Submicrometer structuring of fused silica by laser-induced backside wet etching procedure

Ph.D. theses

Vass Csaba

Supervisor:
Dr. Hopp Béla
senior research fellow

Doctoral School in Physics
Department of Optics and Quantum Electronics

University of Szeged
Faculty of Science and Informatics

Szeged
2010

Introduction and scientific background

Dielectric materials transparent in the ultraviolet (UV) wavelength range (e.g. fused silica, quartz, sapphire, MgF_2, CaF_2, BaF_2) have many application possibilities in several fields of science and industry due to their transparency, high optical quality and chemical stability. These materials are used in some novel areas beside the conventional applications (UV-transparent optics e.g. laser applications): they can be applied as base material of microfluidical and microoptical elements. It is important to find the best processing method which fits the requirements of possible applications: the resolution has to be high enough (micro- and submicrometer) and the machined surface has to be smooth, and the method should have high productivity.

These materials can be microstructured by conventional techniques such as hidrofluidic etching and powder blasting, which are based on lithography techniques. These conventional methods have ~10 μm lateral resolution, their productivity is high, but the processed surface is rather rough. The ion- and plasma etching methods (called dry etching techniques in scientific literature) combined with the lithographic procedures are suitable to reach high resolution (~50 nm, which is less then the diffraction limit of light). Unfortunately, these dry etching methods have some disadvantages: they are time consuming, they have high prices, necessary instruments are complicate; their productivity is low.

The laser-based methods can provide a good alternative for microstructuring of UV-transparent dielectrics: their resolution and productivity can be high enough. The laser-based procedures can be classified as direct and indirect methods. A procedure is called direct method, if the laser beam can etch the target surface itself, and it called indirect, if some other material helps the material removal from the target. The direct processing of these transparent materials can be carried out by using laser beam having wavelength out of the transparency range: e.g. fluorine-laser (λ=157 nm), carbon-dioxide laser (λ=10,6 μm) or soft X-ray laser (λ~10 nm). On the other hand the ultrashort laser pulses can remove a thin layer of the target as a result of complicated mechanism, if the intensity of the beam is high enough to increase the probability of two-photon absorption. The previously mentioned laser-systems (fluorine-, soft X-ray- and ultrashort lasers) are expensive and usually complicated and unmanageable, therefore they can not be used in industrial environment. The UV-transparent materials can be micromachined also by nanosecond UV lasers (mostly excimer lasers), but the quality of the processed surface is not sufficient and the productivity of these methods is too low.

The indirect laser-based methods are competitive procedures compared to the above mentioned direct methods. Excimer lasers and frequency-quadrupled Nd:YAG lasers are used as light sources in indirect techniques. The backside of the target (the laser light comes from its front side through the transparent dielectric) is in contact with an absorber material (e.g. liquid, thin metal or adsorbed hydrocarbon layer), which makes the effective etching possible; or the laser-generated plasma (originating from the absorbing solid state material placed to the backside of the target) helps the effective material removal. All indirect techniques have similar advantages: low etching threshold fluence and relatively good surface quality (low roughness).

The laser-induced backside wet etching, which is the subject of these theses, is a flexible and important method that is the most promising with many advantages for micromachining of UV-transparent materials. The LIBWE was invented approx. 10 years ago. During the LIBWE procedure the backside of the transparent is in contact with a liquid (mostly hydrocarbon solution), which has high absorption coefficient at the laser wavelength. Laser pulses (having sufficient fluence) irradiate the absorber-sample interface through the transparent material and a thin layer is removed from the target surface as a result of a complex processes. The most important advantages of LIBWE are the followings: it is a one-step method (does not need mask preparation on the sample surface); the depth of the etched area can be easily controlled; good etched surface quality; crack- and debris-free etched and surrounding areas; high lateral resolution and relatively low etching threshold fluence.

Aims and methods

After studying the literature of LIBWE method it was obvious that there were several important unanswered questions about the procedure. These questions were partly related to base research, to the material removal process, and partly related to the application possibility of the laser-induced backside wet etching technique. Considering these open questions, I summarized the aims of my work in the followings:

1. My first goal was to study the LIBWE procedure in order to interpret the material removal process with a coherent theory. I applied a new laser type (ArF), which had not been used in LIBWE experiments, and new liquid absorbers (naphthalene/methyl-methacrylate solutions) to achieve my aims (I used fused silica plate as transparent target in all of my experiments). I intended to explain why the fluence-etch rate data points can be fitted by two straight lines.

2. My aim was to prepare a numerical model of LIWBE procedure and to calculate temperature distribution in the target and liquid on the basis of my experimental results to interpret the laser-induced backside wet etching.
3. The best resolution of structures fabricated by laser-induced backside wet etching procedure could not be determined unambiguously on the basis of the literature. Therefore my goal was to study the best resolution of this technique by grating fabrication. My aim was to investigate which parameters can limit the minimal grating periods over the obvious optical limit.

I studied the laser-induced backside wet etched surface of fused silica by atomic force microscope and profilometer in my first experiments. I prepared a numerical model of LIBWE which was based on thermal effects. After studying the accompanying effects and expanding my calculations to other laser types I realized that some phenomenon was not taken into account in my model. Therefore I analyzed the etched surface by X-ray photoelectron spectroscopy and spectroscopic ellipsometry. I completed and improved my first numerical model with the results of ellipsomety. The results of the developed model showed good agreements with the experiments and could help the interpretation of some important phenomenon in material removal by LIBWE.

I studied the resolution limit of the laser-induced backside wet etching technique by fabricating gratings in fused silica surface by combining LIWBE and two-beam interference methods. The gratings were characterized by atomic force microscope and profilometer.

Results

1. I used ArF excimer laser and new liquid absorbers (naphthalene/methyl-methacrylate with a concentrations: c=0.85 and 1.71 mol/dm^3), which were not applied in LIBWE experiments previously, to process transparent fused silica plates. These allowed to achieve removal efficiencies higher than usual, due to the low ArF wavelength and the high absorption coefficient of the liquids at this wavelength. I studied the edge of etched surface and I observed a small hill (which is probably melted and resolidified fused silica) on the unetched area directly around the processed surface, which proved that thermal effects play significant role in the material removal process. I demonstrated that the etch rate (thickness of target layer removed by one laser pulse) depends on the laser wavelength, the type and concentration of the liquid absorber and the laser fluence. The etch rates were found to be between 4 and 55 nm/pulse in the case of applied hydrocarbon solutions (naphthalene/methyl-methacrylate with a concentrations: c=0.85 and 1.71 mol/dm^3 and pyrene/acetone c=0,4 mol/dm^3), and experimental conditions (fluence range for ArF: 200-1000 mJ/cm^2; for KrF: 300-1800 mJ/cm^2). The fluence-etch rate graphs could be fitted by two straight lines in each case. [T1, T2]

   I demonstrated that the surface quality of etched area is the best (the roughness parameter is the lowest - 3-4 nm) in the fluence range of 490 - 620 mJ/cm^2 when using KrF laser and of naphthalene/methyl-methacrylate c=0.85 and 1.71 mol/dm^3 or pyrene/acetone c=0,4 mol/dm^3 solutions. This fluence range has significant importance in the possible application of LIBWE technique.

2. I characterized the etched fused silica surface by X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry to better understand the mechanism of the material removal. My XPS results demonstrated that the etched surface is contaminated by carbon originating from the liquid absorber. The thickness and the optical properties of this modified, carbon contaminated etched fused silica layer were measured by spectroscopic ellipsometer. I demonstrated that its thickness was between 10 and 30 nm, the refractive index for 248 nm wavelength was 1.86, while the absorption coefficient was significant, 1,8-3·10^5 1/cm for ArF and KrF wavelength. [T8]

3. I elaborated a numerical model to calculate the evolution of the temperature of the irradiated fused silica target. This model is the most sophisticated one existing presently and gives results that are in good agreement with the experiments in most of the cases. It takes into consideration the phase changes of the relevant materials, the temperature dependent thermal properties of the materials, the absorption of the modified layer and the removal of boiled fused silica. The measured etch rate was indentified as the thickness of the boiled fused silica layer. My model predicted the etching threshold fluences with accuracy of about ~10 % and gave good estimation on the etch rate at the low fluence range (in the case of ArF laser: 260-440 mJ/cm^2; KrF laser: 400-700 mJ/cm^2). The fluence dependence of calculated thickness of boiled fused silica layer can also be fitted with two straight lines in the case of ArF laser – similarly to the experiments. Based on results of the etched surface analyses and numerical calculation, I can state that the modified, carbon contaminated layer plays important role in material removal. I found that the break-point of fluence-etch rate graph corresponds to the complete removal of the modified layer, and the melted fused silica layer probably plays role in the repeated formation of the modified layer. The differences between the results of model calculations and the experiments can be attributed to the followings: 1. the relevant optical and thermal properties of materials were not known in the whole relevant temperature range; 2. the amorphous carbon was not taken into account due to the insufficient information about its optical and physical properties; 3. the exact process of the formation of the amorphous carbon and the modified layer was not known; 4. I neglected the energy required for the formation of carbon particles from the hydrocarbon solution; 5 the model could not take into account the mechanical effects. [T2, T8]

4. I combined the laser-induced backside wet etching procedure and the two-beam interferometric arrangement (called TWIN-LIBWE; the UV source was the 4th harmonic of Nd:YAG laser) to study the lateral resolution of LIBWE method. I investigated how the grating parameters depend on the laser fluence and the number of laser pulses. I determined the optimal fabrication parameters for 550 and 990 nm period gratings: the best quality gratings can be fabricated by laser fluence of ≈330 mJ/cm^2, and 50-100 pulses. On the basis of this knowledge I produced 266 and 154 nm period grating structure by increasing the incident angle of the laser light. I found

that the decrease of the grating period is accompanied with the narrowing of the range of optimal pulse number and fluence values. [T4, T5, T7].

5. I proved that the lateral resolution of the LIBWE technique is around 100 nm: I fabricated grating structure in fused silica with a period of 104 nm by applying an immersion setup. This period is the smallest grating constant fabricated by laser techniques in fused silica, so far. I demonstrated that the minimal grating period is strongly limited by the heat diffusion in addition to the obvious optical limit [T6, T7].

Publications

Publications related to the theses

[T1] Cs. Vass, B. Hopp, T. Smausz, F. Ignácz: „Experiments and numerical calculations for the interpretation of the backside wet etching of fused silica", Thin Solid Films 453 – 454 (2004) 121–126

[T2] Cs. Vass, T. Smausz and B. Hopp: „Wet etching of fused silica: a multiplex study", J. Phys. D: Appl. Phys. 37 (2004) 2449–2454

[T3] Cs. Vass, D. Sebők, B. Hopp: „Comparing study of subpicosecond and nanosecond wet etching of fused silica", Applied Surface Science 252 (2006) 4768–4772

[T4] Cs. Vass, K. Osvay, M. Csete, B. Hopp: „Fabrication of 550 nm gratings in fused silica by laser induced backside wet etching technique", Applied Surface Science 253 (2007) 8059–8063

[T5] Csaba Vass, Károly Osvay, Béla Hopp: „Fabrication of 150 nm period grating in fused silica by two-beam interferometric laser induced backside wet etching method", Optics Express 14 (2006) 8354-8359

[T6] C. Vass, K. Osvay, B. Hopp, Z. Bor: „104 nm period grating fabrication in fused silica by immersion two-beam interferometric laser induced backside wet etching technique", Appl. Phys. A 87 (2007) 611–613

[T7] Csaba Vass, Károly Osvay, Tamás Véső, Béla Hopp, Zsolt Bor: „Submicrometer grating fabrication in fused silica by interferometric laser-induced backside wet etching technique", Appl Phys A 93 (2008) 69–73

[T8] Csaba Vass, Judit Budai, Zoltán Schay, Béla Hopp: „Interpretation and Modeling of Laser-Induced Backside Wet Etching Procedure", JLMN-Journal of Laser Micro/Nanoengineering 5 (2010) 4347

Other referred publications

[9] T. Smausz, B. Hopp, Cs. Vass, Z. Tóth: "Experimental study on droplet generation during pulsed laser deposition of polyethylene-glycol 1000", Appl. Surf. Sci. 168 (2000) 146-149

[10] B. Hopp, N. Kresz, Cs. Vass, Z. Tóth, T. Smausz, F. Ignácz: "Spatial separation of fast and slow components of pulsed laser plumes", Appl. Surf. Sci. 186 (2002) 298-302

[11] B. Hopp, R. Hegedüs, Cs. Vass, T. Smausz, Z. Bor: "Three dimensional photography and modeling of jets and droplets ejected from the surface of excimer laser ablated molten polyethylene-glycol 1000", Appl. Phys. A 79 (2004) 779-782

[12] B Hopp, T Smausz, N Barna, Cs Vass, Zs Antal, L Kredics and D Chrisey: "Time-resolved study of absorbing film assisted laser induced forward transfer of Trichoderma longibrachiatum conidia", J. Phys. D: Appl. Phys. 38 (2005) 833-837

[13] M. Csete, Cs. Vass, J. Kokavecz, M. Goncalves, V. Megyesi, Zs. Bor, M. Pietralla, O. Marti: "Effect of sub-micrometer polymer gratings generated by two-beam interference on surface plasmon resonance", Appl. Surf. Sci. 247/1-4 (2005) 477-485

[14] M. Csete, N. Kresz, Cs. Vass, G. Kurdi, Zs. Heiner, M. Deli, Zs. Bor, O. Marti: "Sub-micrometer adhesion modulation on polymer surfaces containing gratings produced by two-beam interference" Material Sci. and Engin. C. 25 (2005) 813-819

[15] M. Csete, G. Szekeres, Cs. Vass, N. Maghelli, K. Osvay, Zs. Bor, M. Pietralla, O. Marti: "Surface plasmon resonance spectroscopy on rotated sub-micrometer polymer gratings generated by UV laser based two-beam interference", Appl. Surf. Sci. 252 (2006) 4773-4780

[16] B. Hopp, Cs. Vass, T Smausz, Zs. Bor: "Production of submicrometre fused silica gratings using laser-induced backside dry etching technique", J. Phys. D: Appl. Phys. 39 (2006) 4843-4847

[17] B. Hopp, Cs. Vass, T. Smausz: „Laser induced backside dry etching of transparent materials", Appl. Surf. Sci. 253 (2007) 7922-7925

[18] M. Csete, Á. Sipos, Cs. Vass, V. Megyesi, A. Kőházi-Kis, K. Osvay, Zs. Bor: "Atomic force microscopical and surface plasmon resonance spectroscopical investigation of sub-micrometer metal gratings generated by UV laser based two beam interference in Au-Ag bimetallic layers", Appl. Surf. Sci. 253 (2007) 7662-7671

[19] T. Smausz, T. Csizmadia, N. Kresz, Cs. Vass, Zs. Marton, B. Hopp: „Influence on the laser induced backside dry etching of thickness and material of the absorber, laser spot size and multipulse irradiation" Appl. Surf. Sci. 254 (2007) 1091-1095

[20] R. Böhme, C. Vass, B. Hopp, K. Zimmer: "Sub-wavelength ripples in fused silica after irradiation of the solid/liquid interface with ultrashort laser pulses", Nanotechnology 19, (2008) 495301 6pp

[21] B. Hopp, T. Smausz, C. Vass, G. Szabó, R. Böhme, D. Hirsch, K. Zimmer: „Laser-induced backside dry and wet etching of transparent materials using solid and molten tin as absorbers", Appl Phys A 94 899–904 (2009)

[22] Smausz, T., Megyeri, G., Kékesi, R., Vass, C., György, E., Sima, F., Mihailescu, I.N., Hopp, B.: „Comparative study on Pulsed Laser Deposition and Matrix Assisted Pulsed Laser Evaporation of urease thin films", Thin Solid Films (2009) 517 4299-4302

[23] H. Tóháti, Á. Sipos, G. Szekeres, A. Mathesz, A. Szalai, P. Jójárt, J. Budai, Cs. Vass, A. Kőházi-Kis, M. Csete and Zs. Bor: „Surface plasmon scattering on polymer–bimetal layer covered fused silica gratings generated by laser induced backside wet etching", Applied Surface Science Vol.255, Iss.10 5130-5137 (2009)

[24] K. Zimmer, R. Böhme, C. Vass, B. Hopp: „Time-resolved measurements during backside dry etching of fused silica", Applied Surface Science 255 (2009) 9617–9621

[25] Béla Hopp, Tomi Smausz, Tamás Csizmadia, Csaba Vass, Tamás Csákó and Gábor Szabó: „Comparative Study of Different Indirect Laser-Based Methods Developed for Microprocessing of Transparent Materials", JLMN-Journal of Laser Micro/Nanoengineering Vol. 5, No. 1 (2010) 80-85

Conferences

1. Cs. Vass, B. Hopp, T. Smausz: "Laser induced backside wet etching of fused silica: absorption coefficient dependence", 3rd GR-I International Conference on New Laser Technologies and Applications, Szeptember 4-9. 2002., Patras, Greece, oral presentation

2. Cs. Vass, B. Hopp, T. Smausz, F. Ignácz: "Experiments and numerical calculations for the interpretation of the backside wet etching of fused silica", E-MRS Spring Meeting 2003, Június 10-13., Strasbourg, France, poster

3. Vass Csaba, Csákó Tamás, Smausz Tomi, Ignácz Ferenc, Hopp Béla: „Átlátszó anyagok megmunkálása lézer indukált hátsó oldali nedves maratással", Kvantumelektronika 2003, Budapest, 2003. október 21., poster

4. Vass C, Sebök D, and Hopp B „Comparing study of sub-picosecond and nanosecond wet etching of fused silica", E-MRS Spring Meeting 2005, máj. 31-jún.3, Strasbourg, France, poster

5. Cs. Vass, K. Osvay, M. Csete, B. Hopp: „Fabrication of 550 nm gratings in fused silica by laser induced backside wet etching technique", E-MRS Spring Meeting 2006, máj. 29-jún.2, Nice, France, poster

6. Vass Csaba, Hopp Béla, Osvay Károly és Bor Zsolt: „Átlátszó anyagok lézeres szubmikrométeres megmunkálása", Fizikus Vándorgyűlés, 2007. augusztus 22-24., Eger, oral presentation

7. Csaba Vass, Károly Osvay, Tamás Véső, Béla Hopp, Zsolt Bor: "Submicrometer grating fabrication in fused silica by interferometric laser induced backside wet etching technique", COLA, 2007. szept. 24-28., Tenerife, Spain, poster

8. Vass Csaba, Hopp Béla, Osvay Károly, Bor Zsolt: „Átlátszó anyagok szubmikrométeres megmunkálása lézeres hátsó oldali folyadékos maratással", Kvantumelektronika 2008, Budapest, 2008. október 17., poster

9. C. Vass, J. Budai, Z. Schay, B. Hopp: „Interpretation and modeling of laser-induced backside wet etching procedure", LAMP2009, 2009.jún.27-júl.2., Kobe, Japan, oral presentation