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Fabrication of soft x-ray zone plates using carbon, titanium as sacrificial layer

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ABSTRACT

In this paper, we report a novel process for the fabrication of Fresnel zone plate (FZP) in poly methyl methacrylate (PMMA) using ultra-thin titanium film on carbon as sacrificial layer by electron-beam lithography at 30 keV with proximity correction. The process involves fabrication of free standing structure with high mechanical stability. A study was undertaken to understand the interaction of an electron beam in the resist stack, leading to the optimization of the process for high aspect ratio structures in a single step of exposure and development. The negative tone of PMMA was also utilized to provide mechanical strength to the structure. FZPs of 800 μm diameter were designed and fabricated for a capillary discharge based argon x-ray laser operating at 46.9 nm, to have a focal length of 25 mm. Each FZP had 165 zones with an outer most zone width of 1.34 μm, and a numerical aperture of 17 mrad.

1. Introduction

The refractive index "n" of any material ($n = 1-\delta + i\beta$, where δ is refractive index decrement and β is the part leading to absorption) approaches unity in the x-ray regime and hence significant refraction cannot be obtained within a single absorption length [1]. This makes the focusing of x-rays nearly impossible using the conventional optical techniques and hence alternate methods with multi-elements such as compound refractive lenses [2], multi-layer mirrors [3], zone plates [4] etc. are needed to compensate for the small value of the refractive index change due to a single element. Among these different types of optics, diffractive optical element such as a Fresnel zone plate (FZP) has the highest efficiency in the wavelength range of 0.3 nm–5 nm [1]. Due to small absorption losses, FZPs have become popular focusing elements for soft x-rays and extreme ultraviolet radiation at the synchrotron sources. FZPs find application in high resolution imaging and full field soft x-ray microscopy, micro-diffraction, spectroscopy, and fluorescence experiments where x-ray microprobe is required [1,4–6].

Fresnel zone plate consists of a series of alternate transparent and opaque concentric rings (known as zones) with diameter of each zone being proportional to the square root of the zone number, i.e. $r^2{}_n = n\lambda f$, where n is the number of zones, r_n is the radius of the nth ring, λ is the design wavelength, and f is the focal length in the limit $n < 4f/\lambda$. In the *amplitude* zone plates, the diffracted radiation from the transparent zones adds up in phase at the focus [1] and in the *phase* zone plates, where the opaque zones are replaced by phase shifting material, at the design wavelength the resultant amplitude from each zone adds up in phase [5]. The diffraction efficiency of an FZP depends on the thickness and material of the zones. The smallest feature of a zone plate is the width of the outermost zone and it determines the image resolution. Also, the zone placement accuracy required for achieving this resolution is one third the size of the zone [5]. Due to this stringent pattern placement accuracy, specific fabrication methods like laser patterning [7], holography [8], electron beam lithography [9,10], x-ray lithography [11], ion beam lithography [12], atomic layer deposition based sputter and slice processes [13], and few mechanical processes [14] are used.

Generally, FZPs are fabricated on thin, fragile silicon nitride membranes as support which is very fragile to handle during fabrication processes. Fabrication of soft x-ray zone plates is a challenging task because of the slow and tedious writing process coupled with dry etching and electroplating. Lots of efforts are being made world-wide to develop newer techniques for fabrication of FZPs with the purpose of improving their efficiency, spatial resolution, and mechanical stability. Some work has been carried

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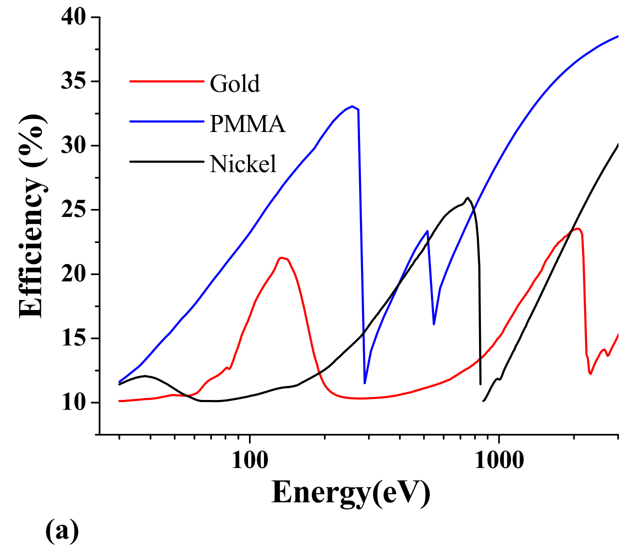
out on PMMA based zone plates using 100 keV electron beam based fabrication techniques [15,16]. In this work, we report fabrication of FZP in polymethyl methacrylate (PMMA) using ultra-thin titanium-carbon films as sacrificial layer. Although the process is well established for intermediate mask fabrication [17], direct fabrication of FZP is not reported using this process, and in the energy range of interest where it is very difficult for any material to be non absorbing, this offers an interesting means of free standing device fabrication (without any support membrane). The FZP fabricated in PMMA film shows very good mechanical strength. The failure point of the various process steps were evaluated and the process was either modified or alternate methods were chosen. Advances have been made in most steps of the process, including the resist, designing pattern for exposure, electron beam exposure, and pattern transfer.

2. Theoretical considerations for the design of FZP for soft x-ray wavelengths

The focusing efficiency is a primary characteristic parameter of zone plates and for a FZP with square zone profile and equal adjacent zone areas is given by Ref. [5].

$$\text{Efficiency}(\eta_m) = \frac{1}{m^2\pi^2}\left(1 + \exp\left(-\frac{4\pi\beta t}{\lambda}\right) - 2\exp\left(\frac{-2\pi\beta t}{\lambda}\right)\cos\phi\right) \quad (1)$$

where 'm' is the diffraction order, 't' is the thickness of the FZP material, 'ϕ' is the phase shift calculated using the expression $\phi = 2\pi\ \delta\ t/\lambda$, for the wavelength λ. The focusing efficiencies [4,5] for different materials at π phase shift condition, for the energy range 30 eV-3 keV have been calculated and are shown in Fig. 1(a) which compares the diffraction efficiency of a phase FZP in soft x-ray regime made with PMMA (the material used in the present work), with nickel (which is the normally used material in the soft x-ray regime), and with gold (which is used for hard x-ray FZPs). It is clear from the curve that the phase shifting efficiency of PMMA in the energy range 30–250 eV increases linearly with log (energy), and is higher than that of gold and nickel. But the advantage of phase shifting is very small as the calculated efficiencies in the range of interest (~30 eV) are very close to that of amplitude zone plates. Fig. 1(b) shows the diffraction efficiency of a phase FZP in PMMA at 46.9 nm. The curve has a peak at a thickness of 107 nm, with a peak diffraction efficiency of 12.2%. However, further increase in thickness decreases the efficiency due to increased absorption (β) and it becomes constant at 10%. From the above theoretical calculations, it follows that for a wavelength of 46.9 nm from the argon x-ray laser [18], the FZP will have a maximum efficiency of 12% for PMMA thickness of 107 nm. As the gain in efficiency by fabrication of phase FZP is very less compared to difficulties in making a mechanically stable, free standing device of 107 nm, hence the structure was fabricated as an amplitude zone plate in a PMMA stack that is measured to be 2.3 μm thick with a theoretical efficiency of 10%. It was targeted to fabricate initially a structure without any support membrane, even though it may be thick and then subsequently modify the processes.



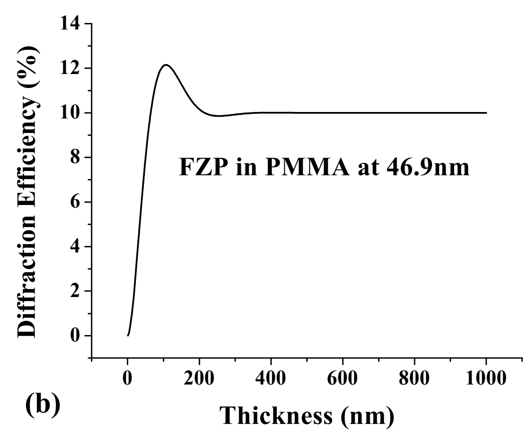


Fig. 1. (a) Maximum theoretical efficiency in the soft x-ray region calculated for PMMA and compared with that for nickel and gold; (b) Variation of diffraction efficiency of phase FZP in PMMA at 46.9 nm.

3. Experimental details

In the present study, for the fabrication of an FZP for 46.9 nm, resist solutions with different molecular weights of PMMA were used. Two resist solutions were prepared, one by dissolving 10 gm of 350 K and another by dissolving 6 gm of 996 K PMMA (99.9% pure, Sigma Aldrich) in 100 ml of anisole (methoxy benzene, 99.5% pure, Merck) in clean room environment. The resist stack was deposited on a float glass substrate. Fig. 2 shows a schematic diagram for the preparation of free standing resist stack and the fabrication of FZP. Low roughness (~0.8 nm) float glass substrates were first degreased in soap solution, washed thoroughly in deionized water, and then dried. Then further cleaning was carried out in methanol and acetone with ultrasonic agitation, and then singe baked at 200 °C for 30 min on hotplate. A carbon layer was coated by thermal arc deposition on the substrate by masking the outer boundary region of ~3 mm of glass substrate during deposition. In the next step, the mask was removed and a layer of titanium (approximately 50 nm thick) was sputter deposited. On this titanium layer, a layer of 10% 350 K PMMA in anisole was spin coated at 2500 rpm, followed by baking at 180 °C in oven for 20 min, the same coating cycle is repeated and then 6% 996 K PMMA in anisole was spin coated on top of 350 K PMMA at 5000 rpm and baked at 180 °C for 4 h in oven. A steel ring was glued to the PMMA stack so as not to impart any stress to the film. After thorough drying, a cut was made along the outer boundary of the ring using a very sharp knife in a single strike. The resist stack was finally housed on an SS ring as the titanium film gets separated from the carbon film very easily. The latter acts as a sacrificial layer. The stack of PMMA was