High-efficiency nickel phase zone plates with 20 nm minimum outermost zone width

M. Peuker

Institut für Röntgenphysik, Georg-August-Universität Göttingen, Geiststrasse 11, 37073 Göttingen, Germany

(Received 1 December 2000; accepted for publication 12 February 2001)

Fresnel zone plates for high-resolution imaging in the soft x-ray regime were fabricated in nickel by a trilevel process, which makes use of electron-beam lithography, reactive-ion etching, and electrodeposition. In order to improve the zone plate’s resolution, which is determined by its outermost zone width, ZEP-7000 electron-beam resist was employed. Residues, which arose during pattern transfer by reactive-ion etching, and which hindered etching in small structures, were suppressed by a cleaning procedure. For improved electrodeposition process control, a nickel electroplating bath was optimized. Zone plates with minimum outermost zone widths of 20, 25, and 30 nm were fabricated, yielding 9.2%, 16.2%, and 18.0% first-order diffraction efficiency, respectively, at $\lambda = 2.4$ nm. © 2001 American Institute of Physics. [DOI: 10.1063/1.1361285]

Microscopy and lithography techniques employing soft x-rays have found numerous applications. In this wavelength range, microscopic Fresnel zone plates (MZPs) are the only available high-resolution imaging optics. A MZP has to combine high resolution with optimal diffraction efficiency to keep exposure times short for all applications and to minimize the x-ray dose applied to the specimen in microscopy.

The first-order spatial resolution $\delta$ of a zone plate, according to the Rayleigh criterion for incoherent illumination, is given by $\delta = 1.22 \lambda / d_{\text{eff}}$, where $d_{\text{eff}}$ denotes its outermost zone width. The first-order diffraction efficiency $\eta_1$, i.e., the fraction of incident radiation that is diffracted into its first order, should be high and uniform even at the smallest zone structures. A decrease in the efficiency with the zone width due to nanostructuring limitations would result in deterioration of the modulation transfer function, and consequently in a loss of image contrast. By applying the coupled-wave theory to a MZP the diffraction efficiency can be calculated for all important parameters.

The aim of this work is to improve the resolution and first-order diffraction efficiency of MZPs for soft x-ray microscopy. The zone height and the zone plate material are the most critical parameters for optimum MZP efficiency. Nickel turns out to be one of the best-suited materials for MZP fabrication for the soft x-ray regime, since it yields high efficiency at moderate zone height at all wavelengths. For $\lambda = 2.4$ nm, which is a typical wavelength for microscopy, a maximum theoretical $\eta_1$ of 23.4% can be obtained using Ni at a zone height of about 250 nm. Hence, for an optimal MZP with an outermost zone width of 20 nm, the aspect ratio is 12.5:1. This is a challenging nanofabrication problem, especially since Ni forms no volatile compounds and therefore cannot be patterned directly by reactive-ion etching (RIE). Thus, electrodeposition techniques have to be used for pattern transfer.

A structured and developed e-beam resist can directly serve as a galvanoform for Ni plating. However, the resist thickness necessary to realize Ni structures of adequate height limits the achievable resolution in e-beam lithography (EBL). To overcome this limitation, trilevel processes were developed that introduce an intermediate copolymer layer for galvanofoming and a hard mask for structure transfer. With a trilevel process the galvanofom height can be chosen independently of the resist thickness. In order to get exact pattern replication in the galvanofom the highly cross-linked copolymer MPEDVB was synthesized from 4-methylphenylethylene and 1,4-divinylbenzene and hardened by high dose x-ray irradiation.

The present work is based on a process using 40 nm PMMA as resist and a 6 nm thick Ti hard mask. The structures were transferred to the Ti by RIE with BCl$_3$, and into the underlying MPEDVB copolymer with O$_2$ (Fig. 1). We have previously shown that at 30 nm linewidth, corresponding to a grating period of 60 nm, galvanofoms with aspect ratios of more than 8:1 can be manufactured. Ni electrodeposition was carried out with a sulfamate-type bath on a plating base of 15 nm Ge and 10 nm Cr. With this process, MZPs with an outermost zone width of 30 nm were made, yielding 15% first-order diffraction efficiency at $\lambda = 2.4$ nm. Considering the x-ray transmission of the plating base and the Si foil substrate of ~70%, the corresponding absolute diffraction efficiency was ~10%. A structured and developed e-beam resist can directly serve as a galvanoform for Ni plating. However, the resist thickness necessary to realize Ni structures of adequate height limits the achievable resolution in e-beam lithography (EBL). To overcome this limitation, trilevel processes were developed that introduce an intermediate copolymer layer for galvanofoming and a hard mask for structure transfer. With a trilevel process the galvanofom height can be chosen independently of the resist thickness. In order to get exact pattern replication in the galvanofom, the highly cross-linked copolymer MPEDVB was synthesized from 4-methylphenylethylene and 1,4-divinylbenzene and hardened by high dose x-ray irradiation.

The present work is based on a process using 40 nm PMMA as resist and a 6 nm thick Ti hard mask. The structures were transferred to the Ti by RIE with BCl$_3$, and into the underlying MPEDVB copolymer with O$_2$ (Fig. 1). We have previously shown that at 30 nm linewidth, corresponding to a grating period of 60 nm, galvanofoms with aspect ratios of more than 8:1 can be manufactured. Ni electrodeposition was carried out with a sulfamate-type bath on a plating base of 15 nm Ge and 10 nm Cr. With this process, MZPs with an outermost zone width of 30 nm were made, yielding 15% first-order diffraction efficiency at $\lambda = 2.4$ nm. Considering the x-ray transmission of the plating base and the Si foil substrate of ~70%, the corresponding absolute diffraction efficiency was ~10%.

---

Figure 1. Trilevel-layer sequence and processing steps for the fabrication of Ni zone plates. After EBL and the development process the structures are transferred via RIE. The resulting galvanofom is filled by Ni electrodeposition. Finally, the mask and the galvanofom are removed by RIE.
To improve the MZP resolution it is necessary to reduce its outermost zone width. However, for periodic structures with line-to-space ratios of 1:1 PMMA resolution is limited to about 60 nm pitch, although single-line resolution can be as low as 5–7 nm. Therefore a new e-beam resist had to be used in the MZP fabrication. Since high resolution negative-tone resist MC6AOAc (Refs. 10 and 14) is too insensitive for exposures of MZPs within a reasonable time with the available EBL system, the positive-tone resist ZEP-7000 (Nippon Zeon Co.) was investigated. Using a 20 nm thick layer of ZEP-7000 resist and n-hexyl acetate as developer, high quality 48 nm period gratings could be made by EBL at 40 kV accelerating voltage. For finer periods the lines became increasingly discontinuous, but even at a 40 nm period a grating with minor errors could be obtained.

Detailed investigations revealed that in the copolymer etching step residues in the trenches hinder pattern transfer, especially for linewidths below 40 nm [Fig. 2(a)]. Linewidth fluctuations are very high in this case. Experiments showed that this effect is independent of the resist used for structure generation. Substituting CBrF₃ or CF₄ for the BCl₃ to etch the Ti decreased the amount of residue significantly, but resulted in unacceptable faceting of the Ti mask.

To overcome these problems, all compounds that can be created in RIE of Ti with BCl₃ were considered. Since all these etching products are soluble in water, RIE was interrupted after Ti structuring and the sample was rinsed with water. Afterwards, the MPEDVB was etched by RIE with O₂. Figure 2(b) shows that after this treatment no more residues exist, and that the linewidth fluctuations are obviously reduced. As a consequence, the etching rate in narrow trenches increased significantly.

For the fabrication of Ni MZPs, precise control of the electrodeposition process is necessary. In order for electrodeposition to occur, a current density greater than threshold has to be applied. At the threshold current density, the plating rate from the commercial nickel sulfamate bath used in previous work is ~10 nm/s. Often the plating current density does not reach threshold immediately upon application. Given the short plating time (10–25 s), a delay of several seconds makes control of the deposited Ni height problematic. Therefore, lower plating rates are desirable.

The sulfamate salt content of the electrolyte was chosen as the parameter for variation of the plating rate, since it can be varied over a wide range without affecting the physical properties of the plated Ni. It was decreased 50% compared to the recommended concentration, resulting in a Ni plating rate of ~2 nm/s and a smooth, pinhole-free Ni deposit.

Using the modified process, structures down to 20 nm could be patterned and transferred. Figure 3 shows scanning electron microscopy (SEM) micrographs of copolymer galvanoform structures with 25 and 20 nm zone widths. The corresponding aspect ratios are 7:1 and 8:1, respectively. It appears that high quality pattern replication in the MPEDVB galvanoform, without structure distortion, and with approximately rectangular zone profiles, can be obtained down to the finest structure sizes. SEM micrographs of fabricated nickel MZP structures are shown in Fig. 4. The zone structures are continuous down to 23 nm, with no bridging. For finer linewidth, the limited e-beam resist resolution results in holes in the MPEDVB zone structures and, consequently, in interconnections between zones in the nickel replication. These defects reduce the local diffraction efficiency of the MZP.

Diffraction efficiency measurements were performed at λ = 2.4 nm at BESSY I. The diffracted first-order radiation was focused into a 5 μm pinhole located in the focal plane and the emerging light cone was detected using a charge coupled device (CCD) camera. Absolute diffraction efficiencies of the measured MZP were obtained by signal integration, and local diffraction efficiencies were calculated based on the geometric setup.

MZPs with minimum outermost zone widths of 20, 25 and 30 nm were fabricated, yielding 9.2%, 16.2% and 18.0% absolute first-order diffraction efficiency, respectively. These efficiencies correspond to 60%, 71% and 83% of the maximum achievable efficiency, based on the optical constants of Ni at λ = 2.4 nm and the galvanoform height. Detailed investigations of the spatially resolved first diffraction order revealed that the theoretical η₁ was obtained down to 50 nm zone width. For smaller structure sizes, the efficiency decreases monotonically with the zone width. For structure
sizes below the e-beam resist resolution limit, an additional efficiency decrease due to the nanostructuring failures was found. But even for 23 and 20 nm wide zones, a local $\eta_1$ of 7.0% and 3.6%, respectively, was measured. The main loss in efficiency for small zone structures can be attributed to a decrease of the nickel plating rate in the narrow, high-aspect-ratio structures, resulting from consumption of nickel ions during electrodeposition, and diffusion-limited electrolyte exchange.\(^{16}\)

Efforts are underway to improve the MZP efficiency homogeneity. For this, the nickel electrodeposition process in small high-aspect-ratio structures will be investigated in detail, making use of variations of the chemical composition of the nickel electrolyte and pulsed plating techniques. Additionally, the structure quality for zone widths below 23 nm is expected to be improved by employing MC6AOAc e-beam resist\(^{14}\) in the nanostructuring process and using a suitable high current EBL system for pattern generation.

The author would like to thank G. Schmahl, D. Rudolph, G. Schneider, P. Guttmann, D. Weinrich, J. Herbst, and T. Gronemann as well as the staff at BESSY I. This work was funded by the German Federal Minister for Education and Research (BMBF) under Contract No. 05 644 MGA.

\(^{5}\) J. Maser, in X-Ray Microscopy IV, edited by V. V. Aristov and A. I. Erko (Bogorodskii Pechatnik, Chernogolovka, Moscow region, Russia, 1994), pp. 523–530.
\(^{7}\) G. Schneider, Appl. Phys. Lett. 73, 599 (1998).