our established fabrication goals.

II. BRAGG–FRESNEL ZONE PLATES

A. Deep-etched silicon

The process for fabricating the deep-etched Bragg–Fresnel zone plates is as follows. First, a plasma deposited tetraethylorthosilicate oxide of 500 nm thick oxide mask layer is grown on clean, 200 μm thick, 8 in. silicon wafers.

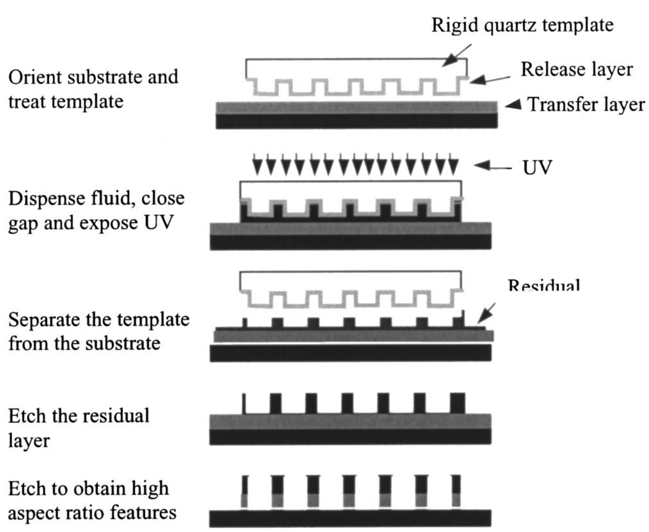

FIG. 3. Processing steps for S-FIL. An e-beam defined quartz template is treated with a release layer and aligned in the University of Texas imprint tool with an 8 in. silicon wafer. A UV-sensitive monomer is dispensed as the template is brought into contact with the wafer. Exposure with UV cures the fluid and the template is subsequently separated leaving the imprint on the wafer. Etching steps transfer the pattern and allow for high aspect ration replication.

The chemically amplified resist UV113 was spun to a thickness of 400 nm and baked at 140 °C for 90 s. Zone plate patterns were designed for various energies, focal lengths, and outermost zone widths. Patterns were written with the JBX-9300FS tool at 100 kV with a base dose of 50 μC/cm^2, which was modulated empirically at various zone radii to account for backscatter effects. The writing time per zone plate of dimensions on the order of 150 μm$\times$1.5 mm varied from 30–60 min, which includes the exposure of a larger area box surrounding the zone plate pattern necessary to isolate the optic from the bulk. A postexposure bake of 90 s at 130 °C was followed by development in an NMD-3 developer (Tokyo Ohka Kogya Co.) for 90 s and a rinse in water. After a spin dry, the entire postexposure process was subsequently repeated with a 20 s bake and a 30 s development step.

After a quick optical microscope check of the resulting patterns in the resist, the zone plates were transferred to an oxide mask with an AMAT 5200, using an EMAX plasma source, for magnetically enhanced reactive ion etching with a freon/oxygen etch chemistry. After the hard oxide mask is patterned, the remaining resist is removed and the remaining oxide is used as a hard mask for the etching of the silicon. The deep silicon etching was done with a specially designed, high throughput advanced silicon etcher which is the result of collaborative development with Agere Systems and STS. The process is a modified Bosch process, which is a time multiplexed deep silicon etch, consisting of two steps: (1) an isotropic etch, with a small bias applied which makes it slightly anisotropic and (2) a sidewall passivation step. This type of etch was previously used primarily in microelectromechanical systems work.

The results are shown in the scanning electron microscope (SEM) micrographs in Fig. 1. The zone plates in Fig. 1 have

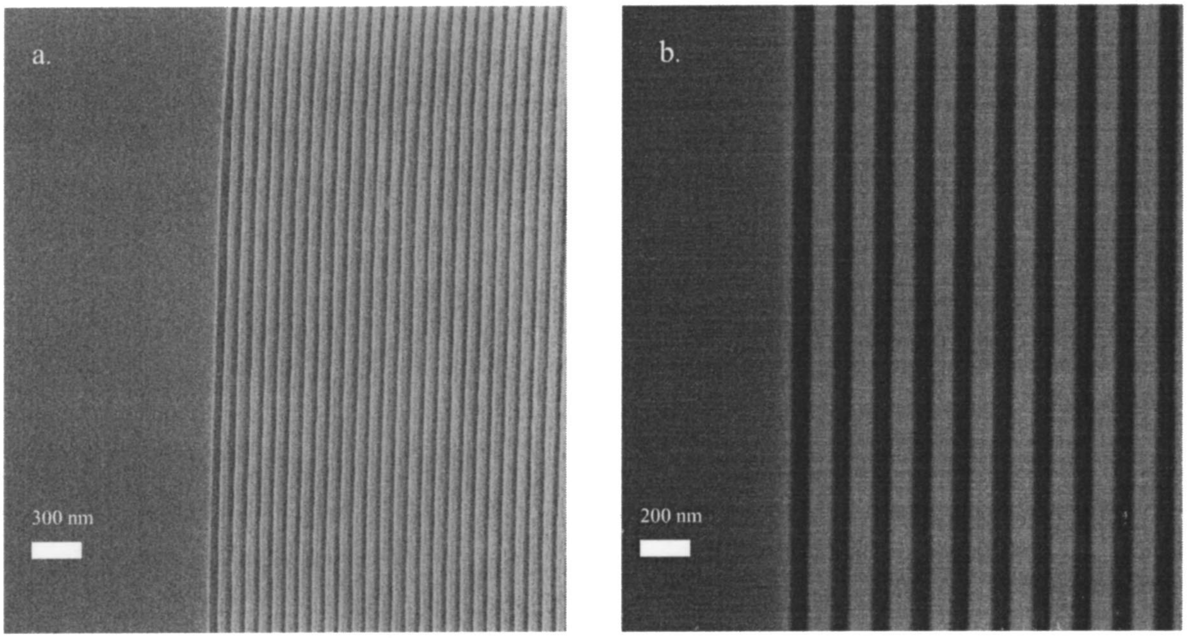

FIG. 4. SEM micrographs of the outer zones of zone plate templates etched in quartz. The zones in the template in (a) are nominally 40 nm wide etched 100 nm deep, and template (b) shows nominally 80 nm zones etched ~100 nm deep.

nominal outermost zone widths of 250 and 400 nm. Figure 1 shows a cross section of the optic with both a full-scale view of all zones and a zoomed-in view of the outermost (smallest) zones. All but the very outermost zones in the 250 nm zone plate survived, while the 400 nm zone plate is perfect to the end. The etch depth for the center zones is over 20 μm while the obviously, etch-lagged outer zones are about 15 μm deep in silicon which well matches the extinction depth for silicon. The aspect ratio is calculated to be 25–100 and the oxide mask is still intact and visible in the micrographs.

The etching process gives the zones a triangular profile, which should not affect the zone plate properties once the proper critical dimension (CD) bias is determined. While a scalloping effect is seen on the edge of the bulk silicon, the result is minimal, if present at all, on the zones themselves. The zones themselves are actually less than their nominal size, with a minimum zone width below 200 nm clearly etched down completely. There is adequate reason to believe that zone plates with features down to 100 nm can be fabricated using this method once the dose and pull-in biases are correctly determined. Experiments on the X16B beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories showed focusing properties for these zone plates.

B. Alternate etch method

To improve resolution limit, narrow zones are needed. To achieve this, an alternate etch process was adopted in which a shallower etch was traded for finer zones. The "shallow" etching for these zone plates was done with a LAM Research 9400, with TCP plasma source, which uses chlorine-based etching of silicon giving an anisotropic profile. Zones down to 80 nm were fabricated at a depth of ~2 μm at an aspect ratio of ~25. The results are shown for bulk silicon in Fig. 2. Testing at the NSLS showed good focusing properties albeit with no background elimination, as expected. In an attempt to remove this background, identical zone plates in SOI have now been fabricated, but focusing properties have not yet been fully characterized.

III. IMPRINTING ZONE PLATES

A. Fabrication of imprint templates

S-FIL[11] is a low cost, high throughput, patterning technique with sub-50 nm resolution capability. It possesses important advantages over photolithography and other next generation lithography (NGL) techniques since it does not require expensive projection optics, advanced illumination sources, or specialized resist materials that are central to photolithography and NGL techniques. Imprint lithography techniques are essentially micromolding processes in which the topography of a template defines the patterns created on a substrate. Several imprint lithography techniques are being investigated as low cost alternatives for high-resolution patterning. Figure 3 shows the general procedure for S-FIL. Investigations by S-FIL group and others in the sub-100 nm regime indicate that the resolution is limited by pattern resolution of the template.[12–14] To date, lines down to 20 nm have been imprinted with a UV monomer using this method, with tests showing the accurately repeatable patterning capability of S-FIL.[14] Using a low-viscosity, UV-curable liquid in conjunction with a bilayer approach makes S-FIL particularly suitable for high-resolution layer-to-layer alignment;[15] insensitive to pattern density variations, and capable of gen-

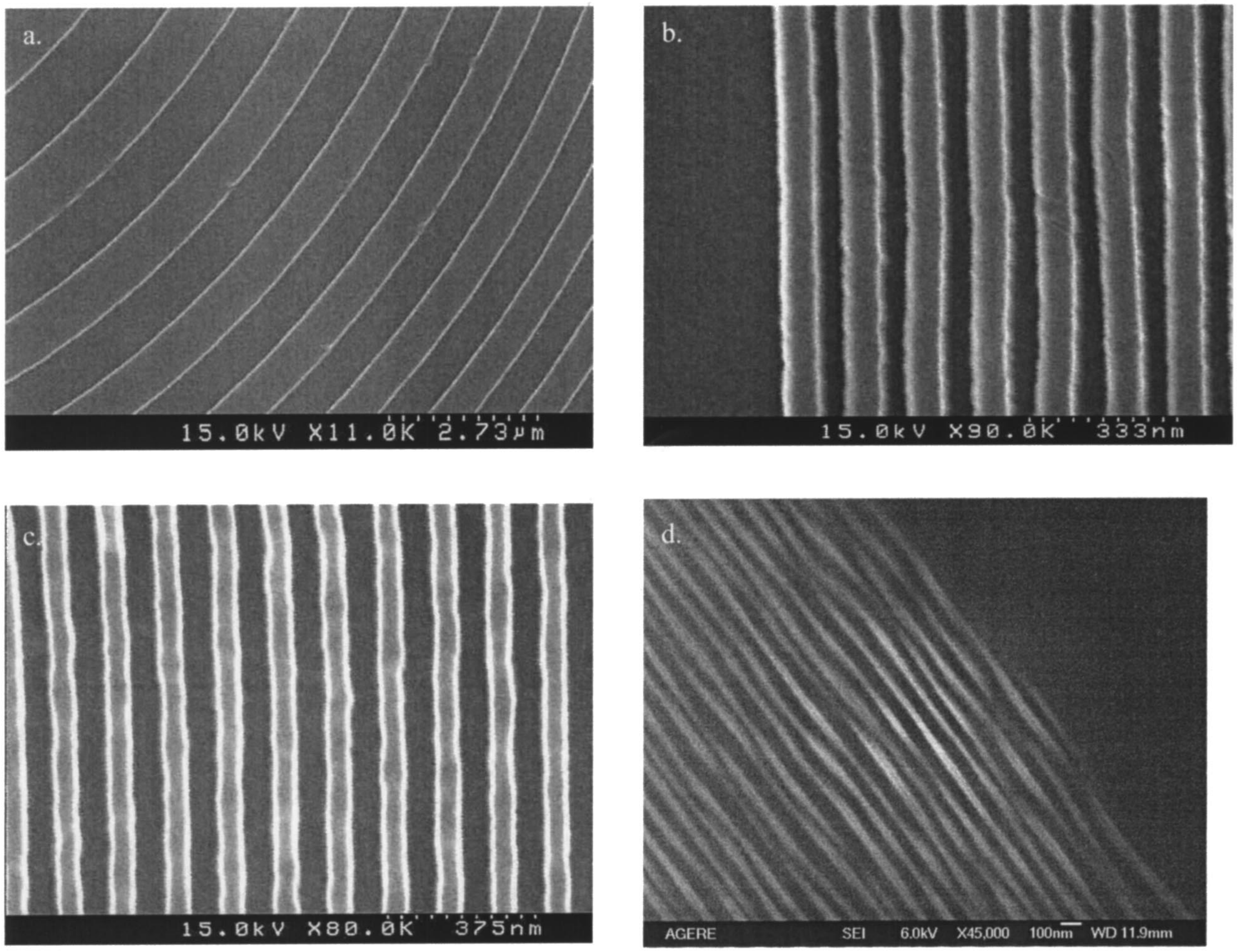

FIG. 5. Overview of imprinting results. SEM images of the 80 nm zone plate pattern transferred into the monomer layer are shown in (a) (inner zones) and (b) (outer zones). Images of the imprinted 40 nm zone plate pattern are shown in (c) (inner) and (d) (outermost). The results show good comparison with the templates in Fig. 4. Zones $<$50 nm were transferred with little aberration, although the 40 nm zones (d) failed to imprint acceptably. Because the template was on a quartz wafer instead of a rigid, 1/4 in. thick piece, these first imprints did not have the required thickness uniformity for etching.

erating high aspect ratio, high-resolution features with high throughput. For these reasons, it was felt that S-FIL was a good candidate for replication and eventual mass production of zone plates, making it necessary to fabricate zone plate patterns in fused silica.

B. Fabrication of quartz template

Quartz wafers (1/16 in. thick) were cut into roughly 1 in.$\times$1 in. pieces and vapor primed in an HMDS oven to improve the adhesion of the resist to the quartz. ZEP520 e-beam resist was spun to a thickness of $\sim$130 nm and baked at 180 °C for 5 min. To avoid charging problems of the substrate during e-beam exposure, the charge-dissipating Showa Denka Espacer 500 was then spun at 2000 rpm and baked at 110 °C for 10 min. Previous tests showed that the Espacer layer made no effect on overall CD.

Various zone plate patterns with minimum features of 80, 40, and 30 nm over diameters of 100–300 μm were exposed in each write using the JBX-9300FS once again. The base dose for the zone plates was 125 $\mu C/cm^2$. After rinsing the Espacer with deionized water, the postexposure development was 2 min in Xylenes and a 45 s rinse in a ZEP rinse (89% methylisobutylketone, 11% isopropanol). The patterns were etched into the quartz via a reactive ion etch with CHF_3; a 2 min etch to obtain $\sim$120 nm etch depth. In general, features below 50 nm, in some cases down to 40 nm, were etched without aberration into the quartz, but the 30 nm zone plates did not transfer well with this process. Figure 4 shows outer zones for the 40 nm and 80 nm zone plate templates in quartz.

C. Imprinting zone plates

The thin template was glued onto a thicker substrate in order to make it adaptable to the template holder of the University of Texas imprint tool.[15] The active area of the template was surface treated to enhance the separation process[16] (Step 4 in Fig. 3). Multiple imprints were patterned on 8 in. Si wafers with a transfer layer using a low-viscosity UV monomer as the imprinting layer.

Some results of the imprints with the zone plate templates are shown in Fig. 5. There is good correspondence between the master and the imprint for the 80 nm zone plates. The 40 nm zone plates also show promising results, although the smallest zones show some deformity from the imprint process. It is likely that the imperfections seen in Fig. 5 are due in large part to the fact that the templates were formed in thin quartz wafers and then glued onto the thicker 1/4 in. pieces as opposed to being written directly into the 1/4 in. quartz as is the normal procedure for the S-FIL process. Similarly, because the template was on a quartz wafer instead of a rigid, 1/4 in. thick piece, these first imprints did not have the required thickness uniformity for etching. Efforts to allow for direct e-beam writing on the thicker quartz are underway as well as investigations into different resist processes to get better adhesion and CD control in the quartz masters. The results are encouraging, nonetheless and represent the first effort to mass produce soft x-ray zone plates down to 30–45 nm outermost zone width.

IV. FUTURE WORK

Initial attempts to marry 100 kV e-beam lithography with established fabrication methods have proven successful. Hard x-ray focusing has been achieved with Bragg–Fresnel optics and more experimentation and testing is planned for the near future. Completed fabrication and testing of the zone plates on SOI will reveal the ultimate usefulness of these reflective zone plates for applications. Optimization of the zone plate patterns to account for the etch undercut of the silicon should provide even better results.

In order to achieve our goal of mass production of useful soft x-ray zone plates, much work is needed. The template fabrication process must be switched over to 1/4 in. quartz pieces to get the best imprint results, and the additional steps of generating nitride windows and nickel electroplating must be realized. Even so, the work so far points to the feasibility of an eventual replication process for zone plates with <50 nm outermost zone widths.

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[1]J. Kirz, C. Jacobsen, and M. Howells, Q. Rev. Biophys. **28**, 33 (1995).
[2]W. Yun, S. T. Pratt, R. M. Miller, Z. Cai, D. B. Hunter, A. G. Jarstfer, K. M. Kemner, B. Lai, H.-R. Lee, D. G. Legnini, W. Rodrigues, and C. I. Smith, J. Synchrotron Radiat. **5**, 1390 (1998).
[3]M. A. Alam, R. People, E. Isaacs, C. Y. Kim, K. Evans-Lutterodt, T. Siegrist, T. L. Pernell, J. Vanderberg, S. K. Sputz, S. G. N. Chu, D. V. Lang, L. Smith, and M. S. Hybertsen, Appl. Phys. Lett. **74**, 2617 (1999).
[4]M. Peuker, Appl. Phys. Lett. **78**, 2208 (2001).
[5]S. Spector, C. Jacobsen, and D. Tennant, J. Vac. Sci. Technol. B **15**, 2872 (1997).
[6]B. Lai, W. Yun, Y. Xiao, L. Yang, D. Legnini, Z. Cai, A. Krasnoperova, F. Cerrina, E. Di Fabrizio, L. Grella, and M. Gentili, Rev. Sci. Instrum. **66**, 2287 (1995).
[7]V. V. Aristov, A. A. Snigirev, Y. A. Basov, and A. Y. Nikulin, in *Short Wavelength Coherent Radiation: Generation and Applications*; Vol. 147, edited by D. T. Attwood and J. Bokor (American Institute of Physics Conference Proceedings, New York, NY, 1986), pp. 253–259.
[8]A. Snigirev, Rev. Sci. Instrum. **66**, 2053 (1995).
[9]T. W. Barbee, Rev. Sci. Instrum. **60**, 1588 (1989).
[10]C. David, Rev. Sci. Instrum. **70**, 4168 (1999).
[11]M. Colburn, S. Johnson, M. Stewart, S. Damle, T. Bailey, B. Choi, M. Wedlake, T. Michaelson, S. V. Sreenivasan, J. Ekerdt, and C. G. Willson, *Step and Flash Imprint Lithography: A New Approach to High-resolution Patterning*, *Santa Clara, CA* (SPIE, Bellingham, WA, 1999), pp. 379–389.
[12]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Science **272**, 85 (1995).
[13]Y. Xia and G. M. Whitesides, Angew. Chem. Int. Ed. Engl. **37**, 550 (1998).
[14]D. J. Resnick, W. J. Dauksher, D. Mancini, K. J. Nordquist, E. Ainley, K. Gehoski, J. H. Baker, T. C. Bailey, B. J. Choi, S. Johnson, S. V. Sreenivasan, J. G. Ekerdt, and C. G. Willson, in *High Resolution Templates for Step and Flash Imprint Lithography*, *Santa Clara, CA* (SPIE, Bellingham, WA, 2002).
[15]B. J. Choi, S. V. Sreenivasan, S. Johnson, M. Colburn, and C. G. Willson, Precis. Eng. **25**, 192 (2001).
[16]T. Bailey, J. Choi, M. Colburn, M. Meissl, S. Shaya, J. G. Ekerdt, S. V. Sreenivasan, and C. G. Willson, J. Vac. Sci. Technol. B **18**, 3572 (2000).