The impact of O/Si ratio and hydrogen content on ArF excimer laser ablation of fused silica

D. Tasche
University of Applied Sciences and Arts, Laboratory of Laser and Plasma Technologies, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany
Laser-Laboratory Göttingen e.V., Hans-Adolf-Krebs-Weg 1, 37077 Göttingen, Germany

C. Gerhard
University of Applied Sciences and Arts, Laboratory of Laser and Plasma Technologies, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany
Fraunhofer Institute for Surface Engineering and Thin Films, Application Center for Plasma and Photonic, Von-Ossietzky-Straße 100, 37085 Göttingen, Germany

J. Ihlemann
Laser-Laboratory Göttingen e.V., Hans-Adolf-Krebs-Weg 1, 37077 Göttingen, Germany

S. Wieneke
University of Applied Sciences and Arts, Laboratory of Laser and Plasma Technologies, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany
Fraunhofer Institute for Surface Engineering and Thin Films, Application Center for Plasma and Photonic, Von-Ossietzky-Straße 100, 37085 Göttingen, Germany

W. Viöl
vioel@hawk-hhg.de
University of Applied Sciences and Arts, Laboratory of Laser and Plasma Technologies, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany
Fraunhofer Institute for Surface Engineering and Thin Films, Application Center for Plasma and Photonic, Von-Ossietzky-Straße 100, 37085 Göttingen, Germany

The impact of stoichiometry and hydrogen content on the ArF excimer laser ablation characteristics of fused silica is investigated. Near-surface substoichiometic SiO_x with $x < 2$ diminishes the ablation threshold as a result of increased absorption. The ablation rate is raised by an elevated hydrogen content. As confirmed by mass spectrometric analysis, the laser-induced formation of substoichiometric near-surface layers within the ablation spot sustains absorption and ablation for consecutive laser pulses.
[DOI: http://dx.doi.org/10.2971/jeos.2014.14026]

Keywords: Fused silica, silicon suboxide, laser ablation, ablation threshold, stoichiometry

1 INTRODUCTION AND PROBLEM STATEMENT

Fused silica of high purity is one of the most important materials for a number of various optical components and devices. Due to its transmission characteristics, far ultraviolet or infrared laser wavelengths usually need to be applied for pure laser micro structuring without auxiliary means. In addition, high fluences are required for ablation, giving rise to thermally-induced disturbing effects such as the formation of melt or micro cracks. In order to achieve high-quality ablation at low fluence, different hybrid laser ablation methods are in hand, as for example laser-induced plasma-assisted ablation (LIPAA) [1, 2], laser-induced backside wet etching (LIBWE) [3, 4], laser etching at surface adsorbed layers (LESAL) [5, 6] and laser-induced backside dry etching (LIBDE) [7]. In the latter case, a thin coating, featuring a high absorption for the particularly used laser wavelength, is deposited onto the fused silica surface. For instance, the ablation threshold fluence is significantly decreased by the use of silicon monoxide (SiO) [8] or silicon suboxide (SiO_x, where $1 < x < 2$) [9, 10] as absorbing coating. In addition to the deposition of a SiO or SiO_x coating onto the surface, a near-surface layer within the fused silica silicon dioxide (SiO_2) bulk material can be chemically reduced to SiO_x with the aid of hydrogenous atmospheric pressure plasmas [11]. This technique represents an alternative solution for decreasing the required laser ablation threshold fluence [12, 13].

Against this background, the influence of silicon suboxide layers of different composition on excimer laser ablation of fused silica was investigated in the present work in order to provide a comparison of the particular ablation thresholds and depths. Further, the chemical composition of such laser ablated fused silica surfaces was determined.

2 EXPERIMENTAL SETUP AND PROCEDURE

Investigations on the influence of different SiO_x compositions on excimer laser ablation were carried out for three different samples and substrates, respectively, all from Heraeus

Received April 15, 2014; revised ms. received June 23, 2014; published July 21, 2014

GmbH: (i) fused silica Suprasil 2B (hereinafter called FS) with a defined stoichiometric ratio O/Si = x of 2, (ii) Suprasil 2A (O/Si = 2), coated with a 77 nm-thick SiO_x-layer from Laseroptik GmbH with x ≈ 1 [14] (hereinafter called c-FS), and (iii) plasma treated Suprasil 2B (hereinafter called p-FS). For p-FS, a gradient oxygen-reduced near-surface layer within the SiO_2 bulk material, reaching its maximum substoichiometric O/Si-value of approx. 1.88 at a sputter depth d_s of 10 nm, was observed in previous work. The maximum depth d_p of the plasma-affected bulk material is approx. 100 nm [11, 15]. For the plasma treatment, an atmospheric pressure plasma jet source with an outlet nozzle diameter of 3 mm [16] was applied, using forming gas 90/10 (90 % N_2, 10 % H_2) from Linde AG as process gas. The gas flow rate was 4.2 l/min. Plasma treatment was performed for 170 minutes at a plasma power 40 mW, applied to an area of 625 mm² (25x25 mm²) on the sample surface via moving the sample by a motorised xy-linear stage. The working distance from the plasma nozzle outlet to the sample surface was 8 mm. After preparing the samples, the transmission T was determined by the use of a spectrometer UV-VIS PE Lambda 19 from Perkin Elmer.

In order to determine the content of hydrogen as well as the stoichiometric ratio O/Si of the investigated samples, secondary ion mass spectroscopy (SIMS) was applied using a SIM spectrometer Quadrupol 4550 from Cameca. Here, the acceleration voltage of the caesium primary ions was 1 kV, where the investigated sputtered area was 0.36 mm² (600x600 µm²). SIMS was performed on the particular reference surfaces before laser ablation and on the bottom of the ablated spots after laser ablation. The initial calibration of the relative sensitivity factor (RSF) was carried out by applying three different standards with defined elementary concentrations, listed in Table 1.

Ablation experiments were performed employing an argon fluoride (ArF) excimer laser LPX 315i from Lambda Physik with an emission wavelength of 193 nm and a pulse duration of 20 ns. In order to achieve homogenous large-scale ablation, a non-imaging beam homogeniser was introduced to the laser beam path as shown in Figure 1.

The back focal length of this homogeniser, consisting of two perpendicularly-crossed cylinder micro lens arrays and a Fourier lens, was 100 mm. The homogeneous area projected onto the sample surface, i.e. the ablation spot area, was 1 mm². As determined by in-situ energy measurements during ablation, the fluences applied to the particular sample surface were in the range from 0.15 J/cm² to 5 J/cm². Front side ablation experiments were performed for the identification of the ablation threshold fluence and for the determination of the ablation depths. For this purpose a surface profiler Dektak 3030 Auto II from Veeco, Inc. with a vertical resolution of 2 nm was employed.

3 RESULTS AND DISCUSSION

3.1 Hydrogen concentration of the different samples

Initially, the content of hydrogen within the investigated samples was determined by SIMS. For untreated fused silica Suprasil 2B, an averaged hydrogen concentration $c(H)_{av}$ of 0.88% was measured. For the Suprasil 2A substrate of the coated samples, $c(H)_{av}$ was 0.58%. A significant increase in $c(H)_{av}$ of 5.15% , i.e. approx. 6-times higher with respect to untreated fused silica Suprasil 2B, was found in the case of plasma treated Suprasil 2B. This high value is most likely explained by diffusion of atomic hydrogen generated by dissociation of the used hydrogenous plasma working gas. This has already been observed in previous work [11]. As a result of the different silicon suboxide compositions and the presence of hydrogen, the investigated samples feature quite differing transmissions T at the laser wavelength of 193 nm, which was applied for ablation. The particular values were T_{FS} = 99.9%, T_{c-FS} = 0% and T_{p-FS} = 92.4%, respectively. Regarding these transmission values, one has to consider that different absorption-increasing mechanisms are involved. In the case of c-FS, absorption is mainly due to the SiO_x layer whereas in the case of p-FS, the near-surface formation of SiO_x as well as the implantation of hydrogen [17]–[19] into deeper regions of the fused silica bulk material contributes to modified optical characteristics of the bulk material.

3.2 Influence of the stoichiometry on ablation characteristics

The ablation threshold fluence F_{th} was defined as the mean value in between the highest applied fluence without any material removal and the lowest one, where considerable ablation was observed. The measured ablation threshold fluences

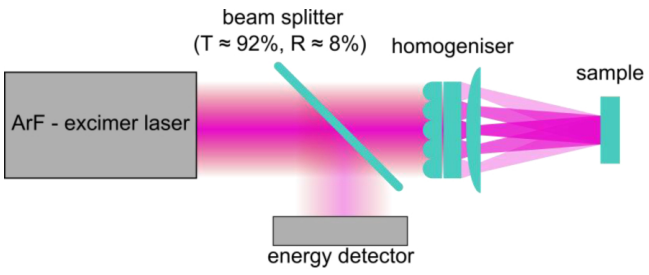

FIG. 1 Experimental setup for laser ablation.

	concentration C in %		
Standard	*silicon (Si)*	*oxygen (O)*	*hydrogen (H)*
silicon dioxide (SiO_2)	33	66	-
hydrogenous amorphous silicon (a-Si:H)	-	-	14
hydrogenous nitrogen doped silicon carbide (SiNC:H)	26.6	-	-

TABLE 1 Elementary concentrations of the applied SIMS calibration standards.

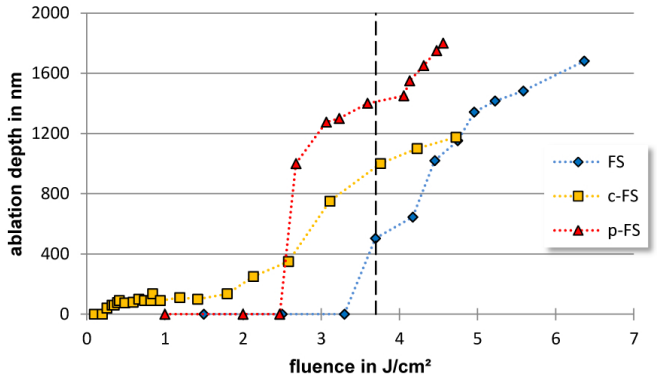

FIG. 2 Ablation depth (10 laser pulses per spot) for FS, c-FS and p-FS vs. fluence.

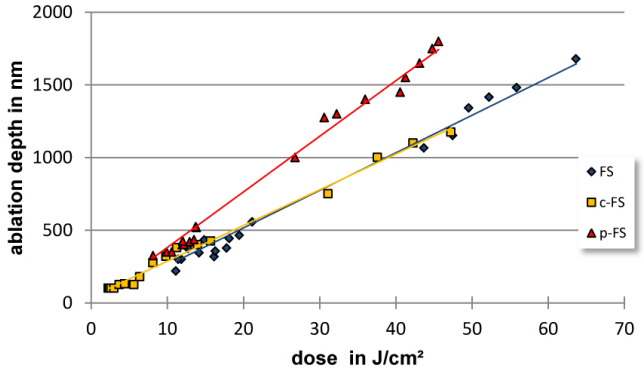

FIG. 3 Ablation depth for FS, c-FS and p-FS vs. dose.

F_{th} for 3 and 10 pulses are nearly identical and lead to an average threshold fluence F_{thaver} of 3.43 J/cm² for FS, 1.08 J/cm² for c-FS and 2,6 J/cm² for p-FS. The threshold for c-FS is given by that value, where the fused silica substrate and not only the coating is ablated. Figure 2 shows the dependency of the ablation depths (10 laser pulses per spot) on the laser fluence Φ for the three different investigated sample types.

For instance, the averaged ablation rate at approx. 3.7 J/cm² (see Figure 2), where ablation took place for all sample types, amounts to 50 nm/pulse for FS, 100 nm/pulse for c-FS and 140 nm/pulse in the case of p-FS. Even though the lowest ablation threshold is found in the case of c-FS, the highest ablation rate was obtained on p-FS. Also for ablation at higher fluences, the highest ablation depth was found in the case of p-FS whereas c-FS and FS feature a comparable ablation behaviour as shown in Figure 3. Here, the particular ablation depths were plotted vs. the applied dose in order to provide a normalised and well-evaluable presentation. The dose is given by the product of the fluence Φ and the number of pulses.

The observed differing ablation characteristics for p-FS on the one hand and both c-FS and FS on the other hand can be explained by the above-mentioned plasma-induced significant increase in hydrogen within the glass bulk material, giving rise to an enhanced coupling of incoming laser irradiation. In contrast, the absorbing SiO_x-coating on c-FS is removed after the first few laser pulses.

For a more detailed investigation of the influence of implanted

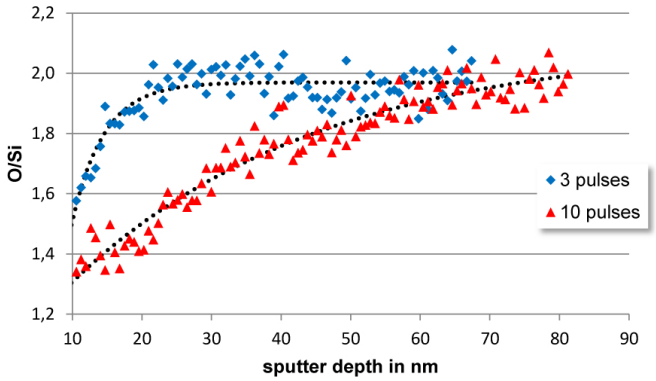

FIG. 4 Stoichiometric ratio O/Si for p-FS samples after 3 and 10 pulse laser ablation including particular fitted progression vs. sputter depths.

hydrogen, SIMS was also performed at the ablation spot bottoms after applying 3 and 10 laser pulses at a fluence of approx. 5 J/cm². For the evaluation, the near-surface layer with a thickness of 10 nm was not considered due to the fact that the measurement was distorted during the formation of a sputter equilibrium between the involved elements and surface-adherent contaminations such as hydrocarbons. Even when excluding the first 10 nm for such analysis, the stoichiometric ratio O/Si was generally decreased compared to that of the non-irradiated material for all investigated samples. After ablation applying 10 laser pulses, the averaged O/Si ratio for a sputter depth range from 10 to 25 nm was 1.92 for both FS and c-FS. However, the most significant reduction was found in the case of plasma treated fused silica, shown in Figure 4, where the O/Si ratio after 10 laser pulses was 1.44 for the above-mentioned sputter depth range. This significant higher laser-induced chemical reduction could be explained by the increased presence of hydrogen, implanted by the plasma pretreatment. Such implanted hydrogen can be assumed to act as reaction partner for oxygen embedded in the SiO_2 network, where the reaction results from laser induced heating of a near-surface layer according to

$$SiO_2(s) + 2H \rightarrow SiO(s) + H_2O(g). \quad (1)$$

The increased effect for ablation with higher numbers of pulses as shown in Figure 4 can thus be explained by the higher dose applied leading to an increased accumulation of reaction products.

Improved ablation of glasses and glassy materials after the first pulse is a well-known phenomenon. It is commonly explained by a number of different, interacting effects such as roughening and crystallisation as a result of short-time melting and re-solidification of the glass substrate material [20]. In the case of LIBWE, an altered state of the absorption coefficient of the fused silica after laser ablation was reported. The authors attributed this modification to the high temperature and the interactions between the fused silica and the pyrene/toluene absorber solution [21]. The above-presented SIMS results provide a further aspect contributing to the explanation of this effect. Since even in the case of pure FS the formation of substoichiometric SiO_x after the first laser pulse was verified it can be stated that the accompanying increase in absorption gives rises to enhanced coupling of incoming laser

irradiation once the surface was ablated. To our best knowledge, this is the first work reporting this effect.

4 CONCLUSIONS

The investigated samples feature considerably different ablation characteristics. The lowest ablation threshold was found for coated fused silica (c-FS) and is easily explained by the high absorption of the applied SiO_x-coating. With respect to pure fused silica (FS), the ablation threshold could be reduced by the presented plasma pre-treatment. For ablation at higher number of pulses and fluences, respectively, the highest ablation rate was found in the case of plasma-pre-treated fused silica (p-FS) which is most likely due to the implanted hydrogen and accompanying effects such as a continuous formation of a new SiO_x-layer on the bottom of the ablation spot after each laser pulse. This assumption is supported by the presented SIMS analysis of the ablated surfaces. It was shown that for all investigated sample types such SiO_x-layers of different stoichiometric composition result from laser ablation.

5 ACKNOWLEDGEMENTS

This work was supported by the European Regional Development Funds (EFRE) and the Lower Saxony Innovation Network for Plasma Technology (NIP), project funding reference number W2-80029388.

References

[1] J. Zhang, K. Sugioka, and K. Midorikawa, "Direct fabrication of micrograting in fused quartz by laser-induced plasma-assisted ablation with a KrF excimer laser," Opt. Lett. **23**, 1486–1488 (1998).

[2] K. Sugioka, and K. Midorikawa, "Novel technology for laser precision microfabrication of hard materials," RIKEN Review **32**, 36–42 (2001).

[3] J. Wang, H. Niino, and A. Yabe, "One-step microfabrication of fused silica by laser ablation of an organic solution," Appl. Phys. A-Mater. **68**, 111–113 (1999).

[4] X. Ding, Y. Kawaguchi, H. Niino, and A. Yabe, "Laser-induced high-quality etching of fused silica using a novel aqueous medium," Appl. Phys. A-Mater. **75**, 641–645 (2002).

[5] R. Böhme, and K. Zimmer, "Low roughness laser etching of fused silica using an adsorbed layer," Appl. Surf. Sci. **239**, 109–116 (2004).

[6] K. Zimmer, R. Böhme, and B. Rauschenbach, "Laser etching of fused silica using an adsorbed toluene layer," Appl. Phys. A-Mater. **79**, 1883–1885 (2004).

[7] B. Hopp, C. Vass, T. Smausz, and Z. Bor, "Production of submicrometre fused silica gratings using laser-induced backside dry etching technique," J. Phys. D Appl. Phys. **39**, 4843–4847 (2006).

[8] J. Ihlemann, "Micro patterning of fused silica by laser ablation mediated by solid coating absorption," Appl. Phys. A-Mater. 93, 65-68 (2008).

[9] J.-H. Klein-Wiele, J. Békési, P. Simon, and J. Ihlemann, "Fabrication of Si02 phase gratings by UV laser patterning of silicon suboxide layers and subsequent oxidation," J. Laser Micro/Nanoeng. **1**, 211–214 (2006).

[10] M. Jahn, J. Richter, R. Weichenhain-Schriever, J. Meinertz, and J. Ihlemann, "Ablation of silicon suboxide thin layers," Appl. Phys. A-Mater. **101**, 533–538 (2010).

[11] C. Gerhard, D. Tasche, S. Brückner, S. Wieneke, and W. Viöl, "Near-surface modification of optical properties of fused silica by low-temperature hydrogenous atmospheric pressure plasma," Opt. Lett. **37**, 566–568 (2012).

[12] S. Brückner, J. Hoffmeister, J. Ihlemann, C. Gerhard, S. Wieneke, and W. Viöl, "Hybrid laser-plasma micro-structuring of fused silica based on surface reduction by a low-temperature atmospheric pressure plasma," J. Laser Micro/Nanoeng. **7**, 73–76 (2012).

[13] J. Hoffmeister, C. Gerhard, S. Brückner, J Ihlemann, S. Wieneke, and W. Viöl, "Laser micro-structuring of fused silica subsequent to plasma-induced silicon suboxide generation and hydrogen implantation," Physics Procedia **39**, 613–620 (2012).

[14] J. Richter, J. Meinertz, and J. Ihlemann, "Patterned laser annealing of silicon oxide films," Appl. Phys. A-Mater. **104**, 759–764 (2011).

[15] C. Gerhard, T. Weihs, D. Tasche, S. Brückner, S. Wieneke, and W. Viöl, "Atmospheric pressure plasma treatment of fused silica, related surface and near-surface effects and applications," Plasma Chem. Plasma P. **33**, 895–905 (2013).

[16] S. Brückner, S. Rösner, C. Gerhard, S. Wieneke, and W. Viöl, "Plasma-based ionisation spectroscopy for material analysis," Mater. Test. **53**, 639-642 (2011).

[17] T. W. Hickmott, "Interaction of Atomic Hydrogen with Glass," J. Appl. Phys. **31**, 128–136 (1960).

[18] Y. Boliang, D.H. Ryan, J. M. D. Coey, Z. Altounian, J. O. Ström-Olsen, and F. Razavi, "Hydrogen-induced change in magnetic structure of the metallic glass $Fe_{89}Zr_{11}$," J. Phys. F Met. Phys. **13**, 217–222 (1983).

[19] I. I. Kitaigorodskii, D. I. Mendeleev, E. A. Fainberg, and L. A. Grechanik, "The influence of certain oxides on reduction of lead silicate glasses in hydrogen," Glass Ceram. **19**, 645–647 (1962).

[20] D. Bäuerle, Laser processing and chemistry (Springer Verlag, Berlin/Heidelberg, 2011).

[21] K. Zimmer, M. Ehrhardt, and R. Böhme, "Simulation of laser-induced backside wet etching of fused silica with hydrocarbon liquids," J. Appl. Phys. **107**, 034908 (2010).