New diamond nanofabrication process for hard x-ray zone plates

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The authors report on a new tungsten-hardmask-based diamond dry-etch process for fabricating diamond zone plate lenses with a high aspect ratio. The tungsten hardmask is structured by electron-beam lithography, together with Cl₂/O₂ and SF₆/O₂ reactive ion etching in a triayer resist-chromium-tungsten stack. The underlying diamond is then etched in an O₂ plasma. The authors demonstrate excellent-quality diamond gratings with half-pitch down to 80 nm and a height of 2.6 μm, as well as zone plates with a 75 μm diameter and 100 nm outermost zone width. The diffraction efficiency of the zone plates is measured to 14.5% at an 8 keV x-ray energy, and the imaging properties were investigated in a scanning microscope arrangement showing sub-100-nm resolution. The imaging and thermal properties of these lenses make them suitable for use with high-brightness x-ray free-electron laser sources. © 2011 American Vacuum Society. [DOI: 10.1116/1.3656055]

I. INTRODUCTION

During recent years it has become important to develop zone plates that can be used with the new and upcoming x-ray free-electron laser sources that operate in the 2–12 keV photon energy range. In addition to the usual challenges with producing x-ray zone plates, i.e., sub-100-nm high-aspect-ratio periodic patterning, these zone plates need to withstand the high heatload that such high-brightness sources will impose upon the optics. Traditionally, high-Z materials, e.g., Ta, Au, Ir, and W have been used for 2 to 12 keV zone plates, but the high heat load can deteriorate the metal or even melt it. Diamond (Di) is considered the optimal zone plate material for such applications due to its high thermal conductivity (2052 W/mK at 300 K) and good optical properties for hard x-rays, i.e., low absorption.

Zone plates focus x-rays by diffraction and can be considered as a circular diffraction grating with radially decreasing linewidth. For focusing and imaging applications, there are two primary properties of the zone plate to consider. Firstly, the resolution is directly proportional to the outermost zone width. Thus a narrow width is desirable, and typical zone widths for fabricated hard x-ray zone plates are in the range of 25 to 100 nm. Secondly, the diffraction efficiency is defined as the fraction of incident light diffracted into a certain diffraction order of the zone plate. Normally, the first order diffraction is considered. The efficiency is primarily determined by the optical material and its thickness but will be decreased due to fabrication errors, e.g., deviation from a 1:1 line-to-space ratio and aspect-ratio dependent etch rate. Figure 1 shows the theoretical diffraction efficiency at 12.4 keV for W, Au, and Di as a function of thickness. As can be seen, the thickness needed for the maximum efficiency requires a very high aspect ratio for narrow zones. In the fabrication, a trade-off must be made between the desired smallest zone width and the highest aspect ratio that can be fabricated. For example, for state-of-the-art hard x-ray Au zone plates, the outermost zone width is 25 nm with a height of 300 nm. Zone plates made from Di have also recently been demonstrated with a width of 100 nm and a thickness of 2.2 μm.

The nanostructuring of Di is primarily achieved via O₂-plasma-based etching. To reach high aspect ratios, different combinations of hardmasks and O₂ recipes have been used. For the Di zone plate, a 500 nm thick hydrogen silsequioxane (HSQ) mask was used with pure O₂ etching. In other published work related to the construction of highly anisotropic Di structures, Ni-Ti and Al have been used as hardmasks.

In the present paper we describe a new nanofabrication process that uses W as a hardmask for making high aspect-ratio CVD Di structures. We present Di gratings with half-pitch down to 80 nm and a height of 2.6 μm. We also show zone plates with 100 nm outermost zones and present the results from diffraction efficiency and imaging experiments conducted at the European Synchrotron Radiation Facility (ESRF) in Grenoble.

II. NANOFABRICATION

Figure 2 shows the nanofabrication process. Electron-beam lithography is used to pattern the zone plate into an e-beam resist. The pattern is then transferred into the Di via three subsequent reactive-ion-etching steps, in which W is used as a hardmask for etching Di. The process steps are described in detail below.

First, the stack of material is prepared. A 400 nm thick layer of W is deposited onto a (5 × 5) mm², 100 μm thick CVD Di substrate (Diamond Materials GmbH) via dc magnetron sputtering (AJA Orion system, 10⁻⁸ mbar base pressure). The sputtering is done at the following parameters: 20 SCCM Ar gas flow, 5 SCCM N₂ gas flow, 3 mTorr pressure,

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75 W power, and 250 °C sample temperature, for a deposition time of 100 min (SCCM denotes cubic centimeters per minute at standard temperature and pressure). Using these parameters yields a low-stress film with little surface roughness. Then, a 20 nm thick layer of Cr is electron-beam evaporated (Edwards Auto 306 System, 10⁻⁶ mbar base pressure) onto the W. Finally, an 80 nm thick positive e-beam resist (Zep 7000, Zeon Chemicals L.P.) is spin-coated on top of the stack and subsequently baked in an oven at 170 °C for 30 min. Electron-beam lithography (Raith 150 system) is used to pattern the e-beam resist. The exposure is done at 25 kV with a typical dose of 100 μC/cm². The pattern is then developed by immersing the sample into hexylacetate for 30 s and then rinsing it in isopropanol and pentane for 15 s and 5 s, respectively. The e-beam pattern is transferred to the Cr layer via reactive ion etching (RIE) (Oxford Instruments, Plasmalab 100 system) in a Cl₂/O₂ plasma at the following parameters: 8 SCCM Cl₂ gas flow, 2 SCCM O₂ gas flow, 20 mTorr pressure, 10 W rf power, 10 W inductively coupled plasma (ICP) power, 20 °C sample temperature, and an etch time of 4 min 45 s. The Cr is then used as a hardmask for etching W with a SF₆/O₂ RIE process. An anisotropic etch in W is important, and good balance between volatile products and sidewall passivation is required. The SF₆ plasma contains radicals that react with W and produce volatile products. O₂ combined with a low temperature produces a nonvolatile film on sidewalls, accounting for sidewall passivation. The recipe used in our RIE system has been optimized with respect to temperature and rf power in order to achieve an anisotropic etch. The recipe parameters are 8 SCCM SF₆ gas flow, 2 SCCM O₂ gas flow, 10 mTorr pressure, 40 W rf power, and a sample temperature of −20 °C. This results in an etch rate of approximately 35 nm/min and an etch time of ~12 min. Some overetching is required in order to clear the W in narrow trenches. A final O₂ RIE step (Oxford Instruments, Plasmalab 80+ system) to etch the Di with W as a hardmask is performed at the following parameters: 10 SCCM O₂ gas flow, 3 mTorr pressure, 100 W rf power, 200 W ICP, and 20 °C sample temperature. The etch rate is 30 nm/min, and thus an etch time of 1 to 3 h is required in order to etch 2 to 5 μm into the Di. Any remaining Cr from the W etch is sputtered away in the O₂ etch within the first 10 min.

Figure 3 displays the anisotropic etch profile of W for 100 and 60 nm half-pitch gratings. The structures are 570 nm high, which yields aspect ratios of 1:6 and 1:10, respectively. Presently, the smallest half-pitch that can be fabricated in W is ~50 nm. This limit is primarily set by the proximity effect in the lithography step, in which incoming electrons are backscattered by the high-Z W, exposing unwanted areas. However, using other resist processes might improve the resolution and make smaller line widths possible.

Figure 4 shows the result of etching Di using W as a hardmask for half-pitches of 100 nm, 80 nm, and 60 nm. When etching the Di, the smallest linewidth that can be transferred from the W pattern is 80 nm. We believe that the main difficulty in etching smaller half-pitches is that W is redeposited on the sidewalls, resulting in the prevention of etching in the narrow trenches. For 100 and 80 nm half-pitch, the gratings are of high quality and yield aspect ratios...
of 26:1 and 32:1, respectively, for a D$_i$ grating structure 2.6 $\mu$m in height. To our knowledge, these are the highest reported aspect ratios in diamond in these small dimensions. As can be seen in Fig. 4 and Fig. 6, a thin white layer (approximately 100 to 200 nm) of W from the hardmask is still present.

Figure 5 shows a D$_i$ zone plate fabricated with the new process. The diameter is 75 $\mu$m and the outermost zone width is 100 nm, resulting in a focal length of 75 mm at 12.4 keV. In Fig. 6, a focused-ion-beam cross-sectional cut of the zone plates has been performed in order to show the zone profile. In the outermost parts with a 100 nm zone width, the etch profile is good and the D$_i$ height is 2 $\mu$m. The O$_2$ recipe results in an aspect-ratio-dependent etch rate, resulting in an etch depth of 4.5 $\mu$m in the inner parts and 2 $\mu$m at the outer zones.

### III. ZONE PLATE CHARACTERIZATION

In order to characterize the fabricated zone plates, diffraction efficiency measurements and 2D imaging were performed at the ID06 beamline at ESRF in Grenoble. The x-ray beam energy during the experiments was 8 keV, and the higher undulator harmonics were suppressed by detuning the monochromator. For these experiments, a zone plate with an outermost zone width of 100 nm, an average D$_i$ etch depth of 2.2 $\mu$m, and a 250 nm remaining W layer was used.

Figure 7(a) shows the experimental arrangement for the diffraction efficiency measurement. A 100 $\mu$m diameter aperture is placed upstream of the zone plate. Behind the zone plate, a 10 $\mu$m pinhole is positioned in the first-order focus in order to record the intensity from this order only. The intensity is measured with an x-ray diode. After a reference intensity measurement (without a D$_i$ window), the ratio of the first-order focus intensity and the reference intensity gives the total diffraction efficiency. In this experiment we...
measured an average efficiency of 14.5%, which corresponds to 80% of the theoretical value at 8 keV. It should be mentioned that in this case, in which a relatively thick hardmask remains, the W contributes to about one-third of the efficiency. Furthermore, the remaining 98 μm thick diamond absorbs about 14% of the radiation. If necessary, i.e., if the zone plate will be used under a very high heatload, any remaining W layer could be removed by a SF6/O2 plasma.

The imaging properties of the zone plate were investigated using an x-ray scanning microscope arrangement, Fig. 7(b). A central stop is placed in front of the zone plate in order to minimize the zeroth order contribution from the beam. An aperture is then positioned a short distance in front of the focus to include only the first diffraction order. Finally, an Au zone plate is placed in the focus as a test sample. The Au zone plate has a 100 nm outermost zone width and a thickness of 700 nm. A piezo-driven stage provides accurate sample translation. The image is reconstructed by recording the intensity at each point and scanning the sample in a raster-fashion. Figure 8 shows a 2D scan of the outermost part of the Au zone plate, where the 100 nm lines and spaces are clearly resolved. The modulation in the image is around 0.04, whereas the contrast in the sample is approximately 0.14. As a first estimation, this would yield a total modulation of 0.28.

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**REFERENCES**


**FIG. 7.** (a) Experimental arrangement for the total diffraction efficiency measurement. (b) Experimental arrangement for imaging, CS = central stop.

**FIG. 8.** 2D image of an Au zone plate with a 100 nm outermost zone width. All zones are clearly resolved, showing the diamond zone plate’s capability of 100 nm resolution imaging.