Micro-optical elements fabricated by metal-transparent-metallic-oxides grayscale photomasks

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One-step gray-tone lithography is the most effective approach to making three-dimensional (3D) microoptical elements (MOEs). Metal-transparent-metallic-oxide (MTMO) grayscale masks are novel and quite cost effective. In this paper, through the successful fabrication of $3D \operatorname{SiO}_2$ MOEs by gray-tone lithography and reactive ion etching, we thoroughly investigate the practical technique needs of MTMO grayscale masks on metallic nanofilms. Design calibration, pattern transfer, resolution, lifetime, and mask protection of grayscale masks have been verified. This work shows that the MTMO grayscale photomask has good practical applicability in the laboratory and in industry. © 2012 Optical Society of America

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1. Introduction

With the development of the micro-optics system, three-dimensional (3D) micro-optical elements (MOEs) are highly desired because of their wide applications in spectroscopy, acousto-optics, optical interconnects, and quantum electronics [1-7]. However, simple and cost-effective fabrication methods for MOEs are still a big challenge. So far, most of MOEs are fabricated by grayscale mask. Many materials have been deeply researched to utilize their unique features for fabrication of lithography masks. Chalcogenide materials, such as Ge₂Sb₂Te₅ [8] and Ge₂Sb_{1.5}Bi_{0.5}Te₅ [9], show very good potential in thermal lithography and inorganic photoresist. Similarly, titanium film is also studied for laser thermal lithography and demonstrates feasible applications in the fields of optical waveguide [10]. As a branch of lithography masks, grayscale masks are required to have more qualifications compared with common ones. Generally, a good grayscale mask should meet the following requirements: (a) continuous-tone gray level, (b) high resolution, (c) simple process, (d) simple and low-cost material system, and (e) good photothermal stability [11]. Currently, mainstream grayscale masks are based on chrome on glass and highenergy-beam-sensitive (HEBS) glass [2,12]. For the former, specifically designed hole arrays with different size/density in the Cr film can offer grayscale patterns with a lower resolution, but it requires complicated fabrication needing many steps including film deposition, lithography, etching, resist striping, etc. For the latter, masks need to be manufactured by expensive electron beam writing on a very complicated material system [12–14]. These two techniques are both too costly for practical applications.

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An attractive MTMO grayscale photomask technique has been developed recently $[\underline{11,15}]$. Using this method, cost-effective grayscale masks with a 200 nm feature size can be simply fabricated only with two steps: metal film deposition and laser direct writing. However, this method as a practical technique needs to be further studied and verified in many aspects, such as design calibration, pattern transfer, resolution, lifetime, mask protection, and so on.

In this study, by using MTMO grayscale masks, we deeply investigated the issues mentioned above by fabricating practical SiO_2 MOEs from masks design to MTMO grayscale mask fabrication to real 3D structure manufacture.

2. Experiments

Sn thin films (20 nm) were deposited on SiO_2 substrates (thickness of 0.5 mm) by radio-frequency magnetron sputtering (ULVAC ACS400-C4) with a power of 30 W and pressure of 0.60 Pa. The grayscale mask fabrication was executed using a home-built laser direct writer adopting a 532 nm laser (Spectra Physics, Millennia Pro 2i) with a repetition rate of 250 Hz and a scan width of 200 nm smaller than the focused laser spot size (~350 nm). The scan adopts single pulse exposure with a pulse width of 1 ms and power ranging from 0 to 10 mW (corresponding energy density $0-100 \text{ J} \cdot \text{mm}^{-2}$) controlled by an acousto-optic modulator. In the process of mask fabrication, the film sample was placed in an X-Y-Zsample stage (PI, precision 2 nm) at the focal plane of the objective lens (Nikon, NA 0.90, 100×). Laser patterning was controlled by a 10 bit bitmap file transferred from a color or grayscale picture.

Three-dimensional microstructures were fabricated via I-line lithography (SUSS MicroTec MJB4) and finally transferred to SiO_2 substrate by reactive ion etching (RIE) (Sentech ETCHLAB 200). The structures were observed and measured by confocal laser scanning microscope (CLSM, Olympus OLS4000) and surface profiler (Veeco Dektak 150). The optical micrographics of the grayscale masks and MOEs were taken by optical microscopy (Leica DM2500). The ultraviolet-visible (UV-vis) spectrum was measured by an UV-vis-near-IR spectrometer (Perkin Elmer Lambda 950).

3. Results and Discussion

A. Grayscale Photomask Design and Calibration

The design procedure of a grayscale photomask is very subtle and detailed. In the process of encoding the optical density (OD) profile designed into a mask pattern, many aspects need to be taken into consideration to avoid negative effects on the fabricating pattern [16,17]. Commonly, diffraction limitation, optical proximity as well as photoresist resolution during UV lithography will affect pattern transfer from a grayscale mask. Therefore, the designed pattern



Fig. 1. (Color online) Comparison of two types of grayscale masks design. (a) Designed pattern and OD distribution without modification. (b) Pattern and OD distribution after modification.

must be modified to obtained perfect patterns in the lithography.

As shown in Fig. 1(a), a Fresnel lens grayscale mask has an accurate optical density distribution. Thus, the mask requires extremely high-precision lithography to faithfully transfer the pattern into photoresist, which is hard to achieve because of many limitations from diffraction, optical proximity as well as photoresist resolution. Therefore, the designed pattern needs to enlarge the gaps between adjacent rings to avoid these negative effects as shown in Fig. 1(b). By the modification, adjacent rings could be fabricated more steeply and have a better lens profile. Similarly, separation distance between adjacent elements for designing the pattern of array of MOEs should be properly arranged according to lithography parameter and resolution of photoresist. In addition, OD calibration, which dealt with three relationships between laser power and OD of the film, height of photoresist and OD of the film, height of surface reliefs in SiO₂, and height of photoresist, should also be taken into consideration. In our case, the laser power can directly match the surface relief of micro-3D structures based on the fixed parameters during lithography and RIE, largely reducing the complexity of fabrication while obtaining highquality MOEs.

B. Mechanism and Resolution of Sn Grayscale Masks

Here, grayscale masks are fabricated by using Sn metal films composed of superfine grains (≈ 30 nm), which can guarantee a high-resolution fabrication. When a laser pulse hits on the film, transparency (*T*) will turn strictly according to the laser dose



Fig. 2. (a) and (b) Optical images of grayscale patterns for Fresnel lenses fabricated in 20 nm Sn films.

(modulating laser power and/or pulse width) [18]. Therefore, different laser doses can produce different oxidizations, resulting in a different percentage between Sn, SnO, and SnO₂. The ratio of opaque metallic Sn to transparent metallic oxides offers the possibility to make continuous-tone grayscale patterns. Figures 2(a) and 2(b) present optical images of grayscale mask for Fresnel lens.

The feature size of photomasks is a critical parameter in lithography. By taking advantage of optothermal effect induced by laser writing, many kinds of nanostructures with a feature size below 100 nm are fabricated on phase-change films [19–21]. This result has been deeply studied and explained by the feature of thermal mode ablation in the laser direct writing process [21]. In our case, the smallest feature size in Sn film can achieve 200 nm, far beyond the diffraction limit of the 532 nm determined by the optical system [22]. This super-resolution mainly results from a match between Gaussian distribution of the laser beam and the oxidation threshold of Sn material. In the laser direct writing process, the Sn film hit by the laser beam will absorb light energy and converts to a Gaussian temperature field. The oxidation area is smaller than the Gaussian temperature field, with the lower temperature area of the film not reaching the oxidation threshold and is not oxidized. Thus, the reason our grayscale masks can be beyond the diffraction limit of the laser spot and achieve high resolution.

Commonly, the feature size of 3D reliefs in graytone lithography is not only decided by mask, but also by the resolutions of photoresist and the UV optical system. Therefore, MTMO grayscale mask is capable of common gray-tone lithography.

C. Fabrication of 3D Microstructures

The fabrication of 3D microstructures includes two steps: UV lithography and RIE. Two-dimensional (2D) patterns in grayscale masks are first transferred to negative photoresist to obtain 3D reliefs.

Regions with a higher transparency of the grayscale pattern can result in a larger height of the negative photoresist. Then, the 3D reliefs are transferred to substrate by conventional RIE. SiO_2 is a good material for optical applications. Therefore, as an example, we take a SiO₂ phase Fresnel lens to demonstrate the process of fabricating micro-optical structures. Figure 3(a) is a tilt view (60°) of a Fresnel lens (AR-N 4400, Allresist) transferred in photoresist from a MTMO mask, showing a smooth surface and desired surface curvature. In order to have a smooth and precise surface profile in good agreement with our design, the RIE process of 3D SiO₂ microstructure needs to keep a fixed etching ratio of photoresist to SiO_2 . We use mixed CHF_3 / SF_6 and O_2 gas as etching gas, in which F^- ion could react with SiO₂, and O²⁻ reacts with organic photoresist. Table 1 shows relative parameters for different etching ratio under a specific experimental condition.

The surface profile and roughness of the Fresnel lens can be observed and measured instantaneously by using CLSM. Figure 3(b) shows the 3D surface of the SiO₂ Fresnel lens. Figure 3(c) depicts a cross section profile along the diameter and gives a height of 2.75 μ m and a diameter of 150 μ m, faithfully reflecting our design. Apart from the single SiO₂ Fresnel lens shown in Fig. 3(b), we have also made other 3D microstructures including convex lens array, Fresnel lens array, etc.

More interestingly, the MTMO grayscale mask is a dark field mask, so that it is very suitable for making 3D reliefs in negative resists (e.g., SU-8 resist). In comparison, the HBES glass is a bright field mask that can match positive resists. Therefore, the MTMO grayscale masks are a complementation of HBES glass.

D. Results of the MOEs

In order to know whether diffractive optical elements (DOEs) made by our approach are practically usable, we investigated focusing and imaging effects of SiO_2 microlens array, which consists of 3×3 lenslets with



Fig. 3. (Color online) (a) SEM image of the photoresist 3D structure, at a tilt angle of 60° . (b) CLSM image of 3D surface profile of Fresnel lens made of SiO₂. (c) Profile curve of the 3D structure measured along radius of (b), showing the height (2.75 μ m) and diameter (150 μ m) of the Fresnel lens.

Table 1. RIE Etching Ratio Under Different Experiment Condition

Etching ratio of SiO2:photoresist (AR-N 4400)	Gas Flow (sccm)			Power	Pressure
	CHF_3	SF_6	O_2	(w)	(Pa)
1:1.0	30	0	2	90	10
1:1.2	50	0	3	90	10
1:2.0	0	30	4	125	10
1:3.0	0	30	6	125	10

 $30 \ \mu\text{m}$ in diameter, as shown in Fig. <u>4(a)</u> and focusing and imaging effect shown in Figs. <u>4(b)</u> and <u>4(c)</u>. These DOEs demonstrate good optical performance. Likewise, a Fresnel lens and its focusing and imaging effect are shown in Figs. <u>4(d)–4(f)</u>, indicating the DOEs made by MTMO grayscale masks are practicable.

In the progress from designed pattern into 3D structures, the precision of surface profile and structure surface roughness are key parameters to evaluate



Fig. 4. (Color online) Optical microscopy images of micro lens array and single Fresnel lens fabricated on SiO₂. (a) Morphology image, (b) focusing image of the lens array, and (c) letter "A" imaged through the micro lens array. (d)–(f) are the corresponding profile, imaging, and focusing of a single Fresnel lens, respectively. All these images demonstrate the practical performance of these DOEs.



Fig. 5. (Color online) (a) SEM image of the optical wedge structure made of photoresist, in which the line on the wedge indicates the path of surface profiler in measurement. (b) Data measured by surface profiler gives out the size and profile of the optical wedge: 122.40 μ m × 1.85 μ m. (c) CLSM image of the central part of Fresnel lens made of SiO₂. (d) Top line shows the line roughness and the rest a curve shows the profile of the lens along radius of (c).



Fig. 6. (Color online) Optical density data before and after accelerated aging experiments showed the stability of grayscale mask. (a) OD of unexposed mask (red curve) and OD (blue curve) of the mask exposed 20 times (10 h) under lithography I-line (365 nm). (b) OD value of grayscale masks at 365 nm after different time duration from 2 h to 10 h.

the grayscale photomasks. For this reason, an optical wedge has been designed to reflect the accuracy of the tilt angle of 3D structures as shown in Fig. 5(a). By using a surface profiler, the wedge's size has been measured as 122.40 µm in length and 1.85 µm in height. The line scan of the wedge shows that the structure has a very straight profile (line roughness $Ra = 0.012 \mu m$) without big hollow, bulge or slope break shown in Fig. 5(b). Furthermore, we measured the surface roughness of the SiO₂ Fresnel lens' central part, i.e., a spherical crown structure in Fig. 5(c). CPLM gives out the detailed information of the structure surface, including surface roughness Sa = $0.023 \ \mu m$ and a profile shown in Fig. 5(d). These data demonstrate that the calibration of grayscale pattern has appropriately assigned the OD value in the pattern and the final product can faithfully reflect the pattern as required.

E. Lifetime of Sn MTMO Grayscale Photomask

Apart from continuous-tone gray level, high resolution, and easily fabricating, an excellent mask should have a long lifetime and possess good economy. It is undoubted that the lifetime of the mask is a crucial factor for micro-optical fabrication, related with exposure time, photothermal stability, period of validity, and so on. As we reported previously, the thin native oxide layer on the surface of the Sn MTMO grayscale photomask is very stable under room temperature and atmosphere environment, providing a natural protective layer. In fact, one mask has been kept for two years while the grayscale pattern has not obviously changed, and grayscale patterns can still be written on, indicating that it has a long period of validity and can be easily stored.

In order to study our masks' photothermal stability, accelerated aging experiments were carried in which a Sn photomask was exposed half an hour under UV light at a power density of 13 mW \cdot cm⁻². After 20 times of such exposure, the mask did not show significant change in transmittance, as shown in Fig. <u>6(a)</u>. Considering only 10 s for a common exposure, the work time of such Sn mask can reach at least 1800 times. Furthermore, the OD value at 365 nm (I-line) also shows that the Sn masks can keep its OD even after a long continuous exposure time [Fig. 6(b)].

For further lifetime increasing, a layer of $(ZnS)_{85}(SiO2)_{15}$ with high transmittance and good roughness, which is widely used as the protective layer of optical discs, has been coated on the masks. By using the $(ZnS)_{85}(SiO2)_{15}$ protective layer, we can avoid possible scratch in contact lithography as well as natural oxidation during storage, further extending the lifetime of Sn MTMO grayscale masks.

Sn MTMO grayscale photomask has a good economy because of the simple two-step fabrication technique and cost-effective single material. The cost of the masks is estimated no more than 10% of that of the HEBS glass. The good stability, continuous-tone gray levels, and excellent performance in lithography together with the low cost insure our grayscale photomasks are good prospects in the fields of MOEs and DOEs.

4. Conclusion

In summary, we proposed a simple and cost-effective way of manufacturing MOEs using self-developed Sn MTMO grayscale photomasks, which have continuous-tone gray levels and present good performance in grayscale lithography. A series of continuous surface relief MOEs exemplified by Fresnel lenses have been successfully fabricated through this method. By means of CPLM and optical microscopy, we have observed the MOEs and inspected their imaging and focusing effects. Accelerated aging experiments demonstrate the Sn grayscale masks have a very long life time under UV light exposure.

The further investigation on the Sn mask indicates that it has not only continuous-tone gray levels and a good pattern transfer in grayscale lithography, but also long lifetime and easy protection. All these results show that Sn MTMO grayscale mask has a good prospect in the fields of MOEs owing to its devisable calibration, simple fabrication, cost-effectiveness, high resolution, and good stability. This work is supported by National Science Foundation of China (NSFC) (10974037, 61006078), National Basic Research Program of China (NBRPC) (2010CB934102), the International Science & Technology Cooperation Project (2010DFA51970), and a European Union (EU)-FP7 Project (No. 247644).

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