X-ray multilevel zone plate fabrication by means of electron-beam lithography: Toward high-efficiency performances

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X-ray microscopy is a research area in which enormous progress has been made in the last years. The advent of third-generation synchrotons, together with the progress made in the fabrication of new optical devices, such as zone plate, are the two main factors that have influenced the interest around microscopy science. The article will treat the fabrication, by means, exclusively, of electron-beam lithography, of high-efficiency zone plates for x rays in the energy range of hard x rays. We were able to fabricate four-level zone plates made of gold and nickel, whose total thickness is 2.1 \( \mu \text{m} \) for gold, and 4.0 \( \mu \text{m} \) for nickel. The resolution, of the last level, is equal to 0.5 \( \mu \text{m} \). These zone plates have experimental efficiency of about 38% in the case of gold, and 55% in the case of nickel, at the first diffraction order and at 7 keV x-ray energy. To our knowledge, the nickel zone plates have the highest efficiency ever obtained at x-ray wavelengths. © 1999 American Vacuum Society. [S0734-211X(99)13806-X]

I. INTRODUCTION

The strong progress done in the last ten years in microfabrication, and in particular, in electron-beam and x-ray lithography, has moved toward interest in the fabrication of diffractive optics and, in particular, to the Fresnel zone plate (FZP). A circular FZP is a diffraction grating whose period is not constant. The period of the concentric rings are designed so that the incident radiation is modulated in amplitude and/or in phase in order to interfere constructively along the axis in a point that, in all senses, represents the lens focus. The first examples of the FZP for visible light were attributed to Lord Rayleigh in April 1871 and Soret.\(^1\) The one century delay necessary to realize the x-ray FZP must be addressed as due to the extreme difficulty in fabricating the microstructures that form the zone plate. The most critical zones to realize are the outer, which have a width well below 1 \( \mu \text{m} \) and diameters bigger than 100 \( \mu \text{m} \) which must be controlled both in size and shape. For this reason proximity corrections for e-beam lithography are very important in dense micro- and nanopatterning because they can improve the quality of lithographic structures from the geometrical and resolution points of view. Moreover, in the case of a phase-shift FZP, the thickness control must fall in the nanometer range.

Besides the binary profile, it is possible to realize the FZP with a multilevel profile. This geometry offers the double advantage of increasing the efficiency and of introducing selection rules that redistribute useless high diffraction order. However, the fabrication of a multilevel FZP includes difficulties beyond that for a binary ZP, requiring the alignment of subsequent levels deposition with an accuracy of a few nanometers. The microfabrication techniques available to satisfy these demands have been borrowed in the last years from the fabrication of the very-large-scale integrated circuit (VLSI). In this article we present gold and nickel multilevel FZPs fabricated by using electron-beam lithography.

II. ZONE PLATE FABRICATION

The FZPs were patterned using a Leica Cambridge electron-beam lithography system EBMF 10 cs/120, at an accelerating energy of 50 keV and a beam current of 0.5 nA. The electron-beam field size was set at 327.68 \( \mu \text{m} \). The resist used was PMMA 7% 900 K molecular weight whose thickness, per each level, was 1 \( \mu \text{m} \) for the gold FZP and 2 \( \mu \text{m} \) for the nickel FZP. The sample was developed in 1:3 methyl–isobutyl–ketone/isopropyl–alcohol (MIBK:IPA) for 1 min at 20°C.

The final metallic features were obtained by electroplating each FZP level on a silicon nitride membrane 1.5-\( \mu \text{m} \)-thick, 0.75 \( \mu \text{m} \) of gold and 1.35 \( \mu \text{m} \) of nickel. It is important to note that we developed a custom alignment procedure to minimize the misalignment errors during the multilevel fabrication process. An analysis using the scanning electron microscope (SEM), and the subsequent optical testing of the FZP, indicated that the alignment between levels is better than 50 nm per each level.

III. MULTILEVEL FZP: DISCUSSION

A circular FZP is shown in Fig. 1. It consists of a series of concentric zone rings, whose position is determined by

\[
r_{n,l} = \sqrt{\frac{\lambda f}{2L} + n - 2},
\]

where \( \lambda \) is the wavelength, \( f \) is the focus length, and \( n \) is the zone index number (in this formula, it can have only even
phase by $\phi = 2\pi \Delta \delta / \lambda$ and attenuates the field amplitude by a factor of $e^{-2\pi \Delta \delta / \lambda}$, where $\delta$ and $\kappa$ are, respectively, the deviation of the real part from unity and the imaginary part of the refractive index $n_r = 1 - \delta + i\kappa$. The integrated amplitude then results in

$$A^m = \frac{C}{2\pi} \sum_{l=1}^{L} e^{-2\pi \kappa i \Delta l / \lambda} e^{-i2\pi \delta i \Delta l / \lambda} \int_{2\pi i(l-1) / L}^{2\pi i/l} d\theta e^{im \theta}. \quad (2)$$

The phase $e^{im \theta}$ takes into account the contribution of diffraction order $m = 0, \pm 1, \pm 2, ...$, where $\Delta l$ is the thickness of each level and $C$ is an arbitrary intensity for the incoming field. When the diffraction condition $\Delta l L \delta = \lambda$ is satisfied, the previous equation turns out to be

$$A^m = C e^{i2\pi(m/L)} - \frac{1}{i2\pi m} \sum_{l=1}^{L} e^{-2\pi \kappa i \Delta l / \lambda} e^{i2\pi l(L)(m-1)}. \quad (3)$$

From Eq. (3) the FZP efficiency can be derived, i.e., the fraction of the incident intensity delivered to the focus, of the $m$th diffraction order that is defined as $\eta^m = |A^m|^2 / C^2$. It is worth noting that the groove asymmetry of the FZP multilevel geometry introduces many phase contributions that, according to the diffraction order, can interfere constructively or destructively. This allows us to condense the photon flux on the first diffraction order, almost completely suppressing the others. The imaginary term of the sum in Eq. (3) accounts for the selection rules for the diffractive order selection. In the limit of zero attenuation ($\kappa = 0$), it turns out that

$$\sum_{l=1}^{L} e^{-i2\pi [(l-1)/L](m-1)} = \begin{cases} L & \text{if } (m-1) = 0, \pm L, \pm 2L, \ldots \text{ otherwise} \\ 0 & \text{otherwise} \end{cases}. \quad (4)$$

The result is that mostly the first order is active (82%) and that the other active orders have periodicity of $L$. The efficiency is $\eta = 2(1 - \cos(2\pi m/L))(L/m)^2$. For a four-level FZP, the first active order beyond the first is when $n = 5$, whose efficiency is decreased for a factor 1/25 compared to the first order. Respect to a binary lens the third order is suppressed. For $m < 0$ (these are not focusing orders and contribute to background), the first active order is $m = -3$ whose efficiency is decreased by a factor of 1/9 compared to the first order. Higher orders are completely negligible.

When absorption is considered, the efficiency of the first order slightly decreases. For a photon energy of 7 keV, it changes from 81.5% to 72% for a FZP made by nickel and to 55% for a gold FZP. On the other hand, absorption allows forbidden orders to appear, however, leaving their intensity negligible. The zero order, whose intensity is < 4%, is higher.

From a fabrication point of view, there are several factors that can occur and diminish the theoretical efficiency. We summarize them in the following points:

1. Linewidth errors with respect to the nominal value.
2. Thickness errors of the phase shifter for each level.
3. Alignment errors between the levels.

The most severe error is that described at point (3). We demonstrated in a previous paper that the total error budget
of points (1) and (2) can each be, when using e-beam lithography, less than 5%. The alignment errors depend strictly on the resolution of the zone plate. To calculate this error contribution it is still convenient to use the phasor method introduced before. We assign a phasor for each level of a zone. The contribution of each phasor is proportional to the area of the zone with the correct phase. When there are misalignments, a fraction of the area of the zone is not overlapped correctly with the underneath zone. This fraction gives the quantitative effect of misalignment onto the efficiency. For our task it is now enough to calculate the misalignment area of the most critical level, i.e., the last level. From geometrical considerations, without giving the details, it can be shown that the area that contributes to a phase error, $A_{\text{err}}$, can be written as

$$A_{\text{err}} = \delta r_n \left(1 + 2 \sqrt{1 - \frac{\delta}{2 r_n}}\right),$$  \hspace{1cm} (5)

where $\delta$ is the lateral misalignment. $r_n(x)$ is given by relation (1). The fraction of the total area $A_{\%}$ for the last level is

$$A_{\%} = \frac{A_{\text{err}}}{A_{\text{rh. zone}}} = \frac{A_{\text{err}}}{\pi[r_n^2(1) - r_n^2(\frac{1}{2})]} = \frac{\delta r_n \left(1 + 2 \sqrt{1 - \frac{\delta}{2 r_n}}\right)}{\pi r_n^2/2}. \hspace{1cm} (6)$$

This formula can be simplified observing that $\delta \ll r_n$, then

$$A_{\%} \approx \frac{3 \delta r_n}{\pi r_n^2(1)} \Rightarrow \delta = \frac{A_{\%} r_n}{2 \sqrt{n}}. \hspace{1cm} (7)$$

This relation shows that the misalignment $\delta$ becomes very important for the outermost zone. When we require a small $A_{\text{err}}$ value we need to obtain from the fabrication process a $\delta$ value of few tens nanometers. As an example, we evaluate the case of the zone plate presented in this article. In this case, the alignment accuracy $\delta$ necessary to have an $A_{\%} = 0.05 (5\%)$ is: $\delta = 0.05 \mu m$.

Of course, for the inner zones the requirement is less severe. For example, for the first zone $\delta$ would have been: $\delta = 0.35 \mu m$. This explains numerically why we need a complex fabrication tool, as an electron-beam machine, to realize multilevel FZP even if they were thought of many years ago.

On the basis of these considerations, we have fabricated a gold [Figs. 1(a) and 1(b)] and a nickel [Fig. 1(c)] FZP lenses tested for the energy range between 5.5 and 8 keV. The geometrical characteristics of our FZP at an energy of 8 keV are the following: focus length=1 m, diameter=150 \mu m, number of levels $L=4$, and outermost zone width for the fourth level = 500 nm.

The zone plates were tested optically at the x-ray microscopy beamline ID21 at ESRF, which can operate over a large energy range (2–8 keV). Zone plate efficiency measurements were performed at 5.5, 6.0, 7.0, and 8 keV. The source is a low beta straight section of the ESRF storage ring equipped with a 1.5-m-long undulator whose period and number of poles are 42 mm and 39, respectively. The wavelength selection is then made by a Si[111] double-crystal monochromator with a spectral resolution of about $\Delta E/E = 10^{-4}$. The zone plate tests were carried out in the scanning x-ray microscope, which is housed in a vacuum chamber located 51 m from the source. The zone plate and the 10 \mu m pinhole in the focal plane were aligned by means of a microscopic mechanical stage within a mechanical resolution of 0.1 \mu m. For finer scanning resolutions, a commercial piezoelectric-driven monolithic X–Y flexure stage allowed pinhole scanning over a range of ±100 \mu m with a positioning resolution of 10 nm. The efficiency measurement consisted in comparing the flux going through the pinhole with the same diameter as the zone plate and the flux in the focus. A 1 mm$^2$ silicon photodiode was used as the photon detector.

At an energy of 7 keV, the gold FZP provided an efficiency of 38%. The highest efficiency of 55% was obtained with the nickel FSZ at 7 keV. At 5.5 and 8 keV the efficiency is, however, still higher than 40%. In Fig. 2(a) are shown the theoretical and experimental efficiency measurements for the FZP made by nickel. The difference between the two behaviors has to be attributed to the fabrication errors: electroplating growth, linewidth errors, and alignment errors. In our opinion, there is a good chance of reducing the fabrication errors by using the present fabrication method, so that in the near future the theoretical curve can fit the experimental measurement. The FZP focusing capabilities have been tested by performing a knife-edge scan obtaining a spot size $\sigma_x \sigma_y = 2 \times 4 \mu m^2$. Figure 2(b) shows the knife-edge measurements along one direction. This value is compatible with the source size $V \times H = 50 \times 140 \mu m^2$ ($V$ is the vertical and $H$ the horizontal direction) divided by a demagnification factor equal to 57 due to the beamline geometry. The geometrical characteristics of the FZP influences the optical gain $g$, i.e., the ratio between the photon density delivered by the FZP on the focus and the photon density impinging on the FZP. By definition, $g = \gamma (r_n/\sqrt{\sigma_x \sigma_y})^2$, where $r_n$ is the FZP diameter. The experimental value calculated for the Ni FZP at 7 keV is 2000. If we worked at the diffraction limit by reducing the source size, we would have expected a resolution and flux gain, respectively, of $\sigma_x \sigma_y = 1.25 \times 1.25 \mu m^2$ and $g \approx 8000$. Another interesting figure of merit for microscopy is the signal-to-noise ratio (SNR) of a focusing optical device. In microscopy, it is commonly used to place an aperture [order setting aperture (OSA)] of a few microns in the path of the optical axis to increase the signal-to-noise ratio. Figure 2(c) is a two-dimensional (2D) intensity map collected at the focal plane with an OSA with a diameter of 10 \mu m. It is important to notice the low background level compared to the intensity peak [in Fig. 2(b) the $z$ axis is in logarithm scale]. This result is due to the multilevel geometry of the FZP that makes possible the suppression of spurious diffraction orders and reinforces the first-order peak leading to a signal-to-noise ratio equal to 680. With this SNR value, the quaternary FZP can be used even without the OSA aperture, similarly to a standard optical lens.
In order to summarize the results, we point out the main feature of the nickel quaternary FZP:
(a) efficiency close to 60%; (b) only first diffraction order effectively active; and (c) experimental flux gain $\sim 10^3$. Maximum reachable gain $\sim 10^4$.

The difference between the theoretical and experimental efficiency can be attributed to the three main fabrication errors as analyzed previously. We estimated an error of 5% for the linewidth and thickness errors and 12% for misalignment errors. We are confident enough about the possibility of misalignment error reduction, by improving our alignment procedure to a value comparable with the other process errors. In other words, we expect to be able to fabricate quaternary FZPs with an efficiency between 65% and 68% at 7 keV.

IV. CONCLUSIONS

Quaternary FZPs were fabricated by using electron-beam lithography. Their optical performances showed efficiency and a signal-to-noise ratio that resulted, in our knowledge, the highest ever obtained at the hard x-ray regime. The applications of this device are, though, mainly for microscopy. Quaternary FZP can be an ideal condenser lens for an imaging microscope where a high photon flux with a low background has to be delivered in a small portion of the sample to be imaged. In fluorescence microscopy and spectromicroscopy, intense x-ray microprobe is particularly suited for the imaging study of transition elements and heavier metals. The rapid growth of the field of bioinorganic chemistry is mainly due to the recognition of the importance of these species in biological processes. In microdiffraction experiments, where high strain sensitivity is required, the high focusing efficiency allows one to get usable x rays within the desired angular divergence. Moreover, the relative intensity of the primary focused beam with respect to the sum of spurious orders that constitute the background is significantly better (almost one order of magnitude) than that of a binary FZP so that a quaternary FZP can effectively be used as a lens in the optical regime. In conclusion, a quaternary FZP realizes most efficiently an optical lens in the x-ray regime.

With the advent of the consolidation of third generation synchrotrons, multilevel FZP will gain a relevant position as the focusing element in research fields where high efficiency and high signal-to-noise ratio are needed in the x-ray wavelength.

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