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Efficient reversible phase mask for TiO₂ submicron gratings directly printed on cylindrical surfaces

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Abstract: In this article we present a radial phase mask specially designed and manufactured for direct micro-structuration under UV photolithography of a cylindrical surface covered by a photoresist TiO₂ film. The period of the phase mask is sub-micron (between 480 nm and 720 nm) and allows direct printing on several types of cylindrical components. With this dedicated reversible phase mask we have demonstrated the feasibility of a TiO₂ grating with a period of 960 nm, printed on a SiO₂ cylinder or inside a SiO₂ tube of 8 mm diameter.

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References and links


1. Introduction

The photolithography for printing (sub)-micron periodic structures on cylindrical substrates is based on an innovative and unique solution previously described in [1,2].

This technique, which is based on an illumination through a phase mask composed of a radial diffraction grating, opens up new perspectives in the direction of micro-structuring cylinders with diameters up to several millimeters. One targeted application concerns for example the structuring of receiver tubes in the solar thermal domain, especially in concentrated power plants (40 to 70 mm diameter) [3]. Other application examples can be found in the field of chemical and biological sensors. Indeed, the association of a grating to
the outside of a cylinder, which is inserted inside a tube containing a grating on the inside has already been envisaged and patented for miniaturized high accuracy optical encoders [4].

Our project aims to use the cylindrical photolithography on layers of photo-patterningable and functional type of sol-gel [5,6], which acts as a negative photoresist under UV insolation and allows micro-structuration in a single lithographic step without additional etching. Indeed, the optical (high index) and photo-catalytic (self-cleaning) properties of the TiO$_2$ sol-gel may enable even more interesting applications for example in the environmental domain (in air [7] or water pollutants cleaning). Validation of the TiO$_2$ structuration on cylindrical surfaces at a small-scale will demonstrate the feasibility of this technique for further extrapolation to large substrates.

The use of sol-gel layers requires the use of a different insolation wavelength compared to what is used most commonly for conventional photoresists ($\lambda = 355$ nm instead of $\lambda = 442$ nm). The optical elements for the cylindrical photolithography bench must therefore be completely redesigned including the phase mask. In this article the design of this new phase mask is presented, as well as a demonstration of the first photolithography at 355 nm wavelength of TiO$_2$ gratings on cylindrical surfaces.

2. Principle of the cylindrical photolithography

The principle of cylindrical photolithography uses a phase mask comprising a radial diffraction grating (radial lines) (Fig. 1a). This grating has a spatial period $A_{r,pm}$ variable as a function of the radial position $r$ ($R_i < r < R_e$) on the mask so that $A_{r,pm} = A_{\phi,pm} \cdot r$. $R_i$ and $R_e$ are respectively the internal and external radii of the mask and $A_{\phi,pm}$ its constant angular period expressed in radians. The grating lines are included inside a ring of width $R_e - R_i$.

An enlarged, collimated laser source ($\lambda = 355$ nm) illuminates the whole grating that diffracts the light. Each of the transmitted orders has a diffraction angle dependent on $A_{r,pm}$ and therefore on $r$, so that the orders diffracted from $R_e$ propagate farther than the orders diffracted from $R_i$ before hitting the surface of the cylinder of radius $R$. The interferogram issued from the orders $+1$ and $-1$ must be the same to have a maximum contrast of the interferogram.

The phase mask is centered and set against a cylinder or a tube [Fig. 1(c)]. The orders do not interfere just beneath the mask but each propagates inside the cylinder or the tube. This emphasizes the first constraint of the cylindrical photolithography: the cylinders must necessarily be transparent to the insolation wavelength, whereas the tubes allow for a wider range of materials to be used because the grating will be printed inside of them and they can thus be absorbing.

Although the propagation of orders from the mask and their interferences are more complex than in the case of a linear phase mask, the two types of mask obey the same rule: in the case of normal incidence and considering interference of orders $\pm 1$ only, the period $A_{cyl}$ of the grating printed on the cylinder is half the period of the phase mask [1]:

$$A_{cyl} = \frac{A_{\phi,pm}}{2}$$

Fig. 1. Principle of the cylindrical photolithography a) radial phase mask, b) interferogram issued from the diffracted orders $+1$ and $-1$ and c) cylinder or tube for grating printing.
It follows that the number of fringes is always the same for a given phase mask and corresponds to an integer strictly equal to twice the number of lines of the phase mask. Moreover, the interference fringes are strictly parallel to the axis of the cylinder.

A previous radial phase mask [1,2], designed for a wavelength of 442 nm, was optimized for radial polarization (TE), and an additional element (radial polarizer) had to be used with this phase mask [1,2] to provide the required polarization. The first lithography with this phase mask was done on glass cylinders covered by an organic positive photosensitive resist. In the current work, the goal is to replace the resist by TiO₂ sol-gel and to avoid the necessity of a polarization transforming element, making it necessary to develop a new phase mask operating at shorter wavelengths (355 nm) and polarization independently.

3. Design of the phase mask

The TiO₂ sol-gel is sensitive at a wavelength of 365 nm (±30 nm), and requires a much longer exposure time than usual organic resists. In order to limit the exposure time and avoid global illumination of the sol-gel layer due to undesired mechanical disturbances, the use of a circular polarized light beam is preferable than a radial one, keeping the number of optical components to minimum, reducing losses in the optical path and greatly facilitating the adjustment of the optical setup. Considering the radial geometry of the phase mask, a circular incident polarization requires that the +1 and −1 transmitted diffraction orders have the same intensity whether they originate from TE or TM incidence. Ideally, this desired TE-TM double functionality of the new phase mask permits to suppress the radial polarizer used before (set-up at 442 nm).

Moreover, as pointed out at the beginning, this phase mask must be used with a cylinder as well as with a tube, so the refractive indices of air, of the substrates (tube and cylinder) and of the phase mask must be adapted. This way the latter should operate in both directions, i.e. for light propagating in opposite directions as shown in Fig. 1c. In the case of the cylinder, the beam is incident in air before being diffracted by the mask, whereas the diffraction orders propagate only in the substrate of the phase mask and in the cylinder, both in fused silica (“from Cover to Substrate” or fCtS). In the case of the tube, the mask is turned in the opposite direction and the light propagates in the phase mask substrate before being diffracted in the air by the mask (“from Substrate to Cover” or fStC). In both cases (fCtS or fStC), the diffraction orders propagate in a single medium: air or fused silica.

The intended application requires a cylinder (or tube) of radius \( R = 4 \) mm, and the period of the grating is close to \( \Lambda_{\text{cyl}} = 1 \) μm. From Eq. (1), these choices thus fix the angular period of the phase mask around \( \Lambda_{\phi-\text{pm}} = 500 \) μrad. A width of 500 μm for the mask ring is chosen so as to slightly enlarge the laser beam and to increase the interference fringes contrast because of nearly similar polarization states of the interfering beams. The mask ring is included between \( R_i = 1 \) mm and \( R_e = 1.5 \) mm with a period in between \( \Lambda_{R_i-\text{pm}} = 480 \) nm and \( \Lambda_{R_e-\text{pm}} = 720 \) nm.

For incidence fCtS, the 1st and 2nd grating’s orders always exist between the minimal and maximal period of the phase mask. However, the 3rd order is also present if \( \Lambda_{R-\text{pm}} > 720 \) nm. In order to avoid additional loss of power in the 3rd order and to keep only the 1st and 2nd orders, the choice was to slightly reduce the angular period to \( \Lambda_{\phi-\text{pm}} = 480 \) μrad, so that \( \Lambda_{R_i-\text{pm}} = 480 \) nm and \( \Lambda_{R_e-\text{pm}} = 720 \) nm. For incidence fStC, the choice of an angular period of 480 μrad instead of 500 μrad is irrelevant because the 3rd order does not exist in any case.

To ensure equality of power between the orders +1 and −1, a symmetric grating is required, with a square profile being the most suitable, since this geometry is easy to achieve by etching. Therefore, the line-space ratio and the aspect ratio (depth / period) of the grating will be the variables to be optimized in order to reach the required conditions.

The modeling of the structure is made using the software “MC grating” [8] based on the RCWA method [9]. The collimated monochromatic light at 355 nm, in normal incidence, is
TE or TM polarized. Figure 2 shows in false colors the power transmitted into the +1 order as a function of the grating period (480 nm < \( \lambda_{r-pm} \) < 720 nm) and depth (from 200 nm to 500 nm) for a line-space ratio of 0.538 (35% - 65%) (best value for highest power). In both cases in Fig. 2, for TE or TM polarization, the power fluctuates little over the chosen period \( \lambda_{r-pm} \) range for a given grating depth but the difference between the two polarizations can be relatively large. In the case of fCtS incidence [Fig. 2(a)], for a TE (TM) polarization, the power transmitted in the +1 order is greater than 40% for a depth between 300 nm (350 nm) and 450 nm (> 500 nm). Thus, only the depths between 350 nm and 450 nm allow satisfying the power equality on the whole periods area and for the two polarizations. Similarly, Fig. 2(b) shows the power calculated in the +1 transmitted order at fStC incidence. The results are substantially identical to those presented in Fig. 2(a). Only a depth of 400 nm leads to a nearly constant power transmitted in the +1 order of about 40% for a TE or TM polarization for a line space ratio of 0.538 and for a period range between 480 nm and 720 nm.

![Fig. 2. Choice of the phase mask depth for TE and TM polarizations and for a normal incident wave a) from cover to substrate and b) from substrate to cover.](image)

The line-space ratio of 0.538 was also determined by modeling using “MC grating” as presented in Fig. 3. This modeling shows the power transmitted into the +1 order as a function of the grating period (480 nm < \( \lambda_{r-pm} \) < 720 nm) and of the width of the SiO2 cell (from 150 nm to 400 nm) for a depth of 400 nm. As the period \( \lambda_{r-pm} \) increases linearly as a function of \( r \), width of SiO2 cell increases linearly too in order to keep a constant line-space ratio. It appears clearly that for TE polarization (for fCtS and fStC) a line-space ratio of 1 (continuous line) does not ensure a constant power above 40% for the transmitted +1 order while this condition is respected for a line-space ratio of 0.538 (dashed line) whatever the polarization (TE or TM) and incidence (fCtS and fStC).
Fig. 3. Choice of the phase mask line space ratio for TE and TM polarizations and for a normal incident wave a) from cover to substrate and b) from substrate to cover.

From this modeling, the design of the SiO\textsubscript{2} phase mask is then fully determined: square profile, angular period of 480 \( \mu \)rad, depth of 400 nm and line space ratio of 0.538. Furthermore, Fig. 2 and Fig. 3 show that the efficiency of the +1 order stays above 40\% for a grating depth of 400 \( \pm \) 50 nm and for a line-space ratio comprised between 0.333 and 0.818.

4. Characterization of the fabricated phase mask

The fabrication of the phase mask was carried out in the clean rooms facilities of the University of Eastern Finland on the basis of the design provided by the Hubert Curien laboratory (France) [Fig. 4(a)]. A 5” quartz mask plate with a 100 nm thick chromium layer was used as substrate. The fabrication process was started by coating the substrate with a 250 nm thick layer of AR-P 6200 electron beam resist. After exposure and development, the patterns were first transferred to the chromium layer using chlorine based reactive ion etching process and subsequently to the quartz substrate using a CHF\textsubscript{3} based reactive ion etching process. In the next phase, the sample was coated again with resist, the grating area was exposed with electron beam, the sample was developed and the remaining chromium on the phase-mask was removed from the grating area by reactive ion etching.

The ring in which the phase mask is printed was characterized by SEM [Fig. 4(b)], in order to check the phase mask geometry.

![Fig. 4. Geometry of the phase mask: a) designed and b) fabricated.](image)

On the outside of the ring (\( r = R_e \)), the period is \( \Lambda_{RE-pm} = 740 \) nm but the line-space ratio is 0.818. Although this ratio is not the expected one, the modeling has shown that this difference is acceptable and that the power differences in the +1 and −1 orders for TE or TM
polarization remain small. On the inside of the ring \((r = R_i)\), the measured period is \(A_{R_i\text{-pm}} = 480\) nm for a line-space ratio of 0.6, which is close to the requested design. AFM measurements (not represented here) were also made on the outside of the ring at \(r = R_e\) and showed a square profile grating with a depth of 350 nm instead of 400 nm, remaining within the tolerances.

Figure 5(a) is a photograph of the projected orders 0 and \(\pm 1\) on a white screen (=10 cm) for normal incidence at wavelength 355 nm. The transmitted orders \(\pm 1\) form a homogeneous cone of light over the entire width of the ring and over 360°.

Due to the divergent nature of the orders \(\pm 1\), they cannot easily be separated in the far-field and analyzed independently. However, their presence is revealed by an interferogram [Fig. 5(b)] of contrast superior to 0.77. The optical characterization of the phase mask is carried out by means of a beam analyzer located in the cone of light relatively far away from the phase mask (1 m) so that it can resolve qualitatively the fringes (around 200 \(\mu\)m) as shown in Fig. 5(b).

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5. Realization of TiO\(_2\) gratings on a cylinder and on the interior of a tube

A TiO\(_2\) sol-gel was formulated and prepared as explained in [5, 6]. A layer of 350 nm thickness is deposited by dip-coating, with 10 mm height on the entire contour of the cylinder (or tube) of 15 mm length and 4 mm radius according to the same experimental protocol.

Then, the set-up shown in Fig. 6 is used to print the TiO\(_2\) gratings on cylindrical substrates. It consists of a 100 mW laser at wavelength 355 nm followed by a beam expander, a linear polarizer, a quarter waveplate and the phase mask.

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![Fig. 5. Phase mask: a) Photograph of the projected diffraction orders at 10 cm b) interferogram.](image)

![Fig. 6. Optical bench for cylindrical lithography.](image)
The tube (fStC direction) or the cylinder (fCtS direction) coated with sol gel TiO₂ material is then set in direct contact with the mask, and subsequently continuously illuminated for approximately 10 min. The sample is then developed in an absolute ethanol bath during less than 60 seconds and gradually reveals a grating.

The grating area is recognizable by the diffraction of white light at the surface of the cylinder, revealing an exposed ring of 3.8 mm length positioned 4.6 mm away from the cylinder edge [Fig. 7(a)]. The position and the length of the grating on the cylinder (or tube) can be calculated as demonstrated in [1]. The photograph of the diffraction grating in Fig. 7(b) is obtained by optical microscopy. Even with a high roughness of the surface, the cylindrical photolithography allows printing a 1D diffraction grating in this photosensitive layer with lines parallel to the axis of the cylinder all around the cylinder. Figures 7 (c) and (d) are a 3D AFM image and an AFM profile of the grating, respectively. The 3D image exhibits a relatively homogeneous grating in depth (100 nm - 150 nm) and a constant line-space ratio in the scanned zone. The printed grating has a measured period of $\Lambda_{cyl} = 960$ nm, as calculated from Eq. (1), its depth and its line-space ratio are respectively 120 nm and 2.0. The same development step in ethanol reveals a diffraction grating printed inside the tube. It extends over a length of 2.9 mm at 3.6 mm from the edge with the same period ($\Lambda_{cyl} = 960$ nm). The holistic printing of the diffraction grating all around the cylinder is visible in Fig. 7.

6. Conclusion

This paper presents the design of a reversible phase mask for printing TiO₂ microstructures on cylindrical surfaces. Since the grating works in both opposite directions, one phase mask can be used to print a grating on a cylinder or inside a tube.

The use of the TiO₂ sol-gel as resist material is adding interesting properties to the realized grating, facilitates the fabrication since no separate etching step is necessary, and the non-conventional substrate geometry (on a cylinder or a tube) makes it possible to envisage various applications in the domain of sensors, solar thermal applications or other.

Further work will aim at realizing this kind of microstructures on cylindrical surfaces at larger scale.

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