Fabrication of SiO_2 Phase Gratings by UV Laser Patterning of Silicon Suboxide Layers and Subsequent Oxidation

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UV transparent phase masks are used in various laser applications like fabrication of Bragg gratings in optical fibers or micro patterning by high power laser ablation. Normally they are fabricated by a costly lithographic process including e-beam writing and reactive ion etching. We propose a new fabrication method based on UV laser ablation. The process consists of three steps. First, a silicon suboxide coating (SiO_x with $x < 2$) with a predefined thickness is deposited on a fused silica substrate. Second, due to its strong UV-absorption, this coating can be removed in defined areas by excimer laser ablation at 193 nm or 248 nm leading to the desired phase pattern in form of a binary depth profile. Third, by applying a thermal annealing process, the remaining SiO_x-coating is oxidized to UV-transparent SiO_2, resulting in a UV-grade surface relief element. The precisely defined interface between substrate and layer allows for ablation with exact depth control and perfect optical surface quality. Such SiO_2 phase masks feature a large processed area, high efficiency for VUV to NIR radiation and can be customized e.g. for perfect zero order suppression. Applications of such phase gratings for materials processing with a UV-femtosecond laser are demonstrated. Using the phase gratings in a mask projection configuration, submicron patterns are created in a variety of materials.

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1. Introduction

Diffractive optical elements have become important tools for beam splitting, beam shaping and the generation of complex irradiation patterns [1]. Especially diffractive phase elements, which do not influence the amplitude but only the phase of light, are often applied for low-loss beam homogenization or efficient mask illumination. Phase gratings, i.e. phase masks providing a periodic phase modulation are used to generate discrete diffracted order beams which are then recombined on a sample to create a periodic intensity pattern. The recombination can be accomplished by far field interference of selected beams (holographic exposure), by imaging the mask plane onto the sample, or by utilizing interference in the near field of the phase mask (proximity illumination) [2-3]. The performance of the respective methods depends on the coherence properties of the used laser beams [4]. One main application of such phase gratings is the generation of fiber Bragg gratings by creating an irradiation induced refractive index modulation in the core of an optical fiber [5]. On the other hand, using imaging techniques with sufficient demagnification factors, phase gratings can also be used for patterning surfaces by material ablation [6-7].

The phase shift function of an element operating in transmission is implemented by a lateral variation of the optical path, i.e. either a variation of the refractive index (generated e.g. by ion exchange methods) or by a variation of the geometrical thickness (depth profile at the surface).

For phase elements to be operated in the UV-spectral range, fused silica substrates with a surface relief structure are applied. This relief is usually generated in the surface by e-beam lithography followed by a reactive ion etching process. This complex fabrication process makes such phase masks rather costly; therefore alternative fabrication processes are highly desirable.

Surface texturing by laser ablation is such a flexible and basically simple process. Laser ablation works well to pattern polymeric materials, whereas the treatment of the classical optical materials like glasses or crystalline dielectrics is rather difficult, mainly due to the weak optical absorption of these materials, which is essential for an effective interaction of the laser radiation with the material. Deep UV lasers at wavelengths of 193 nm or 157 nm are used currently to process glasses. This way optical gratings and multilevel diffractive phase element have been fabricated [8-9]. Precise ablation of fused silica is only possible at 157 nm, and even at this wavelength the depth control is difficult, and a surface of optical quality cannot easily be achieved. A method to improve the ablation results for non-absorbing materials consists in the creation of absorbing states in the surface region. Thus the machinability of glass can be enhanced e.g. by the pre-treatment with Ag ions. This way surface relief gratings have been fabricated at a laser wavelength of 355 nm [10].

However, an alternative approach can lead to even better surface quality and more precise depth control. This approach utilizes the deposition of an optical coating on a transparent substrate. The thickness of this coating is chosen according to the desired phase delay. By ablating the coating in defined areas exactly down to the substrate by laser ablation, an element with precise phase control and perfect surface quality is obtained. This method has successfully been applied using polymeric coatings [11] and

UV-absorbing inorganic coatings [12]. However, for operation of the element in the deep UV, a UV-transparent coating, e.g. SiO_2, is required, which is difficult to process by ablation due to its lack of absorption. To solve this problem, in this paper we present the following procedure:

The coating material is first laser processed in a state with sufficient absorption, and then it is transferred into a non absorbing (functional) state by thermal treatment. In the case of silica glass (SiO_2) there is the absorbing metastable state SiO_x with $x < 2$. The UV-absorption depends strongly on x. After annealing SiO_x to SiO_2, the material becomes highly UV-transparent [13].

2. Fabrication of phase gratings in a three step process

The three step process is shown if fig. 1. *I.* A SiO_x-coating ($x < 2$) with a thickness matching to the required phase delay is deposited on a fused silica substrate. SiO_x ($x < 2$) exhibits considerable UV-absorption and is thus better accessible to UV-laser ablation compared to UV-transparent SiO_2. *II.* This coating is then removed in well-defined areas according to the desired phase pattern using laser ablation.

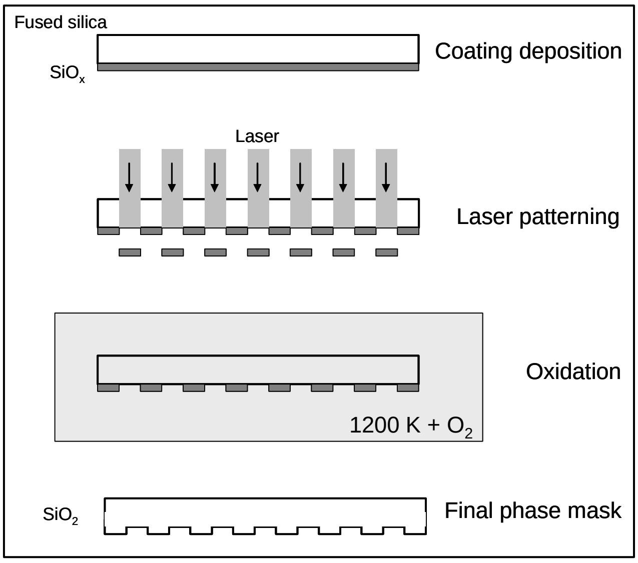

Fig. 1 Process scheme for the laser based fabrication of SiO_2 phase masks

III. By a thermal annealing process (heating to about 1200 K in air) the SiO_x-coating is then oxidized to UV-transparent SiO_2, resulting in a UV-grade surface relief element. Thickness changes during this oxidation have to be taken into account.

For the application as a diffractive beam splitter for optimized 1^{st} order and suppressed 0^{th} order diffraction, a binary phase grating with a duty cycle of 0.5 (equal width of lines and spaces) and a profile depth of $d = \lambda / 2(n-1)$ (λ operation wavelength, n refractive index) has to be fabricated. For our case ($\lambda = 248$ nm, $n \approx 1.5$) a thickness of $d \approx 250$ nm is obtained. Such an element is especially advantageous in combination with a Schwarzschild objective, where in a symmetrical configuration the central beam is obstructed and the 0th order cannot be utilized.

SiO_x thin film deposition was performed by reactive electron-beam evaporation of 99.99% pure SiO_2. A partial oxygen pressure below 10^{-4} mbar was applied to obtain the reduced oxygen content ($x < 2$) in the SiO_x coatings. The substrate temperature was held at 550 K to obtain dense coatings. Typical absorption coefficients of this material are about 1×10^5 cm^{-1} at 193 nm and 2×10^5 cm^{-1} at 248 nm [13].

3. Nanosecond laser rear side ablation of SiO_x

For the patterning of UV-absorbing coatings, ablation in a rear side configuration (the laser light is transmitted through the transparent substrate to the coating layer) has been proven to lead to well defined edges and minimized debris formation [14]. Rear side ablation at a laser wavelength of 193 nm (ArF-excimer laser) was applied here in a mask projection set up. A Cr-on-Quartz mask with 50 µm lines and spaces was imaged into the plane of the coating using a UV-achromate of 100 mm focal length with a demagnification ratio of about 10:1. An achromatic lens was used because in this case the spherical aberration is minimized at the same time. So it is possible to utilize a mask area of 5 mm x 5 mm and process a 0.5 mm x 0.5 mm area with sufficient resolution in one exposure.

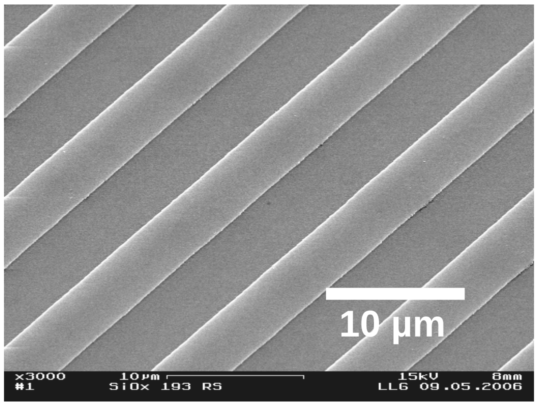

Fig. 2 Pattern of 5 µm lines and spaces made by rear side ablation in SiO_x on fused silica, laser: 193 nm, 20 ns, 540 mJ/cm², 1 pulse

Fig. 2 shows an ablation pattern made with a single laser pulse at a fluence of 540 mJ/cm². Within the irradiated stripes the coating is completely ablated and the substrate is free of residuals. The edge is clear (fig. 3), and the remaining coating as well as the appearing substrate is free of debris. These conditions are achieved within a fluence window of about 400 to 600 mJ/cm². Apparently, similar to what was observed with other coating materials, the coating-substrate interface behaves as a predetermined breaking point, leading to an ablated surface with optical quality. Fig. 4 shows a surface scan made with a profilometer on a sample with about 40 µm wide lines and spaces. The surface roughness in the grooves and on the remaining coating amounts to about 2 nm rms. For comparison, when ablating bulk fused silica at 157 nm, a roughness not better than 15 nm rms could be achieved [9].

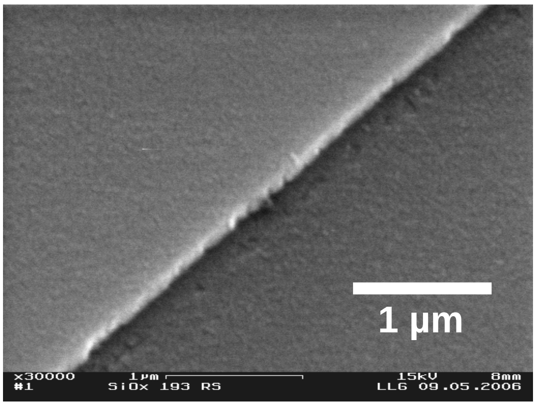

Fig. 3 Ablation edge (detail of fig. 2), step height corresponds to the coating thickness of 250 nm

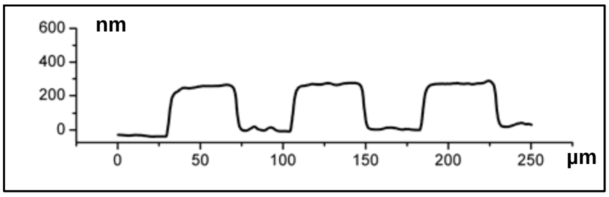

Fig. 4 Surface profile of a SiO_2-phase mask with 40 µm lines and spaces fabricated by the described method; Profile recorded with a Dektak stylus profilometer (note that the ordinate scale is nm, the abscissa is in µm).

4. UV-Femtosecond laser ablation of SiO_x

For the fabrication of high resolution (sub-µm-) patterns the rear side ablation does not seem practicable, because the steepness of the side walls decreases for narrow ablation grooves [14]. On the other hand, front side ablation of such coatings using nanosecond lasers, leads to insufficient quality due to the formation of melt rims [15].

Therefore a short pulse (sub-ps) excimer laser system was used for high resolution patterning of SiO_x. This system delivers pulses of 0.5 ps duration at a wavelength of 248 nm [16]. Front side ablation was performed using mask projection with a Schwarzschild type reflective objective. Using a crossed grating mask the two dimensional periodic patterns shown in figs. 5-6 were obtained. Ablation of the whole layer is achieved with 7 pulses at a fluence of 600 mJ/cm².

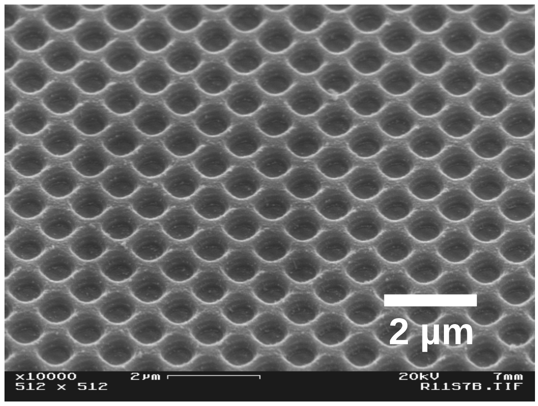

Fig. 5 Two dimensional sub-µm pattern made by front side ablation in SiO_x on fused silica, laser: 248 nm, 0.5 ps, 600 mJ/cm², 7 pulses

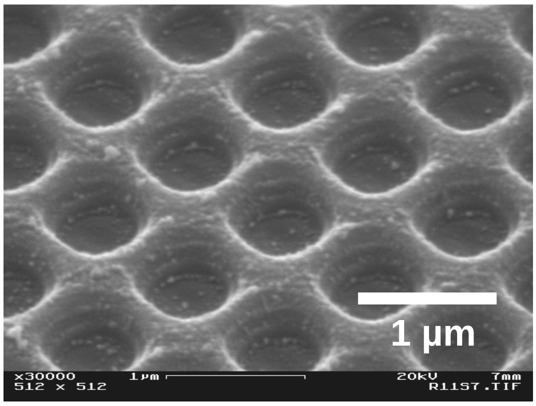

Fig. 6 Detail of fig 5

5. Application of phase masks for sub-µm processing

For the linear phase gratings, diffraction efficiencies of up to 80% in the ± 1st order and suppression of the 0th order down to 1% were measured. These parameters are ideal preconditions for the use of the masks in combination with a Schwarzschild objective: in a symmetric on-axis beam configuration the ± 1st orders interfere in the image plane, and obstruction of the 0th order on the optical axis introduces only a negligible loss. Thus a sinusoidal intensity profile is achieved in the image plane with high transmission efficiency.

The use of such phase masks opens up a wide field of fabrication of periodic surface patterns by laser ablation. Their nearly lossless operation serves for efficient utilization of the provided laser energy. In combination with short pulse lasers, even metals and semiconductors can be patterned with sub-µm resolution. Figs. 7-8 display an example of a periodic pattern fabricated on a steel surface applying mask projection using a mask with 10 µm lines and spaces.

The applied short pulse duration (below 1 ps) ensures a high lateral and depth resolution even in case of materials with high thermal diffusivity, since this pulse duration is typically below the electron-phonon relaxation time, and the thermal diffusion length within the pulse duration (< 1 ps) is negligible. At the same time the applied UV wavelength (248 nm) provides a lateral resolution well below 0.5 µm [17-18]. Moreover, no scanning over the sample surface is necessary since the periodic pattern emerges over a large sample area simultaneously due to the applied mask projection technique. Thus highly efficient fabrication of periodic nano-structures on metal and semi-conductor surfaces can be accomplished, opening up new industrial application fields.

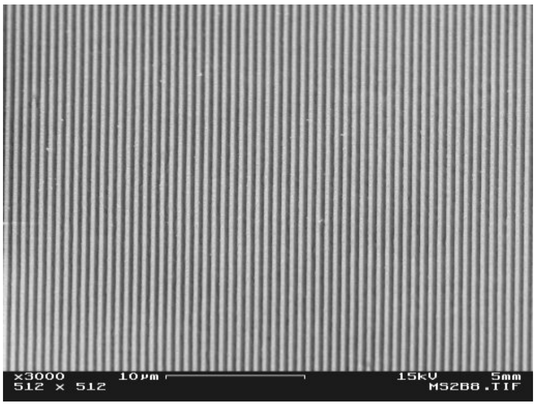

Fig. 7 Sub-µm line pattern ablated in steel, laser: 248 nm, 0.5 ps, 500 mJ/cm², 150 pulses

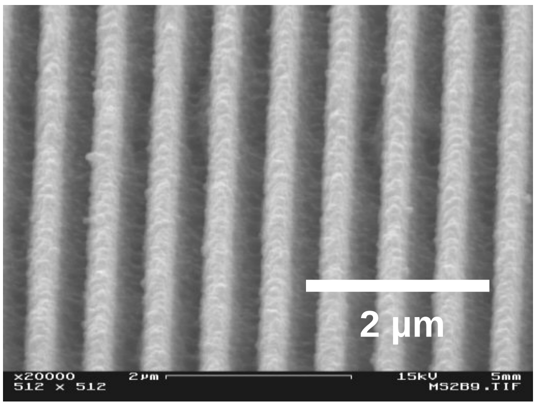

Fig. 8 Detail of fig. 7

Acknowledgments
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