Pulse reverse plating for uniform nickel height in zone plates

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Nickel soft x-ray zone plates are fabricated by through-mask electroplating. The authors report on how a uniform nickel thickness can be obtained over the entire zone plate using pulse and pulse reverse plating. If the plating is carried out at a constant current the nickel thickness has been observed to decrease with radius. This results in lower outer zones and reduced diffraction efficiency in the outer parts of the zone plates. Here they show that the height profile can be controlled by adjusting the current density of the pulses. A high current density is found to primarily affect the edges while a low current density was observed to affect the central parts of the structures. This is true for both cathodic and anodic currents, which means that local plating and dissolution rates can be adjusted to obtain a uniform mass distribution.
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I. INTRODUCTION

Zone plates are diffractive optical elements commonly used in the x-ray spectral range for focusing, imaging, and spectroscopy applications.[1] In order to achieve a high diffraction efficiency, high aspect-ratio features are necessary. In the case of nickel zone plates that are used for soft x-rays, the material is electroplated into a mold. In the following we describe how the electroplating step can be improved by introduction of pulse plating and pulse reverse plating. This results in a uniform mass distribution and an optimal usage of the high aspect-ratio mold.

A zone plate is a circular grating consisting of several hundreds of concentric zones with radially decreasing zone width.[2,3] Zone plates used as microscope objectives typically have a diameter of about 60 μm and an outermost zone width between 20 and 50 nm. An example is shown in Fig. 1. Every second zone is filled with an absorbing or a phase-shifting material separated by a transparent zone (e.g., an empty zone). Two properties are of special interest: outermost zone width and zone height. The achievable resolution in imaging applications and the focal spot size are proportional to the outermost zone width. The zone height and the optical material determine the diffraction efficiency, which is defined as the fraction of the incoming radiation that is diffracted into the first order. Our fabrication is mainly focused on condensers and objectives for soft-x-ray microscopy in the water-window spectral range ($\lambda = 2.4-4.2$ nm).

At these wavelengths, nickel is an excellent material as it has relatively weak absorption and strong phase shift, resulting in a high diffraction efficiency. The optimal zone height varies with wavelength. At $\lambda = 2.48$ nm, which is one of the emission lines from a liquid-nitrogen laser-plasma x-ray source,[4] it is approximately 220 nm which theoretically can give a first order diffraction efficiency above 23%.[5]

Zone plates can be formed either by electroplating the optical material into a mold, as in the case of nickel and gold zone plates, or by etching into the optical material, as with germanium and tantalum.[6,7] The plating mold can be a single layer of e-beam patterned resist or a bilayer or trilayer mold structured by reactive ion etching (RIE). All process steps present their specific challenges. In electron-beam lithography accurate pattern placement and high resolution are needed for aberration-free zone plates with narrow outermost zones.[3] Due to improvements in this field[8] zone plates with outermost zone width of 15 nm have been fabricated.[9] Cryogenic inductively coupled plasma etching has been suggested for reduction of sidewall etching in the etching of high aspect-ratio plating molds.[10] The electroplating step limits the achievable aspect ratio because if the structures in the plating mold are too high they collapse when submerged into the plating solution. We assume that this results from the surface tension forces that occur when the liquid fills the mold. This is similar to the collapse that can occur when high aspect-ratio structures are dried after development.[11] As a result, this is also limiting for the efficiency. To avoid collapse in the plating step efforts have been made to increase the mechanical stability of the plating mold. Using an x-ray hardened polymer zone plates with 20 nm outermost zone width and first order efficiencies as high as 22% have been fabricated.[5] To enable accurate filling of the plating mold we have recently introduced an *in situ* measurement technique, based on light transmission, for accurate control of the plating rate.[12] Another issue is that the plating rate varies over the zone plate so that the filling of the mold is nonuniform. Typically it decreases with radius so that the plated height is the lowest in the smallest features where the aspect ratio of the mold is the highest. Hence, the diffraction efficiency in the outer zones is lowered, which translates into a decreased modulation of the high spatial frequencies in imaging applications. In the present article we report on how pulse and pulse reverse electroplating can be used to obtain a uniform filling of the mold so that its aspect ratio can be fully utilized.

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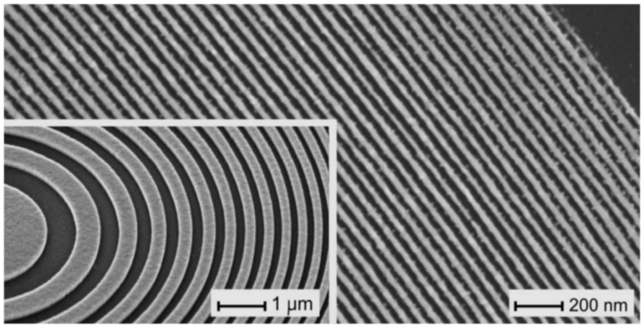

FIG. 1. Outermost and the central part of a nickel zone plate. The outermost zone width is 25 nm and the diameter is 54 μm.

II. FABRICATION PROCESS

Our zone-plate-fabrication process is based on a trilevel resist scheme (Fig. 2). Electron-beam lithography is used for patterning and a plating mold is obtained through two steps of RIE. The polymer mold is then filled by nickel electroplating. In the end, the mold is removed by reactive ion etching. The trilevel stack is prepared on a 50 nm silicon nitride membrane using standard vapor-deposition and spin-coating techniques. The plating base consists of a 5 nm adhesive layer of chromium covered by a seed layer of 10 nm germanium. The plating-mold material is a commercial photoresist (ARC XL-20, Brewer Science). Further details of the fabrication process are found elsewhere.[13]

The electroplating is performed in a commercial nickel sulfamate bath (Lectro-Nic 10-03, Enthone Inc.). When the plating is carried out with a direct current we observe a non-uniform mass distribution. The exact distribution is dependent on the specific mask pattern but two effects generally occur. One is that the plating rate is the highest at the center of the structures and decreases towards the edges. The second effect is that the plating rate in a grating depends on the trench width. Narrow-line gratings plate more slowly than gratings with wider lines. The two effects are illustrated in Fig. 3, which shows height profiles of a $50\times50\ \mu m^2$ unstructured area [Fig. 3(a)] and gratings with different periods [Fig. 3(b)] plated at $\sim5\ mA/cm^2$. In zone plates the effects add up since the zone width decreases with radius. The result is therefore a nickel height that decreases with radius, as shown in Fig. 4(a). This is a problem since it is important to fill the mold completely to achieve high efficiency in the zone plate. At the same time, it must not be overplated since it is then impossible to remove the mold, which results in a

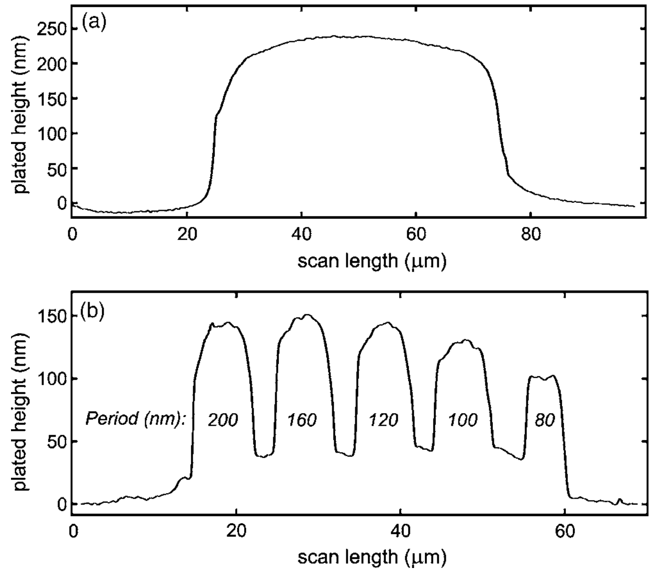

FIG. 3. Profilometer scans showing mass-distribution effects in direct-current plating. (a) Nickel height profile in a $50\times50\ \mu m^2$ unstructured square. (b) Nickel height in gratings of different period.

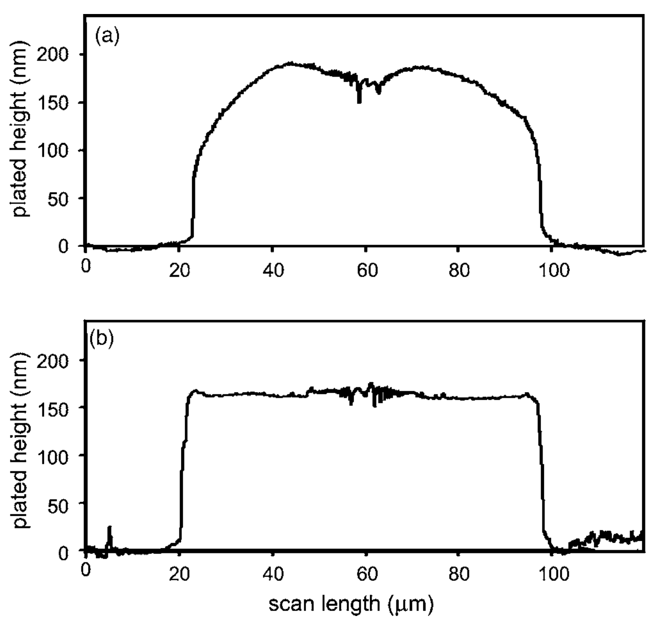

FIG. 4. Height profiles of two zone plates: (a) plated at constant current and (b) plated with optimized pulse reverse plating. The two zone plates are otherwise identical with a 75 μm diameter and an outermost zone width of 50 nm. The oscillations at the middle part of the scans appear because the profilometer tip follows the profile of the relatively large structures at the center of the zone plates.

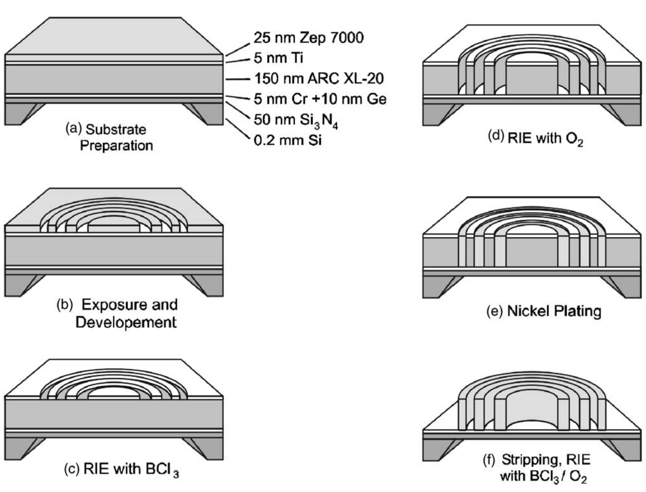

FIG. 2. Trilevel zone plate fabrication process.

useless zone plate (at least for soft-x-ray applications). The observed decrease in plating rate towards the edges of the structures is not expected from basic theory which instead predicts an increased plating rate for these areas.[14] The cause has not been investigated, but one possible explanation is the action of bath additives.[15] The linewidth dependence of the plating rate in gratings, which is shown in Fig. 3(b), could be explained by the fact that the RIE is faster and leaves fewer residues in the wider structures than in the more narrow ones. It is unlikely that mass-transport limitations should be significant since current densities typically below 6 mA/cm^2 were used while good quality deposits are obtained for values as high as 85 mA/cm^2 according to the bath specifications. Although the causes of the described effects are not fully understood the problem with the nonuniform mass distribution can be solved by application of pulse and pulse reverse plating.

III. PULSE AND PULSE REVERSE PLATING

As the name suggests, pulse plating is an electroplating technique in which the current or voltage is pulsed. In pulse reverse the direction of the current alternates so that the sample acts as both cathode and anode. Pulse plating and pulse reverse plating appear in many different applications.[16] In most cases, the motivation is an improved quality of the deposit, such as reduced grain size, increased conductivity, reduced porosity, etc. They have also been suggested for improved mass distribution and deposition quality in plating through holes and vias in the context of copper plating of printed circuit boards.[17,18] In nickel plating, which is most commonly applied in surface treatments for corrosion resistance, pulse plating has been applied for improving deposition quality such as reduced grain size and porosity.[19] Another area where pulse plating and pulse reverse plating are useful is the plating of alloys.[20,21] In the present work we have applied these techniques to obtain a uniform nickel plating of zone plates. Deposit quality has not been investigated. However, there was no indication that the deposit quality was poorer in terms of grain size, stress, or density.

To understand why pulse and pulse reverse plating can be used to address the mass distribution problem described above, it is necessary to understand the influence of current density on mass distribution. If mass-transport effects are ignored, the local current density is determined by the Ohmic resistance in the electrolyte and the resistance associated with the deposition process at the observed point on the cathode surface.[22] The lower the current density, the more limiting the electrochemical reaction at the cathode will be. If the current density is high the mass distribution is instead determined by the resistance in the electrolyte and therefore by the geometry of the sample and the plating cell. As a consequence, the plating rate is normally higher along the boundary of the structures at high currents and a uniform mass distribution is achieved by plating at low current density. In our case we have observed a decreased plating rate near the edges for low current density. Thus, the uniformity is expected to be improved by application of higher current density. With pulse plating it is possible to achieve very high instantaneous current densities at a low mean current. This is important because high mean current density can result in burned deposits due to mass-transport limitations. If the current is reversed (anodic current) nickel from the sample is dissolved. The dependence on current density is basically the same for dissolution as for deposition. In other words, at low anodic current density the rate of dissolution is higher at the central parts of the structure and at high current density the dissolution is faster at the edges. This can be exploited for mass distribution control in pulse reverse plating by finding suitable parameters for the anodic and cathodic current pulses.[23]

IV. EXPERIMENTS AND RESULTS

The electroplating experiments were carried out in a nickel sulfamate bath (Lectro-Nic 10-03, Enthone Inc.) without agitation at a nominal temperature of 52 °C and *p*H of 3.25. A programmable current source (Keithley 6221) was used to drive the current between the electrodes. To be able to control the current density on the cathode a clamp with an isolated contact point was used. The entire bath was mounted on an inverted microscope to enable *in situ* plating rate monitoring.[12] To evaluate the results the height profiles of the samples were measured with a line scan profilometer (Tencor P15). Scanning electron microscopy was also used for height measurements and quality evaluation of the deposit.

In general, and as expected, the relative plating rate along the outer parts was found to increase with increasing pulse current density. However, the parameters needed for uniform mass distribution depend on the type of structure that is plated. For example, a circular disk with a 200 μm diameter was uniformly pulse plated with a pulse current density of approximately 300 mA/cm^2, a pulse length of 1 ms, and an off time between the pulses of 199 ms. In contrast, a zone plate with outermost zone width of 50 nm and a diameter of 75 μm still had a nickel profile that decreased in height towards the edges when plated with a pulse current density of 2.5 A/cm^2, a pulse length of 0.5 ms, and an off time of 499 ms. Thus, the pulse parameters need to be tailored to the specific pattern which is to be plated. Once the appropriate parameters have been determined the results for a specific pattern are reproducible and stable.

Pulse reverse plating was used to further influence the nickel height profile in order to achieve uniform plated thickness in zone plates. High amplitude cathodic current pulses were applied in combination with low amplitude anodic pulses. The cathodic pulses were of high amplitude so that the deposition rate was enhanced in the outer parts of the zone plates. During the low amplitude anodic phase nickel was dissolved most rapidly in the central part. Figure 4 shows the nickel height profile of a zone plate plated at constant current [Fig. 4(a)] and a zone plate plated using pulse reverse plating [Fig. 4(b)]. A clear improvement in uniformity was obtained with pulse reverse plating. The two zone plates were otherwise identical with a diameter of 75 μm and an outermost zone width of 50 nm. The cathodic phase consisted of six pulses with duration of 2 ms each and a peak current density of 2.5 A/cm^2. The off time between the pulses was 498 ms. During the anodic phase a constant anodic current of 12 mA/cm^2 was applied. The overall current was cathodic with mean current density of 4.3 mA/cm^2.

V. DISCUSSION AND OUTLOOK

Pulse plating and pulse reverse plating have become standard procedures in our zone plate fabrication. We have not yet applied these techniques to large area optics, e.g., condenser zone plates, but the results are stable and we expect to apply pulse plating to all types of zone plate optics in the future. It is expected that the uniform nickel height will increase the diffraction efficiency for the outermost zones. For microscopy this would result in improved modulation of high spatial frequencies.

Uniform plating could be useful for fabrication of stacked zone plates. Stacking makes it possible to attain a high aspect ratio, which is interesting for hard x-ray zone plates for which high zones are needed for high efficiency. It also enables the fabrication of multistep zone profiles for increased diffraction efficiency, e.g., blazed zone plates[24] and volume zone plates.[25,26] The stacking can be realized by placing a new resist system on top of the first zone plate and repeating the fabrication process. However, if the plating is nonuniform the errors will add up for every layer. This can be solved by overplating followed by a planarization step. Pulse reverse plating could facilitate the fabrication since there would be no need for planarization if the plating is uniform.

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