Comparative study of fused silica materials for ArF laser applications

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Abstract

We report on a comparative study of a variety of fused silica materials for ArF laser applications, which differ regarding their OH content. Laser induced deflection (LID) technique is applied to measure directly and absolutely the absorption coefficient in fused silica materials at 193 nm as a function of the incident laser fluence in the range 1...3 mJ/cm² before and after applying 20 million shots at a fluence of 5 mJ/cm². In addition the laser induced refractive index change is detected by interferometer measurements after the prolonged irradiation for all samples.

Prior to the long term irradiation, low OH containing fused silica ([OH] < 80 wt-ppm) exhibits both, the lowest absorption coefficient and the lowest absorption increase with fluence (dk/dH) in the range 1...3 mJ/cm². During 20 million laser pulses at 5 mJ/cm², however, the absorption and the dk/dH values show a strong increase for the low OH containing fused silica. In contrast, the absorption of the medium OH containing samples ([OH] = 200...650 wt-ppm) is highest prior to the long term irradiation but is remarkably lowered throughout the 20 million laser pulses. High OH containing fused silica ([OH] > 900 wt-ppm) shows an intermediate absorption level, which only slightly increases or decreases during the irradiation with 20 million laser pulses.

The ArF irradiation induced refractive index change is positive (= compaction) for all samples at the fluence 5 mJ/cm². For analysis, a particular material classification is taking into account. For low and medium OH containing samples, referred to as compaction-dominated, the compaction factor increases with the OH content. For high OH containing samples, referred to as rarefaction-dominated, the resulting compaction factor decreases with increasing H₂ content.

Keywords: Fused silica, ArF laser, absorption, laser induced degradation, compaction

1. INTRODUCTION

For DUV laser applications different modifications of fused silica (FS) are on the market to serve for distinct requirements defined by various applications or even within one application. The most prominent example is the ArF laser lithography where particular requirements regarding absorption and refractive index change need to be fulfilled. The outcome of this for example was the development of fused silica that even at very low application fluences does not show the so-called rarefaction effect, i.e. the decrease of refractive index during prolonged ArF laser irradiation. Another development was the manufacturing of fused silica that changes its absorption only weakly even at a more elevated fluence level. Most of fused silica's modifications have been connected with the tuning of material parameters like the OH and the H_2 contents.

The aim of the present work is to define and carry out an appropriate evaluation that gives insights in the differences between the several fused silica modifications with a particular focus on the absorption behaviour and the refractive index change obtained for the fluence range of a particular application. Furthermore, possible correlations between the obtained optical properties and material parameters have been investigated by measuring the OH and H_2 contents as well as the laser induced fluorescence (LIF).

2. EXPERIMENTAL METHODS

For investigating the absorption behaviour upon ArF laser irradiation, the laser induced deflection (LID) technique is applied. The LID technique is one amongst many photothermal absorption techniques and has been introduced previously and applied commonly to measure residual absorption in bulk materials and thin films [1-3]. The main advantage compared to other photothermal techniques is LID's ability to provide absolute absorption data by using an

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independent electrical calibration. Furthermore, choosing the appropriate sample geometry the bulk absorption coefficient can be determined without the influence of the polished surfaces [4]. The basic LID principle and the experimental setup for the investigations are shown in Figure 1.



Figure 1: a) Sketch of the LID measurement principle including calculated isolines of temperature and refractive index for fused silica as well as the probe beam propagation and b) compact experimental setup for direct absorption measurements using the LID technique

In this work, a total of 16 fused silica samples from different vendors have been investigated, 7 of them show a low OH content of less than 80 wt-ppm. Further 7 samples feature a high OH content of larger than 900 wt-ppm. The remaining two samples are of medium OH content in the range 200...650 wt-ppm. The sample geometry was chosen to be $25x25x20 \text{ mm}^3$ which allows for pure bulk absorption measurements. For 193 nm irradiation an ArF excimer laser (ExciStar S Industrial, Coherent GmbH) with a repetition rate f = 1 kHz was applied. The ArF laser beam has been shaped by a diffractive optical element to achieve a homogeneous intensity distribution (top-hat) of $6x6 \text{ mm}^2$ at the sample's position. For the ArF laser pulses an integral-square pulse width $\tau_{IS} \sim 16 \text{ ns}$ is calculated. For absorption characterization before and after prolonged irradiation, the fluence range $1...3 \text{ mJ/cm}^2$ has been applied according to the applications specifications. The prolonged irradiation has been carried out over 20 million pulses at 5 mJ/cm².

The OH and H_2 contents have been determined by infrared spectral photometric measurements. The ArF laser induced refractive index changes (phase difference) have been detected by interferometer measurements at 633 nm (µPhase Plano 2", FISBA OPTIK). Laser induced fluorescence measurements have been carried out according to a previously described manner [5].

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Definition of test conditions

As a first step, appropriate test conditions have been defined. In order to characterize the absorption behaviour before and after the prolonged ArF laser irradiation the definition of relevant parameters is essential. For fused silica it is physically not reasonable to simply define a two-photon absorption (TPA) coefficient since it has been demonstrate earlier that the absorption increase with fluence is not linear over the entire fluence interval [6,7]. For example, Figure 2 shows fluence dependent absorption data for different fused silica materials which demonstrate the nonlinear absorption increase with fluence. Thus, in contrast to e.g. CaF_2 [8,9], it is not possible to extrapolate the fluence dependent absorption linearly over a wide fluence range to define the two photon absorption coefficient according to Beer's Law. For particular small fluence intervals, however, it is appropriate to define a parameter dk/dH to account for the absorption increase with increasing fluence (here: fluence interval 1...3 mJ/cm²).

Recently it was demonstrated that during the initial ArF laser irradiation, some fused silica materials possess a fast absorption increase followed by a certain period of absorption decrease until a new stationary absorption level is reached [10]. Figures 3a shows this behaviour which is relevant for samples with medium and high OH content. In contrast, Figure 3b shows the results for the initial irradiation of a low OH containing sample.



Figure 2: Fluence dependent absorption coefficients of three different fused silica samples showing the nonlinear absorption increase with increasing fluence



Figure 3: Absorption behaviour upon initial ArF laser irradiation identified by the course of the LID measuring signal a) fast absorption increase followed by an absorption decrease to a new stationary value obtained for medium and high OH containing samples and b) no initial absorption change obtained for low OH containing samples

Therefore, in order to account for the particular initial absorption behaviour of medium and high OH containing samples, the latter have been pre-irradiated with a total dose of about 6 kJ/cm² to terminate most of the initial absorption change. In order to enhance the absorption degradation it is desired to increase the fluence for prolonged irradiation compared to the real application. It is, however, important to prevent microchannel formation during prolonged irradiation [11]. Furthermore, regarding the refractive index change the real application conditions need to be taken into account for deciding about the ability of enhanced testing. In the present study, the application fluence range is 1...3 mJ/cm². Fortunately, all fused silica samples will show a refractive index increase (= compaction) upon ArF laser irradiation [12]. As a result, the prolonged ArF irradiation has been performed with moderately increase fluence of 5 mJ/cm².

Taking all the above aspects into account, the following test conditions have been defined:

- 1. Interferometer measurement at 633 nm of the transmitted wavefront
- 2. Pre-irradiation with comparable dose of 6 kJ/cm^2 if the fast initial absorption change is visible
- 3. Absorption measurements as a function of fluence to define starting values $\rightarrow k_{start}$ and $dk/dH (1...3 mJ/cm^2)$
- 4. Irradiation with 20 Mio. pulses (1 kHz, 5 mJ/cm², $\tau \sim 15$ ns) to simulate 0.5*10⁹ pulses at 1 mJ/cm² (~ 10% of desired lifetime in the application)
- 5. Repeating step $3 \rightarrow$ changes in k and $dk/dH (1...3mJ/cm^2)$
- 6. Interferometer measurement to obtain phase difference at 633 nm
- 7. Measuring OH and H_2 contents
- 8. Laser induced fluorescence measurements

For all measurements the absorption coefficient k is given to the base 10.

3.2 Results of absorption measurements

Starting absorption value at 1 mJ/cm² and its change upon ArF laser irradiation

In order to compare the absorption data prior to the prolonged ArF laser irradiation, the data obtained at the fluence of 1 mJ/cm² are considered. Figure 4a shows the starting absorption k_{start} as a function of the OH content in the investigated samples. Besides the absorption data, a straight line at $k_{start}=5*10^{-4}$ cm⁻¹ is added. This line is drawn as a guide for the eyes to distinguish the data for low, medium and high OH containing samples and does not correspond to any application specifications. It is obvious that the low OH containing samples show a significant lower starting absorption at 1 mJ/cm² than the medium to high OH containing samples (please note the logarithmic scale of the y axis). All k_{start} values for the low OH containing samples are below $1*10^{-3}$ cm⁻¹. The high OH containing materials mainly possesses k_{start} values around $1*10^{-3}$ cm⁻¹ whereas the medium OH containing samples exhibit the highest k_{start} values ranging around $5*10^{-3}$ cm⁻¹.



Figure 4: a) Starting absorption data k_{start} (H = 1 mJ/cm²) as a function of the OH content and b) change of the absorption k (H = 1 mJ/cm²) during prolonged ArF laser irradiation with 20 Mio. pulses at 5 mJ/cm²

The change of the k_{start} values after prolonged ArF laser irradiation with 20 Mio. pulses at 5 mJ/cm² is displayed in Figure 4b. The results clearly show that for the low OH containing samples, having the lowest k_{start} values, the absorption increases significantly throughout the ArF laser irradiation (compare the data with respect to the straight line for $k = 5*10^{-4}$ cm⁻¹). In contrast, for the high OH containing samples only a very weak increase or decrease is found. As a result, the k values of low and high containing samples become very comparable after irradiation of 20 Mio. pulses at 5 mJ/cm². For the medium OH containing samples, the absorption decreases remarkably. However, the remaining absorption is still

clearly higher than for the other samples. The authors assume that for the medium OH containing samples, the initial absorption change requires more laser pulses than for the high OH containing samples and therefore the absorption has been further lowered after the initially applied irradiation dose of 6 kJ/cm^2 due to the consecutive irradiation.

Fluence dependent absorption and its change upon ArF laser irradiation

The fluence dependent absorption dk/dH is determined by linear extrapolation of the absorption data obtained for the fluence range $1...3 \text{ mJ/cm}^2$. Figure 5a shows the dk/dH $(1...3 \text{ mJ/cm}^2)$ data as a function of the OH content in the investigated samples prior to the prolonged ArF laser irradiation. Besides the dk/dH data, a straight line at dk/dH= 1^{*10^4} cm/mJ is added. This line is drawn as a guide for the eyes to distinguish the data for low, medium and high OH containing samples and does not correspond to any application specifications. It is obvious that the low OH containing samples show significant lower dk/dH values than the medium to high OH containing samples (please note the logarithmic scale of the y axis). Mostly the dk/dH values for the low OH containing samples are below $1*10^{-4}$ cm/mJ. The high OH containing materials mainly possesses dk/dH values in the range $1...5*10^{-4}$ cm/mJ whereas the medium OH containing samples exhibit the highest dk/dH values ranging around $1*10^{-3}$ cm/mJ.



Figure 5: Fluence dependent absorption dk/dH obtained for the fluence range $1...3 \text{ mJ/cm}^2$ as a function of the OH content a) prior to the prolonged ArF laser irradiation (= starting values) and b) change of the dk/dH values during ArF laser irradiation with 20 Mio. pulses at 5 mJ/cm²

The change of the dk/dH values after prolonged ArF laser irradiation with 20 Mio. pulses at 5 mJ/cm² is displayed in Figure 5b. The results clearly show that for the low OH containing samples, having the lowest starting values, the dk/dH values increase significantly throughout the ArF laser irradiation (compare the data with respect to the straight line for dk/dH = $1*10^{-4}$ cm/mJ). In contrast and similar to the k values in the previous section, for the high OH containing samples only a very weak increase or decrease is found. As a result, the dk/dH values of low and high containing samples become very comparable after irradiation of 20 Mio. pulses at 5 mJ/cm². For the medium OH containing samples, a stronger absorption decreases is visible. However, the remaining dk/dH values are still clearly higher than for the other samples. The authors assume that similar to the results in the previous section, the initial absorption change requires more laser pulses for the medium OH containing samples than for the high OH containing samples have been lowered somewhat stronger after the initially applied irradiation dose of 6 kJ/cm² due to the consecutive irradiation.

When looking at the results from Figures 4 and 5, a general correlation is found between the starting absorption k_{start} at 1 mJ/cm² and the starting fluence dependent absorption dk/dH. Figure 6 demonstrates that the lower the k_{start} value the lower is the dk/dH value. Therefore, in order to obtain a qualitative comparison between different fused silica materials regarding the dk/dH values, a single measurement within the considered fluence range is sufficient.



Figure 6: Correlation between starting absorption k_{start} at $1mJ/cm^2$ and starting fluence dependent absorption dk/dH for the range 1...3 mJ/cm². The colours of the data points refer to the sample's OH content as shown in Figures 4 and 5.

Laser induced fluorescence (LIF) and correlation to the absorption behaviour

Laser induced fluorescence (LIF) measurements have been carried out to investigate possible changes in defect concentrations during the prolonged ArF laser irradiation in order to find correlations to the observed absorption changes. For that the LIF spectra taken from the irradiated and a non-irradiated part of the samples are compared. It has been found, that for the medium and high OH containing samples the LIF spectra show a comparable qualitative result. In contrast, quite different LIF spectra have been obtained for the low OH containing samples, possibly due to the partially different manufacturing processes. Therefore, this section deals solely with the correlation between LIF spectra and absorption behaviour obtained for medium and high OH containing samples.

Figure 7 displays the characteristic LIF spectra in the wavelength range 200...600 nm obtained for samples with medium to high OH content. In this wavelength range the blue fluorescence of oxygen-deficiency centers (ODC) at around 300 and 400 nm is prominent [5]. It is seen, that after the prolonged irradiation the ODC fluorescence intensity is significantly diminished compared to its original condition. Recently, this behaviour have been described and modelled by defect center transformation and subsequent annealing [10]. Therefore, the authors believe that the initial ODC concentration affects the absorption behaviour of the medium to high OH containing samples.



Figure 7: Comparison of the oxygen-deficiency centers (ODC) fluorescence obtained in the prolonged irradiated and in a nonirradiated part of a sample with medium to high OH content

To proof that, the integral LIF intensity of ODC was taken and compared to the starting dk/dH values. The results in Figure 8a demonstrate that the higher the initial ODC concentration, given by the LIF spectrum between 250 and 550 nm, the higher is the fluence dependent absorption dk/dH. A similar correlation is also valid for the starting absorption k_{start} as easily derived from Figure 6 and therefore not separately displayed. Furthermore, Figure 8b also shows that the k_{start} value and therefore also the initial ODC concentration is correlated to the absorption change during the prolonged ArF laser irradiation. Here, a high k_{start} value (>> 1*10⁻³ cm⁻¹) corresponds to a strong absorption decrease as visible in Figure 4b for the medium OH containing samples. For a very low k_{start} value (< 5*10⁻⁴ cm⁻¹) a significant increase is observed. For k_{start} values around 1*10⁻³ cm⁻¹, only a very weak absorption increase or decrease is observed. Thus, for samples with a medium to high OH content the single measurement of the k_{start} value gives a qualitatively hint about the potential absorption change.



Figure 8: Medium and high OH containing fused silica: a) Correlation between the initial ODC concentration, given by the integral ODC fluorescence, and the starting dk/dH values and b) correlation between the k_{start} value and the absorption change after irradiation with 20 Mio. pulses at 5 mJ/cm²

Refractive index change

Figure 9 shows the phase difference at 633 nm, measured after the prolonged ArF laser irradiation compared to the initial condition of the non-irradiated sample, as a function of the sample's OH content.



Figure 9: ArF laser induced phase difference at 633 nm as a function of the sample's OH content

For all samples, a positive phase difference is obtained corresponding to a refractive index increase (= compaction). The measured phase difference strongly depends on the sample's OH content. A low OH content correlates to a low phase difference, i.e. a low refractive index increase.

In order to correlate the phase difference to material properties one has to distinguish between different material classifications. Low and medium OH containing samples are referred to as compaction-dominated. Therefore, the refractive index change dn due to ArF laser irradiation can simply be explained by [13]

$$dn = k^{(1)} \cdot \frac{N \cdot I^2}{\tau} \tag{1}$$

where $k^{(1)}$ is the compaction factor, N the pulse number, I the irradiation fluence and τ the temporal pulse width. In contrast, high OH containing samples refer to as rarefaction-dominated. Thus, both refractive index decrease (= rarefaction) and refractive index increase (= compaction) occurs simultaneously [13]. The overall refractive index change is determined by the application fluence. In the present study, the overall refractive index change is positive (Fig. 9) and therefore it is appropriate to use a simplified equation to characterize the compaction behaviour [14]

$$dn = k^{(2)} \cdot \left(\frac{N \cdot I^2}{\tau}\right)^{0.6} \tag{2}$$

where $k^{(2)}$ is also defined as compaction factor. The rarefaction effect is taken into account by the reduced weighting. Figure 10a shows the correlation between the calculated compaction factors $k^{(1)}$ and the OH content for low to medium OH containing samples. It is evident that the compaction factor increases with the OH content. Therefore, a low OH content is favorable when a low refractive index increase is required. For the low to medium OH containing samples, no influence of the H₂ content is observed. In contrast, Figure 10b shows that the compaction factor $k^{(2)}$ for high OH containing samples correlates with the sample's H₂ content and no correlation is found to the OH content. The authors believe that this can be explained by the rarefaction effect that increases with increasing H₂ content. Therefore, a high H₂ content corresponds to a stronger compensation of the refractive index increase.



Figure 10: a) compaction factor $k^{(1)}$ (Equ. 1) as a function of the OH content for low to medium OH containing samples and b) compaction factor $k^{(2)}$ (Equ. 2) as a function of the H₂ content for high OH containing samples

4. SUMMARY

A comparative study of different fused silica modifications for the use in ArF laser application is presented. The investigated fused silica materials are divided into samples with low OH content ([OH] < 80 wt-ppm), medium OH content ([OH] = 200...650 wt-ppm) and high OH content ([OH] > 900 wt-ppm). The evaluation procedure and the test parameters have been based on the irradiation conditions for particular applications. Therefore, the authors compared the samples regarding their starting absorption k_{start} at the fluence 1 mJ/cm² and their fluence dependent absorption dk/dH in

the range 1...3 mJ/cm². Furthermore, the change of these parameters upon prolonged ArF laser irradiation with 20 Mio. pulses at a moderately increased fluence of 5 mJ/cm² as well as the irradiation induced refractive index change at 633 nm have been measured. Applying a fluence of 5 mJ/cm², e.g. slightly higher than the application range 1...3 mJ/cm², serves for an enhanced degradation while being low enough to prevent the formation of microchannels in the samples.

The investigations have shown that the low OH containing fused silica exhibit the lowest values for both, k_{start} and the initial dk/dH whereas for the medium OH containing samples the highest values are obtained. As a result of the prolonged ArF laser irradiation, however, the k and dk/dH values for the low OH containing samples strongly increase whereas for the medium OH containing samples a strong decrease is observed. For the high OH containing samples, only a weak increase or decrease is measured for the k and dk/dH values, respectively. It is remarkable, that after applying 20 Mio. pulses at 5 mJ/cm², low and high OH containing samples exhibit very comparable k and dk/dH values. As a general correlation it is found that the lower the initial k_{start} value the lower is the fluence dependent absorption dk/dH.

The measured phase difference at 633 nm after prolonged ArF laser irradiation is positive for all samples indicating that compaction is dominant for all samples at the applied irradiation fluence of 5 mJ/cm². When comparing the total phase difference, the low OH containing samples show the smallest compaction values. After classifying the materials into either compaction-dominant (low and medium OH content) or rarefaction-dominant (high OH content) we have calculated the sample's compaction coefficients. We found that for compaction-dominant samples, the compaction factor increases with the OH content and shows no dependence on the H₂ content. In contrast, for rarefaction-dominated samples the compaction coefficient decreases with increasing H₂ content whereas no dependence have been found on the OH content.

In addition, laser induced fluorescence (LIF) measurements have been performed to correlate certain defects in fused silica to the obtained absorption behaviour. For the medium to high OH containing samples it is found that the observed absorption behaviour correlates to the initial oxygen-deficiency center (ODC) concentration indicated by a blue fluorescence in the wavelength region 250...550 nm. Therefore, short-time LIF tests are very promising to qualitatively evaluate the absorption properties of fused silica materials with medium and high OH contents.

In the case of low OH containing fused silica no correlation was found between LIF and absorption, possibly due to the usage of stronger varying manufacturing processes than applied for the other fused silica material.

As a final conclusion, selecting the most appropriate fused silica material in the DUV strongly depends on the actual application conditions. In particular, the application will define whether the change of absorption or refractive index is the critical figure of merit. Therefore, to gain the best performance out of a DUV optical system may require the usage of more than one fused silica modification.

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