

Simultaneous measurement of bulk absorption and fluorescence in fused silica upon ArF laser irradiation

Ch. Mühlig*, S. Kufert, W. Triebel; Institut für Physikalische Hochtechnologie, Jena, Germany
F. Coriand; Schott Lithotec AG, Jena, Germany

ABSTRACT

A new setup was established to simultaneously record the bulk absorption of fused silica at 193 nm and its laser induced fluorescence (LIF). Bulk absorption coefficients in the $10^{-3}/\text{cm}$ range are measured in a compact setup with small samples of $20 \times 20 \times 10 \text{ mm}^3$ using an ArF pump laser and recording the ArF laser induced deflection (LID) of a diode probe laser beam. LIF is measured through an optical fiber coupled to an intensified gated CCD camera.

Within the first few pulses of ArF laser irradiation the bulk absorption coefficient and LIF emission around 300 nm and 400 nm (oxygen deficient centers, ODC) decrease considerably, sometimes to a fraction of their initial values. In some fused silica samples additional fluorescence in the green-yellow wavelength region is found. This fluorescence increases in a strongly nonlinear way with the fluence. Assuming fluorescence excitation by single photon absorption the observed behavior can be explained by saturation of the absorption transition which put limitations on the fluence applicable in the experiments. Summarizing the obtained results a measurement instruction for precise absorption measurements of fused silica at 193 nm laser irradiation is suggested and fused silica samples have been investigated concerning their dependence of the absorption coefficient on the fluence. The results, in combination with transmission measurements of 300 mm long fused silica samples, confirm the nonlinear increase of the absorption with increasing fluence.

Keywords: fused silica, laser induced absorption, laser induced fluorescence, pump and probe technique

1. INTRODUCTION

Nowadays the majority of optical elements for optical lithography are made of high-purity fused silica. Very important parameters of this material are the excimer laser induced density and refractive index changes and, above all, the initial absorption coefficient and its change upon prolonged DUV laser irradiation. Since the absorption coefficients α of fused silica have become very low down to the $10^{-3}/\text{cm}$ range precise and highly sensitive measurement techniques are required. To determine these small absorption values by conventional transmission measurements large sample sizes are required. As an alternative, background-free direct absorption measurements have become attractive due to their high sensitivity¹. Currently, two photo-thermal techniques have been established, calorimetry²⁻⁴ and laser induced deflection (LID)⁵⁻⁷. The first method measures the temperature rise in the investigated sample to calculate the absorbed averaged power including surface absorption. To discriminate between surface and volume absorption, samples of different thickness are measured and the bulk absorption is calculated from a plot of the absorption versus sample thickness⁸. The LID technique uses the deflection of a probe laser beam induced by the local changes of the refractive index due to the temperature increase within the sample ("thermal lens"). It was demonstrated, that surface absorption does not contribute to the beam deflection and thus the bulk absorption values are obtained directly for each single sample⁷.

Within the last two years, the European CHOCLAB II project has brought together several groups performing direct absorption measurements in order to critically evaluate the existing work instructions for absorption measurements. For their extension to ArF excimer lasers so-called round-robin tests were carried out. Fluence dependent absorption measurements performed with equivalent fused silica samples and different experimental setups are compared to each other⁸. The deviating results have shown, that the measurement of the small absorption coefficients of fused silica is apparently a challenging task. Laser induced absorption and relaxation processes in fused silica are influenced by the

* christian.muehlig@ipht-jena.de; phone: +49-3641-302633; fax: +49-3641-302603; <http://www.ipht-jena.de>;
IPHT e.V., P.O.B 100239, 07702 Jena, Germany

experimental parameters like pulse repetition rate, laser pulse shape and fluence. Therefore, detailed investigations were initiated and first results presented recently⁷.

Earlier absorption measurements of fused silica at 193 nm revealed an absorption decrease within the first laser pulses of irradiation⁸. On the medium time scale absorption assumed a constant value, which can be considerably lower than the intermediate value shortly after starting the irradiation. Therefore, it is necessary to irradiate the sample until its absorption reaches the stable value. Often, the initial effect was attributed to surface cleaning by laser irradiation. However, this effect is also detected when measuring pure bulk absorption by the LID technique⁷. Additionally, a sample was stored at ambient conditions for a couple of days immediately after the laser induced decrease of absorption. No change of absorption was registered when irradiating the same sample with its new surface contamination. Therefore, we assume that the initial absorption decrease is due to laser induced bulk processes instead of surface cleaning. This interpretation is corroborated by the visually observed blue fluorescence behavior. Blue fluorescence in fused silica is induced by single photon absorption and attributed to oxygen deficient centers (ODC)⁹⁻¹². For clarification, the influences of selected defects on the parameters of absorption measurements upon ArF laser irradiation are investigated by laser induced fluorescence (LIF) and a work instruction is derived and proposed for measuring small absorption in fused silica.

2. EXPERIMENTAL SETUP

A scheme of the experimental setup for absorption, transmission and LIF measurements is shown in figure 1.

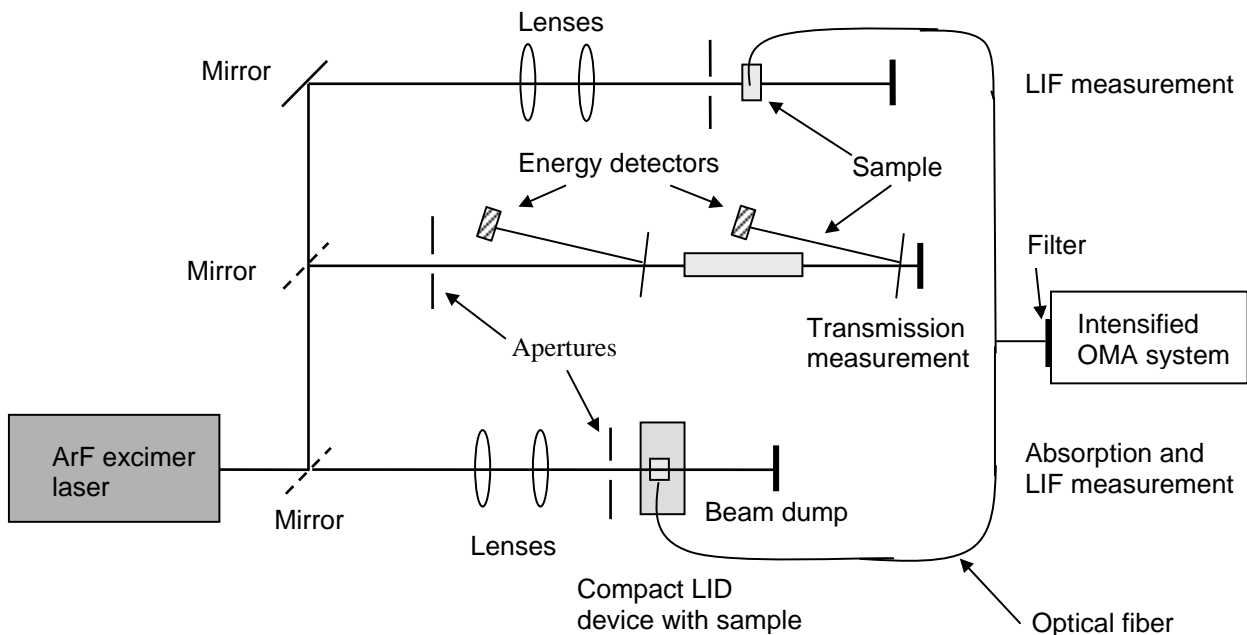


Figure 1: Scheme of the experimental setup to measure absorption, transmission and laser induced fluorescence

OH rich fused silica was irradiated by an excimer laser LPX 240i (Lambda Physik AG) at 193 nm. For simultaneous LID and LIF measurements (lowest measurement arm) the beam was shaped to a size of $5 \times 5 \text{ mm}^2$ at the sample ($20 \times 20 \times 10 \text{ mm}^3$) which is placed in a compact capsuled setup⁷. To record the LIF spectra an optical fiber was added to the compact LID. The combined LID and LIF investigations have been performed at a fluence of 20 mJ/cm^2 and a repetition rate of 50 Hz. For pure LID measurements repetition rates of 200 and 250 Hz and fluences ranging from 5 to

20 mJ/cm² have been applied. The LID signal is registered by an oscilloscope (LeCroy LC334A) whereas the LIF signal is recorded by an intensified gated OMA system (S&I).

Separate LIF investigations (upper measurement arm) were carried out with both, an unshaped beam of 15 x 5 mm² size and a lens shaped beam of 5 x 3 mm² size to measure the LIF signal over a wide range of fluences at a repetition rate of 10 Hz.

The transmission of 300 mm long fused silica samples (central measurement arm) was measured by energy monitors (Precision Systems and Instruments) in front and behind the sample. The unshaped laser beam was confined to a size of 15 x 5 mm² by an aperture. The repetition rate was 100 Hz at fluences of 2 – 10 mJ/cm².

3. RESULTS AND DISCUSSION

It was previously found that both, the visible blue fluorescence and the absorption of OH rich fused silica, are changing upon ArF laser irradiation. Therefore it appears attractive to directly compare the temporal evolution of the blue fluorescence and of the ArF laser absorption. For convenience of presentation the results of the LIF investigations are bundled in the following part and the absorption and transmission measurements are shown thereafter.

A typical ArF laser induced LIF spectrum related to the blue fluorescence is shown in figure 2a. Two bands ODC(a) and ODC(b) are seen which are attributed to two modifications of oxygen deficient centers ODC⁹⁻¹¹. The spectrum was recorded with a 100 μs time gate after the ArF laser pulse. The time gate width is much longer than the emission lifetimes of 0.48 μs and 0.38 μs determined for the ODC(a) and ODC(b) fluorescence, respectively.

To quantitatively evaluate the visible bleaching of the blue fluorescence, the time and energy integrated LIF signals of ODC(a) and ODC(b) were registered in intervals of 7 seconds during ArF laser irradiation and the two bands deconvoluted. The temporal evolution of these signals and their sum is sketched out in figure 2b and confirms the visual observations.

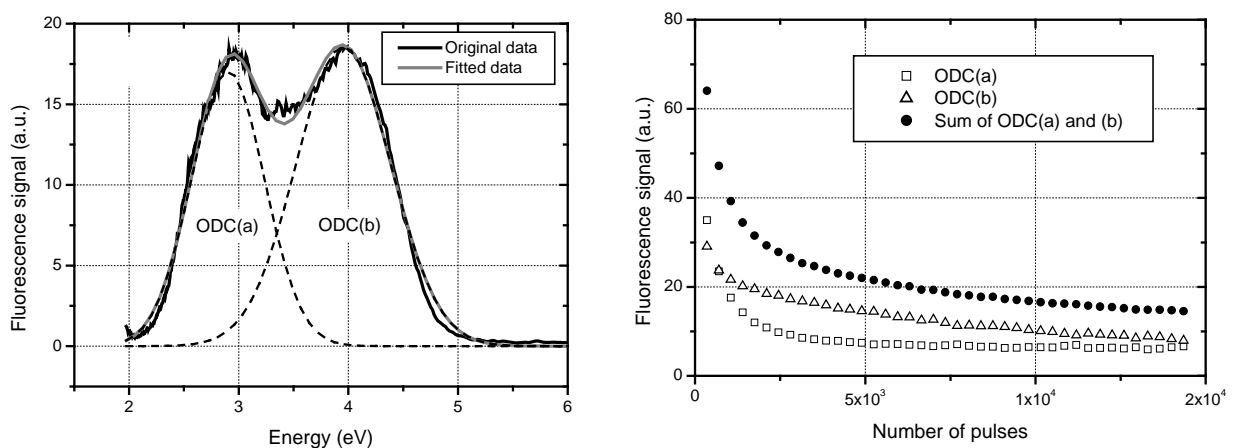


Figure 2: (a) Typical LIF emission spectrum of fused silica in the range between 2 and 6 eV showing two ODC fluorescence bands which are simulated by Gaussian functions.

(b) Time and energy integrated LIF signals: temporal development upon ArF laser irradiation

It is easily seen that the emission from ODC(a) decays much faster than that from ODC(b) and reaches a constant value before the end of the applied number of laser pulses. On the other hand, the decrease of the ODC(b) emission is still present at the end of the irradiation. The sum of the two ODC LIF signals also decays with the number of laser pulses and is assumed to reflect a diminishing number of oxygen deficient centers. It is further evident that the decrease has not yet stopped when switching off the laser.

One of the most interesting investigations of fused silica upon laser irradiation is the fluence dependence of its optical properties. Therefore, fluence dependent LIF measurements were carried out. The ODC fluorescence was registered after reaching a constant value (figure 3). Apart from the ODC fluorescence some LIF spectra of OH rich fused silica samples indicated an additional green-yellow fluorescence^{13,14} with a virtually constant intensity during ArF laser irradiation. The origin of this fluorescence is still not fully understood, but previous investigations using a fluorescence spectrometer have indicated that, similar to ODC, single photon absorption is the primary excitation process. Since earlier published investigations using a KrF excimer laser have already shown, that a saturation of the green-yellow fluorescence is evident for high fluences¹³, the fluence dependence of this green-yellow fluorescence at ArF laser irradiation was additionally investigated for a particular sample with the same recording conditions as for the ODC fluorescence (figure 4).

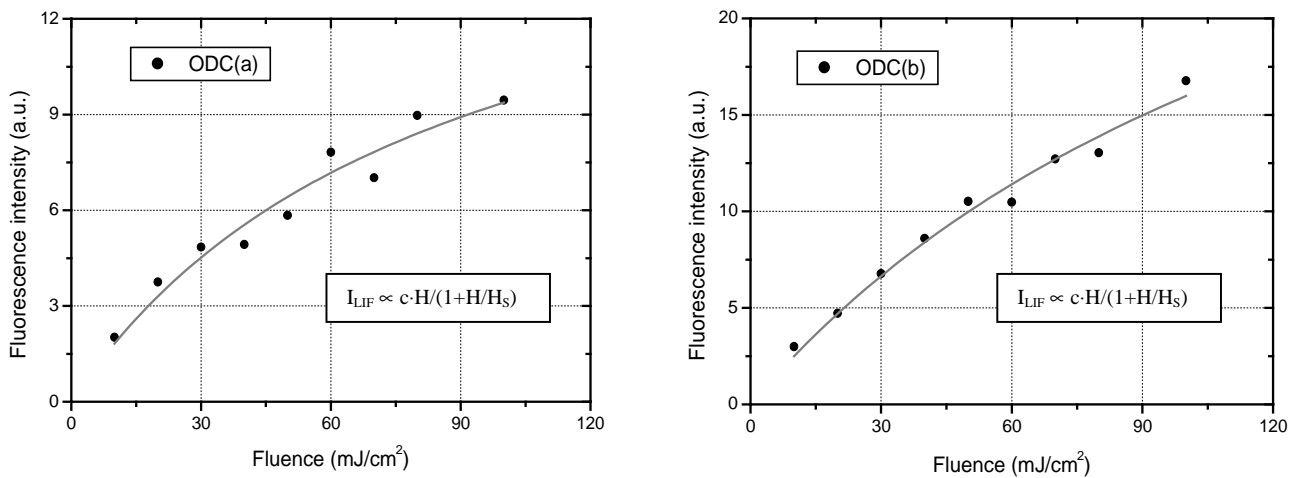


Figure 3: Time and energy integrated LIF intensities of the different ODC fluorescence bands with increasing fluence indicating the saturation of both ODC fluorescence bands. The displayed fit function is derived from assuming a saturation of the related absorption transition (see equation (1)).

The results in figure 3 and 4 make evident that both, the ODC and the green-yellow fluorescence intensities do not increase in a linear way with the fluence. For the ODC(a) and (b) the beginning of a saturation of the LIF signal is evident for high fluences whereas for the green-yellow fluorescence the saturation is already present at very low fluences.

With the knowledge of a single photon absorption process being the origin of the ODC and the green-yellow fluorescence, the fluence dependence in figure 3 and 4 can be explained by assuming a saturation of the primary absorption transition. Thus, the absorption coefficient for the corresponding single photon absorption process would follow the relation:

$$\alpha = \alpha_0 \cdot \left(1 + \frac{H}{H_S} \right)^{-1}, \quad (1)$$

with α_0 indicating the absorption coefficient at zero laser fluence and H_S the saturation fluence when the value for α has dropped to $\alpha_0/2$.

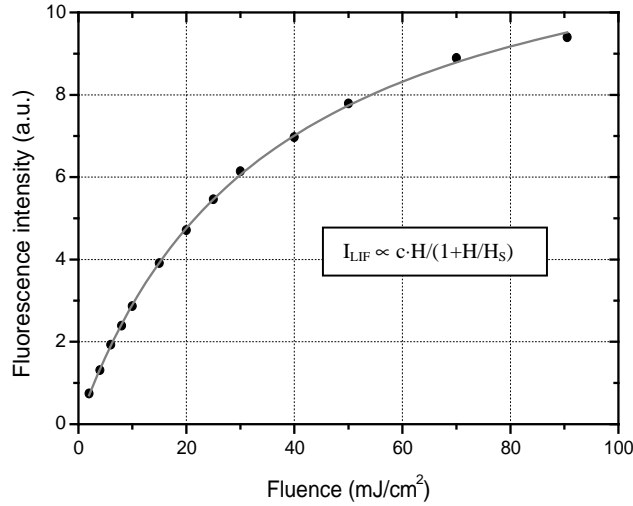


Figure 4: Time and energy integrated LIF intensity of the green-yellow fluorescence band with increasing fluence indicating the saturation of the fluorescence. The displayed fit function is derived from assuming a saturation of the related absorption transition (see equation (1)).

Applying a fit function derived from equation (1) to the results in figures 3 and 4, saturation fluences H_S of 85 mJ/cm² for ODC(b), 150 mJ/cm² for ODC(a) and 35 mJ/cm² for the green-yellow fluorescence are obtained. Thus, if a saturation of the corresponding absorption transition is the explanation of the behavior shown in figure 3 and 4 the range for fluence dependent absorption measurements has to be well below H_S or equation (1) has to be taken into account in the data analysis.

In the following the results of absorption and transmission measurements of OH rich fused silica samples will be presented. The results of the absorption measurements performed by LID simultaneously with the LIF measurements in figure 2b are displayed in figure 5a. Looking at the development of the absorption coefficient as a function of the incident ArF laser pulses a decrease is found. The course of the absorption decay (fig. 5a) differs from that of the summarized ODC related LIF (fig. 2b). However, the measured absorption is related to oxygen deficient centers and to E' centers obtained by conversion of ODC into E' centers¹², whereas the LIF measurements exclusively show oxygen deficient centers. Nonetheless, since there is so far no other observed contribution to the absorption decrease of fused silica, we assume from the obtained results, that the absorption decrease of fused silica upon ArF irradiation is due to the laser induced reduction of originally present oxygen deficient centers.

Furthermore, figures 2b and 5a reveal that the applied number of laser pulses are not sufficient to reach constant values for the absorption coefficient and the ODC fluorescence. Prolonged irradiation of three identical OH rich fused silica samples at 200 Hz and different fluences (5, 10 and 20 mJ/cm²), however, revealed constant absorption coefficient values after applying a dose D of 4 to 5 kJ/cm² with D = pulse number N x fluence H (fig. 5b). In addition, figure 5b

shows at the end of the irradiation that the absorption coefficients increase with the fluence indicating nonlinear absorption processes.

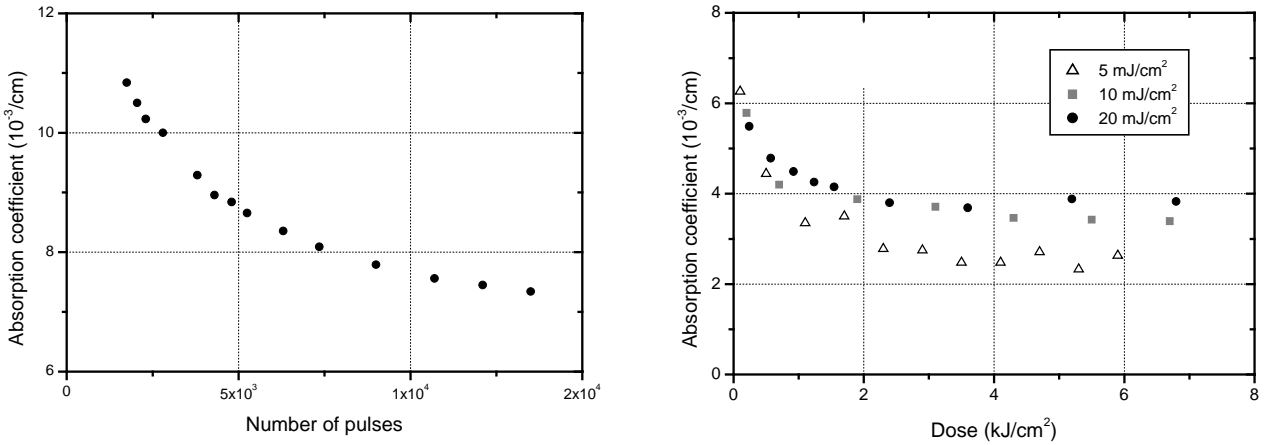


Figure 5: Absorption coefficients determined by LID (a) as a function of incident ArF laser pulses (20 mJ/cm^2 , 50 Hz) and (b) as a function of the irradiation dose $D = N * H$ (N = number of laser pulses, H = fluence)

To verify the results obtained by LID in figure 5b, transmission measurements were performed with three different OH rich fused silica samples of 300 mm length at a constant fluence of 5 mJ/cm^2 and a repetition rate of 150 Hz. Figure 6 shows similar decays for all samples whereas the decay amplitudes are different. It can again be assumed from figure 6 that a dose of 4 to 5 kJ/cm^2 is sufficient to terminate the absorption decrease.

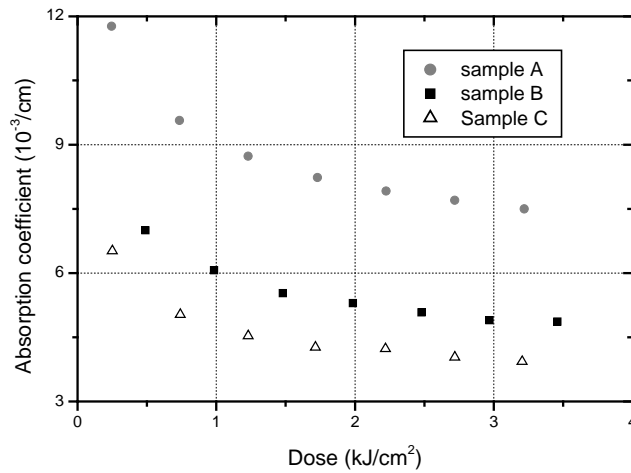


Figure 6: Absorption coefficients of 3 different 300 mm long OH rich fused silica samples determined by transmission measurements upon ArF laser irradiation with the same fluence of 5 mJ/cm^2 .

Summarizing the above investigations of OH rich fused silica using ArF laser irradiation and those previously published^{sandiego2001}, a measurement instruction is suggested for precise fluence dependent absorption measurements of OH rich fused silica upon ArF excimer laser irradiation and for a better comparison of the results obtained by different groups.

1. Before starting the measurements, a pre-irradiation dose $D = N \times H$ (N = number of pulses, H = fluence) of about 4 to 5 kJ/cm² has to be applied to ensure the end of the absorption decrease due ArF laser induced reduction of oxygen deficient centers. To avoid permanent laser induced absorption changes during pre-irradiation due to well-known two photon absorption processes a low fluence (few mJ/cm² range) is recommended.
2. The fluence dependent absorption or transmission measurements should be performed at a nearly constant integral-square pulse width τ_{IS} ¹⁵ because of its influence on the nonlinear absorption processes⁷. In a first approximation this can be ensured by keeping the laser discharge high voltage constant and varying the fluence by beam attenuators. Nonetheless, the laser pulse shape should be frequently measured to avoid substantial changes of τ_{IS} due to ageing of the laser gas.
3. For the repetition rate a value of 200 Hz or higher is recommended since previous experiments pointed out, that for values below 200 Hz the absorption of fused silica diminishes with the repetition rate at a constant fluence because of known relaxation processes between consecutive laser pulses⁷. For repetition rates higher than approximately 200 Hz, no significant change of the absorption is obtained⁸.
4. LIF investigations are recommended in addition to the absorption or transmission measurements to verify the occurrence of the above described fluorescence bands. Because of the saturation of the ODC and the green-yellow fluorescence, the fluence range for the absorption measurements should be either well below the found saturation fluences. Otherwise, possible saturation of a part of the small signal absorption needs to be involved in the subsequent analysis of the results.. Especially, the occurrence of the green-yellow fluorescence with its saturation fluence of 35 mJ/cm² puts strong limitations on the applicable fluence range.
5. The applied fluence range should include low values (few mJ/cm² range) to achieve a high accuracy when extrapolating results to zero fluence.

The above work instruction was used to investigate the absorption of several OH rich fused silica samples at different fluences by LID and transmission measurements. Prior to these measurements, LIF investigations revealed that all the measured samples showed ODC fluorescence only. Therefore, absorption measurements using the LID technique were carried out at 200 or 250 Hz and in a fluence range between 5 and 20 mJ/cm² which is well below the found two ODC saturation fluences. Thus, the assumed saturation of the ODC absorption transitions at high laser fluences is not considered here. The results (fig. 7a) show that the absorption coefficient of OH rich fused silica does not increase in a linear way with the fluence. Our results are in contrast to previously published ones at partially much higher fluences which have been analyzed by a modified Beer's law^{2,4,8} including a linear fit function.

To verify the LID results, fluence dependent transmission measurements of several OH rich fused silica samples of 300 mm length were carried out. Due to the experimental conditions for the transmission measurements the repetition rate was fixed to 100 Hz which is lower than the recommended value of 200 Hz or higher. The fluence was varied between 2 – 10 mJ/cm². Therefore, the absorption coefficients obtained by transmission measurements can not be compared quantitatively to those achieved by LID. However, the obtained fluence dependence of the absorption coefficient (fig. 7b) clearly confirms the nonlinear behavior shown in figure 7a.

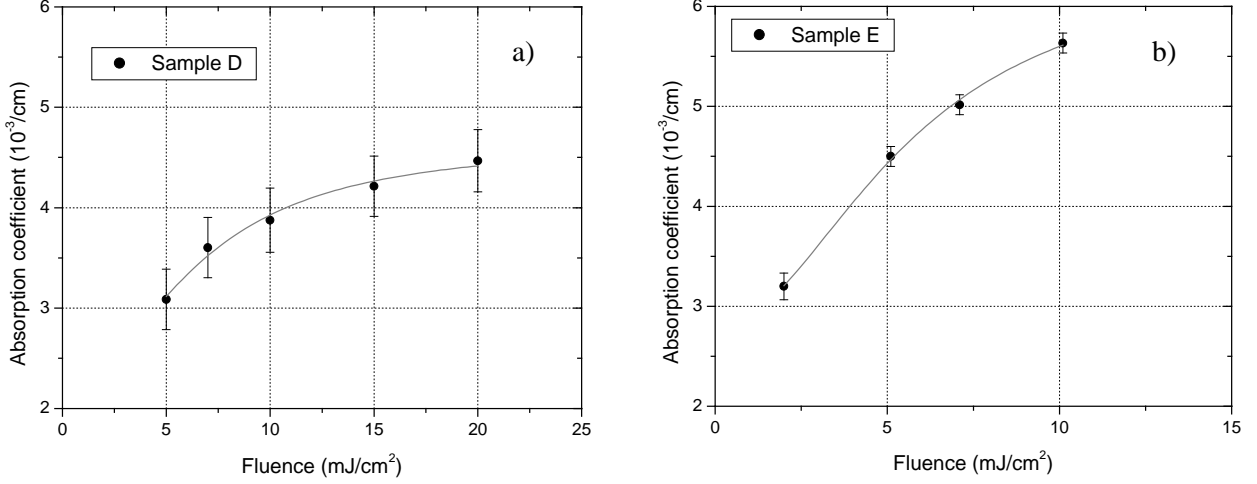


Figure 7: Absorption coefficient α of fused silica determined by LID (a) and transmission measurements (b) as a function of the incident laser fluence. The experimental data were fitted using the first and third term of equation (2).

The nonlinear dependence shown in figure 7 can be explained by the mechanisms of pulse laser induced absorption in fused silica. Previously, investigations of different groups indicated, that the pulse laser induced nonlinear absorption is caused by two photon excitation followed by a single photon absorption of the generated defect center (E' or $NBOH$)^{16,17} which forbids the application of Beer's law. Without going into detail, the energy transmission^{18,19} of ArF laser pulses and their nonlinear effects in fused silica are consistent with a fitting model for the absorption coefficient α which has the structure:

$$\alpha = \alpha_1 + \frac{\alpha_2}{1 + \frac{H}{H_s}} + \frac{c_1 \cdot H^2}{1 + c_2 \cdot H^2}. \quad (2)$$

Here α_1 denotes the constant part of the small signal absorption coefficient. The second term takes into account a possible fluence dependent small signal absorption coefficient (see equation (1)). The third term results from the nonlinear absorption due to two photon absorption followed by single photon absorption. The material dependent constants c_1 and c_2 contain information about defect relaxation and physical properties of the relevant absorption transitions like single and two photon absorption cross sections. Applying the first and third term of equation (2) to the results in figure 7 yields a very good agreement with the obtained experimental results.

However, there is still work to be done to analyze the fitting results with respect to the constants c_1 and c_2 for a more quantitative evaluation of different OH rich fused silica material. In addition, prolonged LID absorption measurements are in preparation to obtain information about the present absorption increase upon long lasting laser irradiation. In contrast to common marathon tests²⁰ the experiments will be performed at moderate higher fluences ($\sim 20 \text{ mJ/cm}^2$) to reduce the irradiation duration to a fraction of the time usually necessary at lithography application fluences. Due to the very small sample thickness (10 mm) required for LID measurements prohibitive effects like microchannel formation can be avoided. This is a serious problem when investigating extended fused silica samples at higher fluences by transmission measurements.

4. SUMMARY

Applying a new experimental setup, simultaneous LIF and absorption measurements (LID technique) of OH rich fused silica were carried out. It was demonstrated, that the absorption decrease during the first few pulses of ArF excimer laser irradiation is not due to surface cleaning, but results from a diminishing of absorbing oxygen deficient centers. Furthermore, the experiments gave evidence, that a pre-irradiation dose D with $D = N \times H$ (N = pulse number, H = fluence) of $4 - 5 \text{ kJ/cm}^2$ is necessary to terminate the ODC related absorption decrease. Fluence dependent LIF measurements indicate, that the laser induced fluorescence of ODC and a still to clarify defect center showing green-yellow fluorescence saturate for high fluences. This might be explained by the saturation of the corresponding absorption transitions. Especially, a very low saturation fluence of 35 mJ/cm^2 was found for the green-yellow fluorescence. As a consequence of the experimental data a new measurement instruction was derived for precise fluence dependent absorption measurements of OH rich fused silica using ArF excimer laser irradiation. Applying this measurement instruction a nonlinear increase of the absorption with the fluence was found by direct absorption (LID) and transmission investigations. Based on the common understanding of pulse laser induced defect generation and annealing in OH rich fused silica, the consideration of the energy transmission of laser pulses in fused silica yields a fitting model which shows a very good agreement with the obtained experimental data.

ACKNOWLEDGEMENTS

This work was supported by the Bundesministerium für Bildung und Forschung (BMBF) as part of the EUREKA project EU 1269 (CHOCLAB II). The authors would like to thank the Schott Lithotec AG for providing the fused silica samples.

REFERENCES

1. S. L. Logunov, "Measurements of optical losses in thin films," *Proc. of CLEO Europe*, **CthA4**, p. 279, 2000
2. E. Eva, K. Mann, "High-resolution calorimetric absorption measurements on optical components for excimer lasers," *Proc. of SPIE*, **2966**, 1996.
3. E. Eva, K. Mann, "Calorimetric measurement of two-photon absorption and color-center formation in ultraviolet-window materials," *Appl. Phys. A*, **62**, pp. 143-149, 1996
4. E. Eva, K. Mann, "Nonlinear absorption phenomena in optical materials for the UV-spectral range," *Appl. Surface Science*, **109/110**, pp. 52-57, 1997
5. M. Guntau, W. Triebel, "Novel method to measure bulk absorption in optically transparent materials," *Rev. Sci. Instrum.*, **71**, pp. 2279-2282, 2000
6. W. Triebel, S. Bark-Zollmann, C. Mühlig, A. Voitsch, F. Coriand, J. Alkemper, "Evaluation of Fused Silica for DUV Laser Applications by Short Time Diagnostics," *Proc. of SPIE*, **4103**, pp. 1-11, 2000
7. Ch. Mühlig, S. Kufert, S. Bark-Zollmann, W. Triebel, "Measuring small absorption losses of laser pulses in fused silica by a pump and probe technique," *Proc. of SPIE*, **4449**, pp. 13-21, 2001
8. U. Natura, Ch. Mühlig, W. Triebel, U. Leinhos, K. Mann, E. Eva, A. Pfeiffer, "Characterization of 193nm light absorption in fused silica by various measurement techniques," *Proc. of the 6th International Workshop on Laser Beam and Optics Characterization (LBOC)*, Munich, 2001
9. D. L. Griscom, "Optical properties of defects in silica glass," *J. Non-Cryst. Solids*, **99**, pp. 899-916, 1991
10. A. V. Amosov, S. I. Vavilov, A. O. Rybaltovsky, "Oxygen-deficient centers in silica glasses: a review of their properties and structure," *J. Non-Cryst. Solids*, **179**, pp. 75-83, 1994
11. A.O. Rybaltovskii, E. M. Dianov, K. M. Golant, I. V. Nikolin, A. A. Frolov, Yu. S. Zavorotny, P. V. Chernov, "Photoluminescence of Silica Glasses Prepared by Plasma-Chemical Oxidation of SiCl_4 in Gas Phase under Oxygen-Deficient Conditions," *Glass Physics and Chemistry*, **25**, pp. 137-144, 1999
12. Y. Kawaguchi, N. Kuzuu, "Characteristics of Excimer-Laser-Induced Luminescence of the Ground Surface of Silica Glass," *Jpn. J. Appl. Phys.*, **39**, pp. 180-185, 2000
13. Ch. Mühlig, S. Bark-Zollmann, D. Grebner, W. Triebel, "Pulsed UV Laser Raman and Fluorescence Spectroscopy of Large Area Fused Silica Photomask Substrates," *Proc. of SPIE*, **4000-1**, pp. 632-638, 2000

14. Ch. Mühlig, W. Triebel, S. Bark-Zollmann, D. Grebner, "In situ diagnostics of pulse laser-induced defects in DUV transparent fused silica glasses," *Nucl. Instr. Meth. Phys. Res. B (NIMB)*, **166-167**, pp. 698-703, 2000
15. T. P. Duffey, T. Embree, T. Ishihara, R. Morton, W. N. Partlo, T. Watson, R. Sandstrom, *Proc. of SPIE*, **3334**, p. 1014, 1998
16. J. Moll, "Assessing Damage for UV-Laser-Resistant Fused Silica," *Photonics Spectra*, **April**, pp. 78-81, 2002
17. W. Triebel, M. Guntau, Ch. Mühlig, A. Wiese, "Time Resolved Investigation of Pulse Laser Induced Defects in Optical Glasses of High UV-Transmission," *Glass Sci. Technol.*, **71C**, pp. 67-72, 1998
18. S. Belke, I. Kapp, W. Triebel, B. Wilhelmi, *Picosecond Phenomena II*, Springer Series in Chem. Phys. 14, p. 367, 1980
19. A. Dragomir, J. G. McInerney, D. N. Nikogosyan, P. G. Kazansky, "Two-photon absorption properties of commercial fused silica and germanosilicate glass at 264 nm," *Appl. Phys. Lett.*, **80**, 2002
20. V. Liberman, M. Rothschild, J. H. C. Sedlacek, R. S. Uttaro, A. Greenville, A. K. Bates, C. Van Peski, "Excimer-laser-induced degradation of fused silica and calcium fluoride for 193-nm lithographic applications," *Optics Letters*, **24**, 1999