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Fabrication of low blaze angle gratings by replication and plasma etch

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ABSTRACT

We suggest a new method of making ultra-low blaze angle gratings for synchrotron application. The method is based on reduction of the blaze angle of a master grating by replication followed by a plasma etch. A master blazed grating with a relatively large blaze angle is fabricated by anisotropic wet etching of a Si single crystal substrate. The surface of the master grating is replicated by a polymer material on top of a quartz substrate by nanoimprinting and then transferred into quartz by a plasma etch. Then a 2nd nanoimprint step is applied to transfer the saw-tooth surface into a resist layer on top of a Si grating substrate. The plasma etch through the patterned resist layer provides transfer of the grooves into the Si substrate and results in reduction of the blaze angle due to the difference in etch rates of the resist and Si. We investigated the impact of the replication process on the groove shape, facet surface roughness, and diffraction efficiency of the fabricated 200 lines/mm low blaze angle grating.

Keywords: ALS-U, x-ray diffraction gratings, blaze angle, saw-tooth gratings, nanoimprinting, plasma etching, angle reduction, diffraction efficiency

1. INTRODUCTION

Highly efficient blazed diffraction gratings with very small blaze angles are required for x-ray instrumentation utilized at synchrotron and free electron laser (FEL) facilities for a number of x-ray applications such as tender x-ray scattering and spectroscopy [1]. For example, monochromator of the new Tender beamline of Advanced Light Source-Upgrade (ALS-U) will be equipped with blazed gratings with groove density of 240 – 305 lines/mm and the blaze angles of 0.27 -0.37°. Similar low blaze angle (LBA) gratings are needed for the new Flexon and Cosmic beamlines of the ALS-U [2].

It is challenging to achieve perfect saw-tooth grooves with blaze angles smaller than 1° by existing grating fabrication methods such as mechanical ruling [3], ion beam blazing [4], anisotropic wet etching [5] etc. Several methods for blaze angle reduction were proposed. Ion beam etching (IBE) with Ar ions through a ruled gold layer provides transfer of the saw tooth surface into Si substrate [6]. The reduction of the groove profile is provided by different sputter rates for gold and Si. Adding some amount of oxygen ions introduces a chemical component of the IBE process and enables high reduction factor. We suggested a blaze angle reduction process for low groove density gratings, which allows achievement of extremely low blaze angles [7]. The method schematically shown in Fig. 1a is based on planarization of a high blaze angle grating by a resist layer followed by Reactive Ion Etch (RIE). The reduction of the groove depth and the blaze angle by a reduction factor, R, is achieved due to difference in etch rates, V_{Si} and V_{resist}, of Si and the resist:

$$R = \frac{1}{1 - V_{Si}/V_{resist}} \qquad (1)$$

We demonstrated successful reduction of the blaze angle down to an ultra-low angle of 0.04° and achievement of high diffraction efficiency for the grating coated with a Mo/Si multilayer in the EUV wavelength range [7]. Equation (1) though shows two complications of the planarization/etching approach. To achieve a high reduction factor that is required for the low blaze angle gratings, the plasma etch should provide almost the same etch rates for Si and the resist, i.e. $V_{Si} / V_{resist} \approx 1$. This, however, makes the reduction factor very sensitive to tiny variations of the etch rate ratio, i. e. small deviation of the etch rate ratio from an optimized value results in a huge error in the reduction factor. For example, as the etch rate ratio changes from 0.94 to 0.96 the reduction factor increases from 17 to 25. This can impact the final blaze angle accuracy and in practice requires at least one extra planarization/etch cycle with a low reduction factor to tune the blaze angle to the goal value precisely [7]. Another consequence of the high etch rate ratio is that the resist surface is transferred into the Si with almost no changes. All possible imperfections of the resist surface such as roughness, residual non-planarity, global

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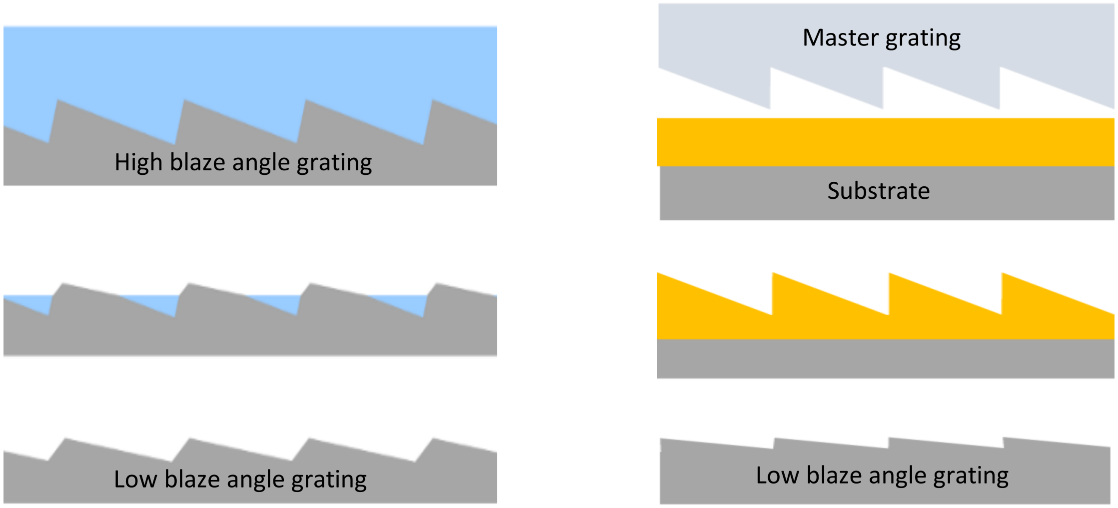
thickness non-uniformity, as well as non-uniformity of the plasma etch process will be transferred into the grating substrate and can compromise the quality of the x-ray optics surface.

In this work we investigate an alternative method of achieving a low blaze angle which is potentially free of the shortcomings of the planarization/etching approach. The concept of the new process is depicted in Fig. 1b. A master blazed grating with relatively high blaze angle is replicated by nanoimprint and then the saw-tooth grooves are transferred into a grating substrate by a plasma etch (Fig. 1b). The oxygen-based plasma etch through the patterned resist layer provides transfer of the grooves into the Si substrate and results in reduction of the blaze angle due to a difference in etch rates of the resist and Si. For the replication/transfer process the reduction factor is directly defined by the etch rate ratio:

$$R = \frac{V_{resist}}{V_{Si}} \qquad (2)$$

The replication/etch process is expected to be less sensitive to the errors in the etch rate calibration owing to linear dependence of the reduction factor on the etch rate ratio. Moreover, any imperfections of the resist surface as well as imperfections of the master grating are expected to scale down by the same reduction factor.

In principle a single replication/etching cycle can provide the required reduction of the blaze angle. In many cases however a double replication is desirable. To replicate the saw-tooth surface of the maser Si grating to the Si grating substrate in a single step one should use a thermal nanoimprinting. The replication/etch cycle should be done twice if a UV curable resist is used: the 1st step is to transfer to a quartz plate and then the 2nd transfer from the quartz mold to the Si grating substrate provides the final reduction of the blaze angle. Also, a single replication step results in flipping of the facet tilt as well as the facet curvature, and the double replication process is needed for Variable Line Spacing (VLS) gratings to preserve the original sign of the slope of the master grating facets along the downstream direction to provide blazing conditions for a positive or negative diffraction order. In this work we report on the first results of a proof-of-principle experiment on fabrication and characterization of a 200 lines/mm blazed grating with the target blaze angle of 0.2° by the double replication process.



(a) (b)

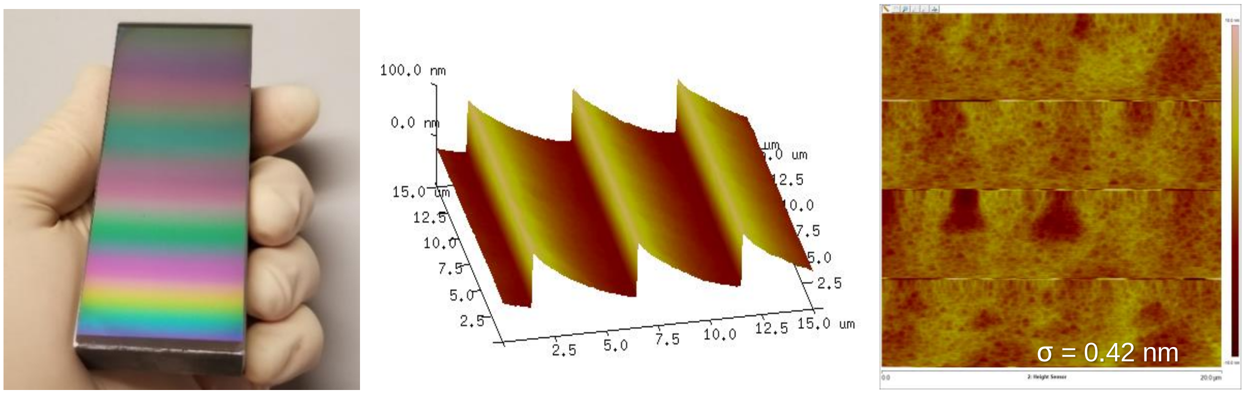
Figure 1. The concept for the blazed angle reduction process via (a) planarization and plasma etch and (b) replication and plasma etch.

2. RESULTS AND DISCUSSION

2.1 Master grating fabrication

A master blazed grating was fabricated by anisotropic wet etching of a 100 mm × 40 mm × 18 mm single crystal Si substrate (Fig. 2a). The surface of the substrate was close to the Si (111) planes and had a miscut angle of 1.8° towards the nearest <110> direction. The fabrication process was described in detail elsewhere [8-9]. Briefly, a 200 lines/mm grating pattern was transferred from a mask to the substrate by a lithography process. Then a lift-off process was applied to create a hard mask composed of one micron-wide stripes of Cr on top surface of the substrate. An anisotropic wet etching with a 20 wt. % KOH solution was applied at room temperature for 2.5 hours to make the slanted facets of the grating. The triangular groove shape was finalized with an isotropic etch in RCA-1 solution.

An AFM image of the grating is shown in Fig. 2b. The blazed facets are substantially curved and the average slope of 1.15° of the facets is much smaller than the miscut angle of 1.8°. This is caused by the low anisotropy of the etching process for the small miscut angles since the deviation of the substrate surface from (111) planes is very small and the difference in the etch rates is small too. This makes KOH etching not efficient for blaze angles smaller than 1° [5]. In principle blazed facet flatness can be improved by longer KOH etching and the blaze angle can approach the miscut angle. However, very long etching is not desirable since it may result in development of etching pits and result in facet surface roughening. A number of defects such as triangular conical pits seen in Fig. 2c results in rather high roughness of the facet surface and causes medium or poor quality of the master grating which is expected to be improved during the blaze angle reduction process.



(a) (b) (c)

Figure 2. A photograph (a) and AFM images (b, c) of the 100 mm × 40 mm × 18 mm Si master grating made by anisotropic etching.

2.2 Quartz mold fabrication

We used UV-curable resist mr-UVCur26SF for the nanoimprint replication of the master grating to a quartz plate of 100 mm × 40 mm × 6 mm in size (Fig. 3a). The master grating and the quartz plate were covered with an anti-sticking coating and an adhesion promoter respectively. A uniform pressure was applied using an air cushion nanoimprint setup [10] and then the resist was cured by UV light. After separation the replica was inspected with AFM (Fig. 3b). The nanoimprint process provided almost perfect replication of the saw-tooth grooves by the resist material (Fig. 3). The groove depth of 95 nm for the resist replica is slightly reduced compared to the 102 nm for the master grating due to nanoimprint resist shrinkage. Since the surface of the blazed facets is concave for the master grating the facets are convex for the replica.

The saw-tooth resist surface was transferred into the quartz plate surface by RIE plasma etch. We used CF_4 gas plasma of 30 W power, which provided an etch rate ratio of 2.1 for the resist and the quartz. As a result of the plasma etch the saw-tooth groove shape with convex facets was well preserved while the depth was reduced from 95 nm down to 45 nm. The patterned quartz plate was used as a mold for the second replication/etching cycle.

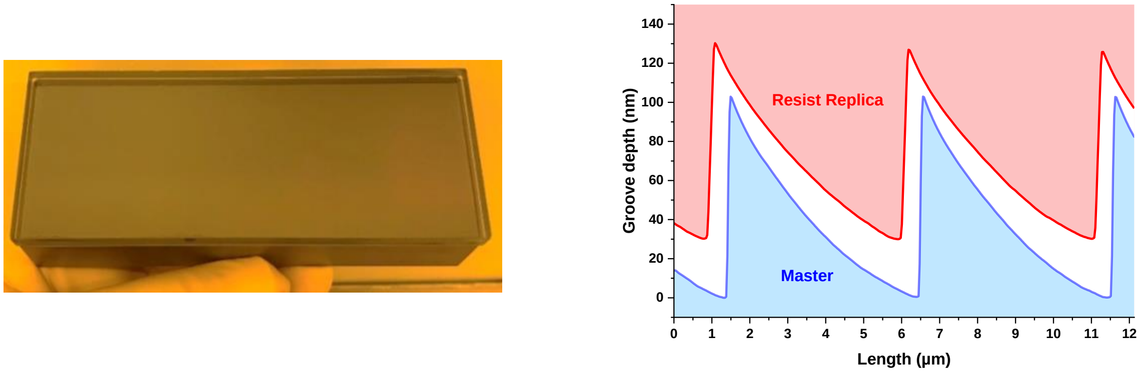


Figure 3. A photograph (a) and profiles of the grooves (b) of the Si master grating and the resist replica on top of the quartz plate.

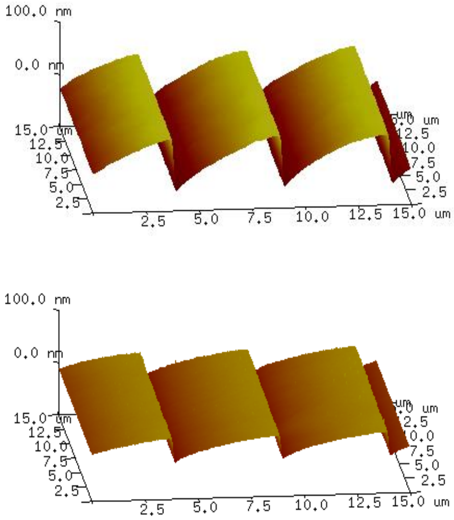


Figure 4. AFM images of the saw-tooth surface of the resist replica (upper) and the saw-tooth surface transferred to the quartz plate by CF_4 RIE plasma etch (bottom).

2.3 Low blaze angle grating fabrication

The same nanoimprint process was repeated to replicate the saw-tooth surface of the quartz mold to the resist layer on top of the Si grating substrate (Fig. 5). Again, the replica preserves the groove shape but the convex facets of the mold converted into the convex facets of the replica, so the original curvature sign of the master grating facets was recovered by the 2nd replication. An RIE plasma etch mixture of CHF_3 and O_2 provided etch rate ration of 2.25 for the resist and Si, and resulted in reduction of the groove depth from 45 nm down to 20 nm (Fig. 6).

The net blaze angle reduction for the double replication process is 5.1. AFM profiles for the master grating and the final low blaze angle grating are shown in Fig. 7a. One can see that the saw-tooth shape of the master grating was highly preserved during the blaze angle reduction process. The apex of the grooves remained sharp, and the width of the anti-blazed facets is unchanged. The slope of 7° of the anti-blazed facets is high enough as compared to grazing angles of incidence of 2° - 3° typical for the soft x-ray domain. The average blaze angle of 2.2° is somewhat higher than the target angle of 2.0° but still within the 10% tolerance.

The double replication results in substantial scaling down of the imperfections of the master grating. Pits and other middle frequency irregularities of the facet surface reduce significantly along with the groove depth during the reduction process (Fig. 7b and 7c). At the same time, a number of small pits are observed on the facet surface (Fig. 7c). These defects were not observed for the master grating and were generated during the plasma etch due to damage of the resist material by the plasma. This problem requires further investigation and a search of materials that are more stable during the plasma etch. Although the number of the pits is high the total area of the pits does not exceed a few percent of the area and should have a limited impact on the diffraction efficiency.

The low blaze angle grating was coated with a 30 nm thick Au coating with a 5 nm thick Cr adhesive sub-layer deposited by dc-magnetron sputtering using Ar sputtering gas.

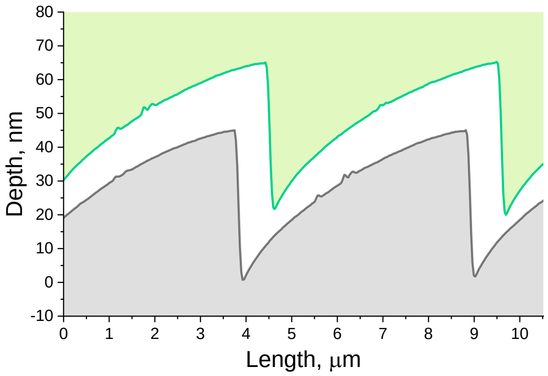


Figure 5. AFM profiles of the grooves of the quartz mold (gray) and the resist replica (green) on top of the grating substrate.

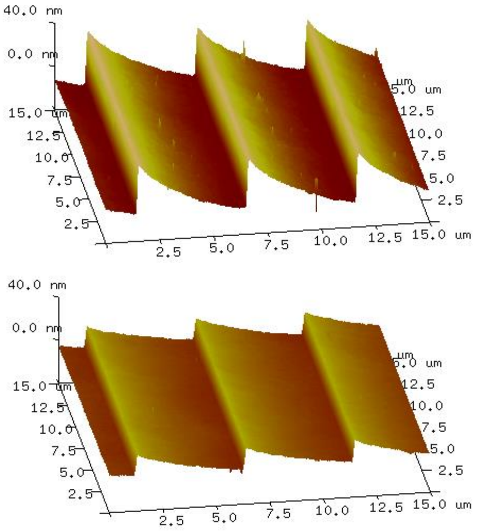


Figure 6. AFM images of the saw-tooth surface of the resist replica (upper) and the saw-tooth surface transferred to the Si grating substrate by ($CHF_3 + O_2$) RIE plasma etch (bottom).

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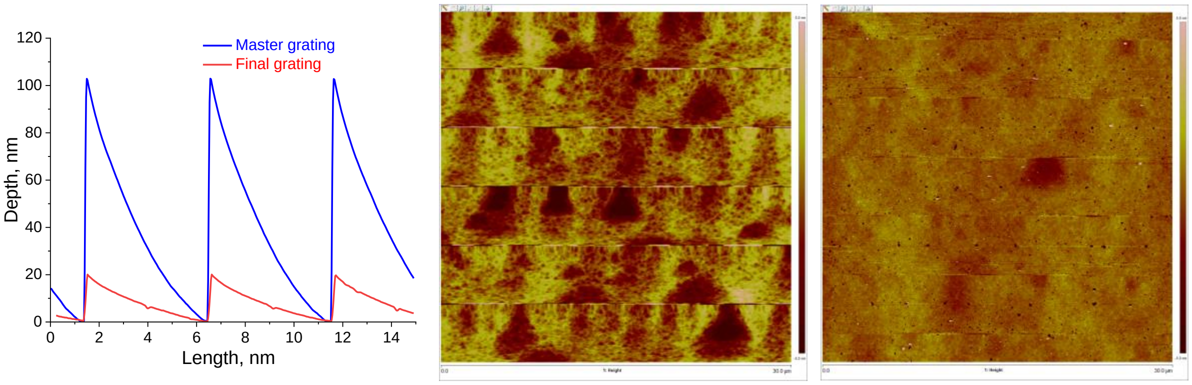

Figure 7. AFM groove profiles (a) and AFM images of the master grating (b) and the final low blaze angle grating (c). The color scale bar corresponds to 10 nm.

2.4 Diffraction efficiency simulations and measurements

Accuracy of the blaze angle reduction process and quality of the fabricated low blaze angle grating were evaluated by diffraction efficiency simulations. The efficiency simulations were performed using the Rigorous Coupled Wave Analysis (RCWA) method using the open source RETICOLO software [11] for ideal grooves with blaze angles of 2.0° and 2.2° as well as for real groove profile measured by AFM (Fig. 8a). The saw-tooth groove profile was discretized over 100 layers and the computations were made with 20 Fourier orders. The refractive index for the grating material (gold) was taken from the CXRO database [12].

The grating is designed to operate at a constant included angle of $2\theta = 174°$ in the energy range of 250-1100 eV. Absolute efficiency of the 1st positive diffraction was computed over the energy range at the respective angles of incidence. Maximum diffraction efficiency of an ideal blazed grating with plane blazed facets and the target blaze angle of 0.2° is expected at an energy of 675 eV (blue curve in Fig. 8b). The efficiency curve for the ideal 0.22-degree blazed grating is slightly shifted towards lower energies (green curve). Non-planarity of the facets of the fabricated low blaze angle grating causes minor reduction of the diffraction efficiency (red curve) versus the ideal grating.

The diffraction efficiency of the gold-coated low blaze angle grating was measured at beamline 6.3.2 [13] of the ALS in the energy rage of 250-1250 eV. The measurements were performed by detector angular scan at incidence angles in the range 87.11°-87.54°, calculated for each energy according to the constant included angle scheme. The measured efficiency shown in Fig. 8b by star symbols is in excellent agreement with the one predicted by the simulations.

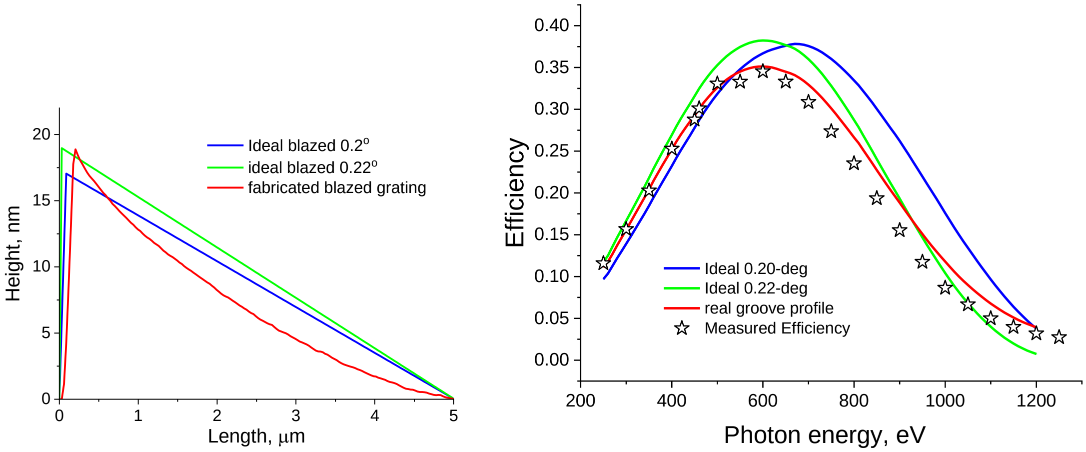

Figure 8. Groove profiles (a) and calculated diffraction efficiency (b) for an ideal grating with the blaze angles of 0.2° (blue), 0.22° (green), and the fabricated low blaze angle grating (red). Experimentally measured diffraction efficiency is shown by star symbols (b).

3. SUMMARY

We developed a new process for low blaze angle x-ray gratings based on blaze angle reduction. The reduction is performed by replication of a master blazed grating with a relatively large blaze angle by a nanoimprint process followed by a plasma etch for the replica. The reduction of the groove depth is achieved owing to the difference in the etch rates of the nanoimprint resist and the Si grating substrate. The process provides achievement of a target low blaze angle with high accuracy and at the same time preserves the saw-tooth groove shape of the master grating. Although the plasma etch of the resist generates some high frequency defects and should be improved in future, the overall quality of the grating improves during the reduction process owing to scaling down of middle frequency imperfections of facets of the master grating. The suggested blaze angle reduction process was verified by fabrication of a 200 lines/mm grating with a blaze angle of 0.22°. The low blaze angle grating demonstrated diffraction efficiency of 35% in the soft x-ray range, which is close to the theoretical value.

ACKNOWLEDGEMENTS

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DISCLAIMER

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