Generation of phase-only holograms by laser ablation of nanoparticulate ITO layers

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Abstract
Phase holograms offer great potential e.g. for laser beam shaping and imaging applications. However, the generation of these structures typically requires multi-step processes which tend to be time-consuming and expensive, especially if high-quality structures are required. In this work we demonstrate a flexible and inexpensive method which allows for the production of binary phase-only holograms by laser ablation of ITO nanoparticle layers. Since these layers are ablated free of residues, accurately defined phase shifts can be achieved. While arbitrarily shaped structures can be generated, the ITO layer thickness can be adjusted in order to freely tune the phase shift for the desired wavelength. In the diffraction patterns generated by the holograms we observed an excellent zero order suppression.

Keywords: hologram, binary, ITO, thin film, laser, ablation, nanoparticle

(Some figures may appear in colour only in the online journal)

1. Introduction
Due to their high optical transmission phase diffractive optical elements offer great potential e.g. for laser beam shaping applications. During the last decades many different methods for the creation of such structures were proposed. The most common methods are lithographic processes that in most cases include a subsequent etching step [1, 2] and mechanical material structuring by diamond turning [3]. Also replication of diffractive elements by hot-embossing or injection-molding in the case of polymers [4, 5] and compression molding for glass materials [6] has been demonstrated. Recently, an appealing approach that includes laser ablation of an UV-intransparent sputtered SiO₂ layer from a SiO₂ substrate and subsequent oxidation of the residual layer parts to SiO₂ at high temperatures was reported [7, 8]. Also the direct ablation of bulk glass and polymer substrates was demonstrated [9, 10]. However, the resulting surface roughness achieved by this technique is not sufficiently low to achieve a constant defined phase shift at visible wavelengths. The ablation of polymer layers from glass substrates by laser irradiation in order to achieve defined phase shifts has been proposed in [11]. Here, the quality of the resulting structure is influenced by uncertainties due to incomplete removal of the polymer coating. In this work we propose a simple and flexible method to generate well-defined binary phase holograms by direct laser ablation of transparent ITO nanoparticle layers from transparent glass substrates. We show the residual free ablation of these layers resulting in an optical quality surface with the average surface roughness of the glass substrate.

2. Methods

2.1. Sample preparation
In our experiments, we used ITO nanoparticles commercially available from Evonik Industries AG. The particles display sizes in the range from 20 nm to about 120 nm according to...
dynamic light scattering measurements, while the primary particle size is about 20 nm. We prepared an ITO suspension by dispersing the nanoparticles in ethanol at a 20 wt% loading. We added 2-[2-(2-Methoxy-ethoxy) ethoxy] acetic acid, also known as trioxycdecanoic acid, acting as a steric stabilizer. This way, agglomeration of the particles prior to deposition of the suspension on a substrate was prevented. A more detailed description of the production of the suspensions can be found in [12]. In order to create ITO nanoparticle layers of uniform thickness by spin coating, we deposited 200 μl of the suspension on 25 mm × 25 mm × 1 mm soda-lime glass substrates and spun at 3000 rpm for 20 s. For fine adjustment of the thickness of the generated layers, we diluted the particle suspensions by addition of ethanol prior to the deposition [13]. A dilution of the initial suspension in the proportion 1:3 (ethanol:initial suspension) resulted in a layer thickness of 540 nm ± 20 nm. To determine the roughness of the layer surface as well as the roughness and diameter of the laser ablations, we used a laser scanning microscope (LSM, Olympus, Lext OLS4000). We also used this device to determine the film thickness. Therefore we introduced scratches on the sample surface and measured several height profiles of these structures. We measured the optical transmission of the films by a UV–Vis spectrometer (Shimadzu, UV-3600).

2.2. ITO layer ablation

If defined structures shall be produced from the ITO layers by laser ablation, the ablation properties i.e. the ablation threshold and the achievable ablation quality in terms of surface roughness need to be investigated. In order to determine the ablation threshold, we prepared several particle layers with a thickness of 540 nm ± 20 nm on soda lime substrates. It has been found previously that the ablation threshold of particulate [14] as well as dense [15] ITO layers slightly depends on the layer thickness and thus needs to be determined for the layer thickness of interest.

For the localized ablation of the particle layers, we used a femtosecond laser (Spectra Physics Spitfire) with a wavelength of 800 nm, a pulse length of about 100 fs, a raw beam diameter of 7 mm and a maximum power of 2.5 W at a repetition rate of 1 kHz. For fine tuning of the laser power we used a polarizing attenuator in the raw beam path. We focused the laser beam onto the sample surface by a 20 × 0.4 NA microscope objective and moved the sample perpendicularly to the laser beam by a xy-stage. In order to ablate the layers, we fired single laser pulses with pulse energies ranging from 4 μJ to 36 μJ onto the ITO samples and pulse energies ranging from 20 μJ to 65 μJ onto the glass substrates.

We measured the diameter of the circular ablations by the LSM. The outcome of the experiment is plotted according to Liu [16] in figure 1. Here, the focal spot diameter used to calculate the laser fluence is also estimated according to Liu to avoid errors arising from defocussing. The ablation threshold is then estimated by linear extrapolation as seen in figure 1. An ablation threshold of 0.63 J cm⁻² ± 0.06 J cm⁻² was found for the ITO layers while the ablation threshold for the glass layer was determined to be 4.17 J cm⁻² ± 0.1 J cm⁻². This difference allows using a laser fluence high enough to ablate the ITO layer while the glass substrate remains unchanged.

To determine the ablation quality we measured the surface roughness within the ablated areas with the LSM. The measurement revealed an average roughness of 2.7 nm ± 0.5 nm along an ablated line with a length of 80 μm. Since the surface roughness of the uncoated substrate displays the same value, a residual-free ablation of the ITO layer down to the glass surface was concluded. The surface roughness of the layer itself over an equally long line turned out to be as low as 8.5 nm ± 0.5 nm.

It is worth mentioning that the steric stabilizer is still present in the particle layers under consideration and coats each particle with a layer of approximately 1 nm in thickness. This estimation is based on the length of the chemical bonds of the stabilizing agent assuming that single molecules of the acid are attached normal to the particle surface. While we believe that the stabilizer does not noticeably influence the optical properties of the layer itself, it has been found in our previous work that the layer ablation is likely to be mediated by the presence of the stabilizing agent [14]. We believe that the particles absorb the incident light and heat up the surrounding stabilizer resulting in its evaporation which efficiently removes the particle layer.

2.3. Hologram generation

We used the commercially available software VirtualLab to calculate a binary phase hologram with a phase shift of π. The desired far field diffraction pattern was calculated to form the letters ‘LPT’. In order to achieve a reasonable quality of the diffraction pattern a hologram size of 500 × 500 pixels was chosen. A 21 × 22 pixel fraction of the obtained hologram structure is shown in figure 2(a). For the unambiguous determination of the diffraction efficiency of the holograms a second benchmark hologram was designed which in the far field only generates a circle in the first quadrant.
The hologram read-out wavelength was exemplarily tuned to 532 nm. The desired layer thickness \( d \) leading to a phase shift of \( \phi \) can easily be calculated by \( \phi \pi \frac{\lambda}{n} = -\frac{d_n}{2} \) (1)/532nm with the real part of the particle layer effective refractive index for a wavelength of 532 nm given by \( n_{532\text{ nm}} = 1.492 \) [17]. The layer thickness \( d \) resulting for \( \phi \pi \) is approximately 541 nm.

As the refractive index of soda-lime glass depending on its chemical composition ranges from 1.5 to 1.6 [18], no significant amount of light will be reflected at the interface between the substrate and the porous layer. A transmission spectrum of an exemplary particle layer on soda lime glass as well as the transmission spectrum of the bare soda-lime glass substrate (red dashed line).

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We used the laser setup to transfer the calculated hologram structure onto the ITO layer by ablation. Two laser pulses with pulse energies of 3 \( \mu \)J were fired at each pixel to ensure complete ablation. The resulting average ablation diameter was 3.7 \( \mu \)m ± 0.2 \( \mu \)m.

Figure 2(b) shows a fraction of the generated structure. It can be directly compared to the corresponding region of the hologram shown in figure 2(a). An exemplary ablation profile of an ablated pixel can be seen on figure 2(c). It clearly shows a very smooth region in the bottom of the ablated area indicating full ablation of the layer.

3. Results

In order to evaluate the quality of the generated structures, we used the collimated beam of a diode-pumped frequency-doubled Nd:YAG laser with a wavelength of 532 nm at a power of 10 mW to illuminate the hologram from the glass side at normal incidence. A photograph of the observed diffraction patterns on a white screen placed perpendicularly to the incident non-diffracted beam at a distance of 1.4 m from the sample hologram is shown in figure 4. The desired structures appear bright to the naked eye while the zeroth and higher orders remain at an acceptable level. The intensity of the zeroth order as well as the diffraction efficiency of the hologram were evaluated by introducing a customized spatial filter behind the hologram and integrating the intensity diffracted into the solid angle of interest by focusing it on a calibrated photo diode [19]. This measurement is particularly simple for the benchmark hologram since the diffraction orders do not overlap and can be easily focused to the detector due to their circular shape. In total for the LPT hologram 52.6% of the diffracted light contribute to the desired diffraction pattern equally distributed among the +1 and −1 order of the hologram while only 5.3% of the total intensity are going to the zeroth order. The benchmark hologram showed even a slightly better performance with an average of 27.9% of the diffracted light going into each the +1 as well as the −1 order (summing up to a total of 55.8%) while 3.8% are going to the zeroth order.
4. Discussion

An ideal binary phase hologram can distribute 40.5% of the incident light intensity into the +1 and −1 order [20]. This fact can easily be understood by considering the simple case of a binary grating with a fill factor of ½ i.e. equally wide areas with a phase shift of 0 and π. It can be shown that such a structure also displays a first order intensity of 40.5% while no light goes to the zero order [21]. A binary hologram can be regarded as a structure being constituted of a sum of binary gratings with different periods. Our measurements did show first order intensities of 26.3% for the LPT hologram and 27.9% for the benchmark hologram. The zero order intensity was 5.3% and 3.8% respectively. While the surface roughness measurement revealed an optical quality surface of our structure, the very low zero order intensities indicate an accurate shift of the phase of light by a value of π.

Obviously a deviation from the ideal case persists. The layer height and surface quality are greatly influencing the diffraction efficiency of such a hologram. However, in the case of our structures the limiting factors are imperfect ablations in between two pixels and the shape of the ablated pixels. While the former causes rather homogeneous scattering the latter causes a variation of the effective fill factor of the grating along a line under consideration.

Considering the residual free ablation process and the tunability in layer height, the approach in general should be very capable of reaching diffraction efficiencies closer to the ideal case. We are currently investigating different methods. A possible approach is improving the ablation process by introducing overlaps between adjacent ablations. A further improvement for pixel sizes on the order of tens of microns can be achieved by introducing an appropriate beam shaping mechanism e.g. square shaped pixels in order to tune the shape of the individual ablations.

5. Conclusion

In this work we demonstrated a simple and flexible method for the generation of arbitrarily shaped binary phase only holograms by laser ablation of ITO nanoparticle layers from glass substrates. The layer generation is done by spin coating of particle suspensions and produces optical quality surfaces under ambient conditions. Due to residual-free layer ablation an accurately defined phase shift i.e. high quality true binary steps can be introduced. Since the dispersion of the material is known accurately, the magnitude of the phase shift for a particular wavelength can be tuned by adjusting the layer thickness. Due to the high transparency of ITO over the entire visible spectrum holograms can be prepared for all visible wavelengths. Compared to approaches like ablation of bulk material, the laser fluence only controls the lateral size of the ablations while the ablation depth is fixed at a desired value. The produced holograms already showed a very low zero order intensity, and the diffraction efficiency has a good potential to be increased by improving the ablation process e.g. by introducing spot overlaps or by beam shaping.

While the demonstrated hologram structure was only about 2 mm by 2 mm in size, it should be easily extendable to a size up to a few centimeters. Using a high repetition-rate ultra-short pulsed laser the processing time should remain on the order of tens of seconds. Being simple and inexpensive, the approach can be used for the production of individual phase masks e.g. for beam shaping or imaging applications.

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