Summary of the Ph.D. thesis

Production and analysis of optical gratings and nanostructures created by laser based methods

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Introduction

After the invention of lasers the favorable features of laser light have been widely utilized by numerous fields of applications. Consequently, the lasers, laser systems and laser-based instruments and diagnostic methods have become essential tools of both basic and interdisciplinary (medical, biophysical, and chemical) scientific research, and also of industrial production.

The micro- and submicrometer size surface structures are usable as free standing or integrated parts in diverse application fields as optical spectroscopy, microelectronics and sensorics. In these applications, sometimes necessary to create microstructured surface pattern on a transparent substrate, on films deposited on a substrate or on the tip of an optical fiber. The micropattern could be a periodically modulated surface or a surface with special morphology, which consequently has physical activity. Example to the prior is one of the most important periodic pattern, the *diffraction grating*, while example to the latter is the substrate for *surface enhanced Raman scattering*.

The diffraction gratings established and supported the progress of spectroscopy since the end of 19^{th} century, with the opportunity to reveal the energy states of atoms and molecules of the (visible) universe, by the examination of emission and absorption spectra of various specimens. In present, the production of the spectrum of a source (the light decomposed to its components having different wavelength) is routinely made by instruments which disperse the input light by a diffraction grating. Moreover, the grating coupled waveguides - which consists of a grating created in a film deposited onto a substrate – can couple discrete modes of lightwaves in and out from the film. It is possible to make sensors by the help of such waveguides, which are highly sensitive to chemical and biological components.

Several techniques have been developed to microstructure transparent materials, from which the indirect laser based techniques proved to be more efficient than direct ablation methods. One of them is the *laser-induced backside wet etching*, in which the backside of the transparent sample is etched by consequence of the laser energy deposited in a liquid absorbed, which is in contact with the backside of the target. The resulted surface quality and the controllability of the process is exceptionally high.

The present study is based on my results achieved by the *laser induced backside wet etching* technique regarding the fabrication and examination of transmission gratings etched into plane transparent targets, the replication of those into bulk metal samples, and the production of nanostructures on optical fiber tip. During my work I aimed to create and examine surfaces which are relevant for present applications and/or will have application in some field in the future.

Scientific background

Numerous methods have been developed in the last decades to produce permanent surface structures into solid targets with submicrometer resolution.

The **multistep methods** can be grouped regarding that the desired surface pattern is realized by a procedure involves the preparation of (resist) mask on the target and subsequent etching, or the pattern is created by a casting (master-replica) process, where the surface of a mold (master) is transferred into the replica.

Upon a master-replica process first the etalon mold (master) is created by a method requires high accuracy, then its surface pattern is transferred (without imaging) into numerous samples (replica). This method is used, for the series production of diffraction gratings, where the master gratings created by the help of special ruling engines or by holographic recording technique. During the replication a liquid resin layer is deposited on a substrate and it is mechanically contacted and pushed to the master grating, which procedure results that the inverse surface profile of the master's is transferred into the replica.

The lithographic techniques are based on the preparation of a high resolution mask, recording, selective etching of exposed parts and the subsequent etching of the target material uncovered by the resist mask by various etching techniques. The removing of material of the target is generally realized by ion beams created by the acceleration of heavy ions, which removes the material through mainly physical interaction (ion beam etching), or by the acceleration of parts which etch the material by both physical and chemical interactions (reactive ion etching). The production of the high resolution mask is the step, which makes the overall procedure expensive and time consuming, because a mask with few hundred nanometers resolution requires the use of optical or electron beam lithography, which are inherently multistep methods. However, the industrial spreading of UV laser-based optical lithography have significantly facilitated the progress of computer technologies; the processors and memory modules are made by this method, in industrial quantity.

In contrast to above described procedures, the laser-based direct and indirect methods requires less sophisticated technological infrastructure and far more affordable, which makes them suitable for ordinary laboratories. The **pulsed laser ablation** is based on photothermal and photochemical changes in the target induced by the absorption of the majority of incoming laser energy. Above the threshold laser fluence, the material of the target is removed. The linear absorption of the sample is of major importance, on the basis of that, one can distinguish highly absorbing and transparent materials. In case of absorbing targets the ablation process results in good controllability and relatively large processed area.

In case of transparent materials where the energy of laser photons is generally not enough to tear the chemical bonds, the increase of peak intensity (shorter pulse duration) supports the induced nonlinear (multiphoton) absorption, which makes the ablation more efficient. Still the ablation of transparent targets have serious difficulties, which are consequently limiting the quality and size of processed surface.

Methods

The **indirect laser-based techniques** can overcome the problem mentioned above: the material removal is realized by the help of an intermediate medium (this is why it is referred as indirect technique). The laser pulses pass through the transparent target with negligible attenuation, and the majority of its energy is absorbed by the medium, which can remove a thin layer of the target through heat diffusion and plasma induced processes. Among the several indirect methods proposed so far, I used the **laser-induced backside wet etching (*LIBWE*)** in my experiments. The backside of the transparent target is in contact with a liquid absorber (hidrocarbonic solution or liquid metal), which heats up drastically due to absorption of laser energy and significant amount of that energy is transferred to the sample by heat diffusion. Above the threshold fluence a thin layer of the sample surface is removed by melting and boiling. The threshold is depends on the material properties of the sample and the absorber, and on the wavelength of illuminating source. One of the most important advantage of *LIBWE* – and all of the indirect methods – is the low threshold and high surface quality (low roughness, straight edges).

Combining the wet etching with a two-beam interferometric arrangement (***TWIN-LIBWE***), submicrometer period grating can be etched into transparent targets in a single step. In this geometry, the spatially and temporally overlapping pulses create an interference pattern with spatially modulated intensity distribution. The spatial period of this pattern, and so the period of the gratings can be continuously tuned.

Several studies published about the optimization of the fabrication of transmission gratings etched into fused silica plates by *TWIN-LIBWE*, however the efficiency of the gratings have not been investigated so far.

Moreover, only bulk targets have been microstructured by the method, transparent thin films have not been tested yet, although they have several applications. The applications rely on grating couplers such as *grating coupled interferometry* and o*ptical waveguide lightmode spectroscopy* are good examples of such techniques.

Optical fiber tips have not been etched by any of the indirect methods, although the fibers have quite diverse applications from imaging to sensorics.

The fused silica is a mechanically hard and chemically stable material which makes it ideal to serve as a master grating in methods such as **direct nanoimprint lithography** (*D-NIL*), in which the mold is transferred directly into the target sample (by pressing them together) while the target material is heated up to an optimal temperature (for soften/melt the target). Probably reflection gratings in bulk metals also can be fabricated by the method, which have been already proved for metal films.

Aims

When I started my work in the Department of Optics and Quantumelectronics in the University of Szeged, after studied the relevant literature, I aimed to create and examine microstructures which could have application later.

My aims are listed as the followings:

1. One of the most important property of a diffraction grating is its efficiency. Based on the efficiency one can decide that a given grating is suitable for an application or not. For this reason I aimed to determine the efficiency of micrometer period (bulk) fused silica transmission gratings made by *TWIN-LIBWE,* at three (commonly used) laser wavelength.
2. The thin film gratings have applications in the sensorics as grating coupled waveguides, for which several measurement techniques have been developed. For this reason, I aimed to produce micro- and submicrometer period transmission (coupler) gratings into wide wavelength range transparent thin films by *TWIN-LIBWE*, and determine the optimal parameters of fabrication of the gratings.

3. Generally, the reflection gratings are consist of a metal film evaporated onto a substrate having the desired groove profile. It is shown, that such structure has lower laser induced damage threshold than a grating created into a bulk of metal. For this reason, I aimed to fabricate micro- and submicrometer period reflection gratings into bulk tin by a suitable imprinting (master-replica) method, for which I use the fused silica gratings made by *TWIN-LIBWE* as master molds.
4. Beyond telecommunication applications, the optical fibers are widely used in numerous fields of sciences and are basic elements of several measurement techniques and instruments. Since fiber tips have not been etched by any of the indirect techniques, the testing of the etching of fiber target seemed to be a promising opportunity. I aimed to etch a fiber tip by *LIBWE* technique, and to find application for the created surface.

Results

The majority of the results presented in my thesis are connected to an indirect laser-based surface patterning technique, namely the laser-induced backside wet etching (LIBWE) and the minor part of my results is connected to an imprinting technique. I have aimed to produce and examine surface structures which are relevant for present applications and/or will have application in some field in the future. For this reason I have determined the efficiency of diffraction gratings, created gratings into dielectric thin films and bulk metal, and nanostructured the tip of optical fiber.

The summary of my scientific results are listed as the followings:

1. I have determined for the first time, the diffraction efficiency of the TWIN-LIBWE made fused silica surface relief transmission gratings (with periods of 0.95, 2.12 and 3.71 μm) by the combination of measurements and simulations for three laser wavelengths (266, 532 és 654.5 nm), and for all the allowed diffraction orders. The presented method takes into account the inhomogeneous distribution of modulation depth which can be fitted well by symmetric functions, and it is based on the weighting of simulated efficiencies by the relative grooved area belongs to a given (single) modulation depth. I have found that by TWIN-LIBWE it is possible to fabricate gratings which has maximal diffraction efficiency in the $\pm 1^{st}$ orders, in some specific cases above 50%. Consequently, these gratings most probably suitable for further applications [T1].

2. I have fabricated micrometer and half of micrometer period surface relief gratings into thin films (SiO_2, Al_2O_3 and Y_2O_3) deposited onto fused silica substrate for the first time by TWIN-LIBWE method. I have found that the etching threshold for SiO_2 film is 285 mJ/cm^2 , which is equal to the known bulk's threshold, and I have found that the modulation depth can be adjusted within a large interval by the adjustment of laser parameters during etching. I have measured the threshold of 240 and 220 mJ/cm^2 for Al_2O_3 and Y_2O_3, respectively, and I have found that the optimal etching parameter set and consequently the scalability of modulation depth are significantly narrower than for SiO_2 film and bulk. I have demonstrated that by TWIN-LIBWE it is possible to produce gratings into thin films which are capable to couple the light into the waveguide film [T2].

3. I have produced replica reflection gratings in bulk tin (Sn) by a "master-replica" method (melt-imprint technique) from TWIN-LIBWE made fused silica grating molds. The period of both replicas and masters cover an order of magnitude (266, 505, 1045, 2120 és 3710 nm); I have compared the modulation depth of replicas and of masters for all periods. I have concluded that the modulation depth of replicas are nearly constant for a given period, i.e. independent of the depth of its master; however this typical groove depth – similarly as the master's - is increasing with increasing groove spacing. Moreover, I have demonstrated that by illuminating the produced replicas, all of the allowed diffraction orders are appear [T3].

4. I have fabricated phorous sub-100 nm characteristic size nanostructures on the tip of multimode optical fiber having fused silica core by metallic LIBWE (M-LIBWE) arrangement based on liquid gallium (Ga) as absorber. I have measured the etching threshold of fiber core to 450 mJ/cm^2, and the etching rate between 20 and 37 nm/pulse in the 450-1060 mJ/cm^2 fluence range. I have showed that the method supports the production of surface structures which after coated by a thin metal film, proved to be a proper substrate to produce surface enhanced Raman scattering (SERS) signals [T4].

Publications

Peer reviewed journal publications related to the theses:

[T1] B. Kiss, Cs. Vass, P. Heck, P. Dombi and K. Osvay: „*Fabrication and analysis of transmission gratings produced by the indirect laser etching technique*", J. Phys. D: Appl. Phys. 44 (2011) 415103 (5pp)

[T2] B. Kiss, F. Ujhelyi, Á. Sipos, B. Farkas, P. Dombi, K. Osvay and Cs. Vass: „*Microstructuring of Transparent Dielectric Films by TWIN-LIBWE Method for OWLS Applications*", JLMN-Journal of Laser Micro/Nanoengineering Vol. 8, No. 3 (2013) 271-275

[T3] B. Kiss, R. Flender and Cs. Vass: „*Fabrication of Micro- and Submicrometer Period Metal Reflection Gratings by Melt-Imprint Technique*", JLMN-Journal of Laser Micro/Nanoengineering Vol. 8, No. 3 (2013) 287-291

[T4] Cs. Vass, B. Kiss, J. Kopniczky and B. Hopp: „*Etching of fused silica fiber by metallic laser-induced backside wet etching technique*", Appl. Surf. Sci. 278 (2013) 241–244

Other publication in peer-reviewed journals:

[1] B. Hopp, T. Smausz, T. Csizmadia, Cs. Vass, Cs. Tápai, B. Kiss, M. Ehrhardt, P. Lorentz and K. Zimmer: „*Production of nanostructures on bulk metal samples by laser ablation for fabrication of low-reflective surfaces",* Appl. Phys. A Vol. 113, Issue 2 (2013) 291-296

[2] Cs. Vass, B. Kiss, R. Flender, Z. Felházi, P. Lorenz, M. Ehrhardt and K. Zimmer: *„Comparative Study on Grating Fabrication in Transparent Materials by TWIN-LIBWE and Ultrashort Pulsed Ablation Techniques",* JLMN-Journal of Laser Micro/Nanoengineering Vol. 10, No. 1 (2015) 38-42

[3] B. Kiss, R. Flender, J. Kopniczky, F. Ujhelyi, Cs. Vass: *„Fabrication of Polarizer by Metal Evaporation of Fused Silica Surface Relief Gratings"*, JLMN-Journal of Laser Micro/Nanoengineering Vol. 10, No. 1 (2015) 53-58