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In situ diagnostics of pulse laser-induced defects in DUV transparent fused silica glasses

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Abstract

Excimer laser pulses ($\lambda = 248$ or 193 nm) induce transient and permanent defects in optical glasses of high UV transparency. Such defects are causing additional absorption and changes of density and refractive index, respectively (compaction). The interaction of each laser pulse with different OH-rich fused silica samples was investigated by real time measurements of laser-induced fluorescence (LIF) and of Raman spectra excited by the 248 nm KrF-excimer laser. The irradiation of the glasses with energy densities of about 10 mJ/cm^2 and more induces E' and NBOH defects simultaneously. The laser-induced fluorescence of NBOH defect centres at 650 nm characterises the kinetics of defect generation and relaxation. The primary absorption process is the two-photon absorption of KrF laser pulses. The relaxation of defects in the time interval between the laser pulses is mainly influenced by diffusion limited processes. Locally resolved LIF and Raman spectra allow the investigation of homogeneity and laser damage stability in large area substrates (e.g. for mask blanks). Raman spectra excited by KrF laser pulses are measured to detect precursors and intermediates of laser-induced defects and molecular hydrogen in the glass matrix. The detection limit of H_2 molecules is in the range of 10^{17} cm^{-3} . A correlation between LIF intensities and H_2 concentrations is found. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Synthetic fused silica of high DUV transmission is widely used in scientific and industrial applications. In order to develop fused silica as a basic material for optical components in DUV

laser lithography, it is necessary to characterise the material's behaviour under the influence of pulsed excimer laser radiation. Excimer laser pulses ($\lambda = 248$ or 193 nm) induce transient and permanent defects in optical glasses of high UV transparency. Such defects are causing additional absorption and changes of density and refractive index, respectively (compaction). It is necessary to investigate the correlation between excimer laser-induced defect formation and selected species (e.g. molecular hydrogen). One goal of such

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investigations is the development of a model of radiation-induced ageing processes in glasses. Another aim of the investigations is the determination of relationships between intrinsic material parameters of fused silica and technological conditions.

2. Characterisation of materials and applications

The investigated materials are pure fused silica glasses with a high OH content (around 800 until 1200 ppm) from several material providers. They are used as optical components for UV laser beam shaping and guiding and UV laser microlithography. Today the mainly used wavelengths for these applications are 248 nm (KrF excimer laser) and 193 nm (ArF excimer laser).

In the near future the applicability of optical materials like selected fused silica ('dry' material) and CaF_2 must be tested at shorter wavelengths (e.g. 157 nm F_2 laser).

The typical application conditions of the OH-rich fused silica materials at 248 and 193 nm are characterised by pulse repetition rates in the range of 400 Hz until 1000 Hz, where the fluences range from 0.5 to 10 mJ/cm^2 . A guaranteed lifetime of about 10^{11} pulses is requested. An important quality demand for these materials is a low change $\Delta\alpha \leq 1 \times 10^{-3} \text{ cm}^{-1}$ of the absorption upon laser irradiation of about 10^{11} pulses.

3. Experimental

Three different techniques have been developed and applied to investigate excimer laser-induced changes of the optical properties of OH-rich fused silica. The excitation and detection method during the laser irradiation is demonstrated in Fig. 1.

Raman scattering is detected during the first 100 pulses. The H_2 -peak in these spectra is used to calculate the H_2 concentration of the fused silica with an error of about $\pm 10\%$ for concentrations higher than 10^{17} cm^{-3} .

Measurements of laser-induced fluorescence (LIF) are made after a distinct irradiation time

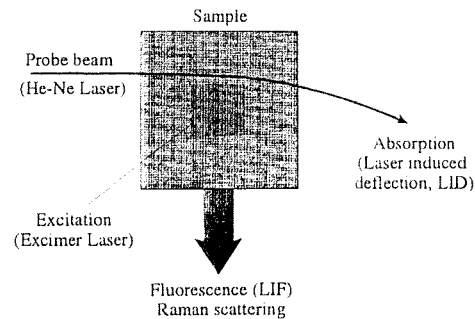


Fig. 1. Excitation and detection methods of pulse laser interaction in fused silica samples.

(about 2000 pulses). At this time the NBOH-LIF signal at 650 nm [1] has reached a steady state [2]. The LIF signal was evaluated by comparing the signal of the investigated sample with that of a reference sample. A LIF value was defined as the ratio of the two signals with an error of about ± 0.05 . The LIF value is used to characterise the laser degradation stability of the fused silica materials. The experimental experience shows that low LIF values predict a high laser stability against degradation.

The deflection of a probe beam due to a temperature-dependent refractive index gradient is used to detect the laser-induced absorption effects (LID) with a detection limit of about 10^{-4} cm^{-1} . The LID method was discussed in detail in [3].

The experimental set-up is shown in Fig. 2. Measurements are performed with the help of an excimer laser (248 nm, narrowband emission and 193 nm) at repetition rates of 10 Hz and energy densities of 300 mJ/cm^2 per pulse (LIF) or up to 1 J/cm^2 (Raman). The Raman and fluorescence spectra are detected by means of a gated OMA system. There are two possibilities of irradiation:

- Central irradiation and 90° detection for locally resolved investigations of different rectangular samples ($20 \times L \times 10 \text{ mm}^3$, L variable up to 60 mm)
- Front-face irradiation under nearly 45° to the surface and detection perpendicular to the incident laser beam for locally resolved evaluation of substrate materials for mask blanks (6'' and 9'').

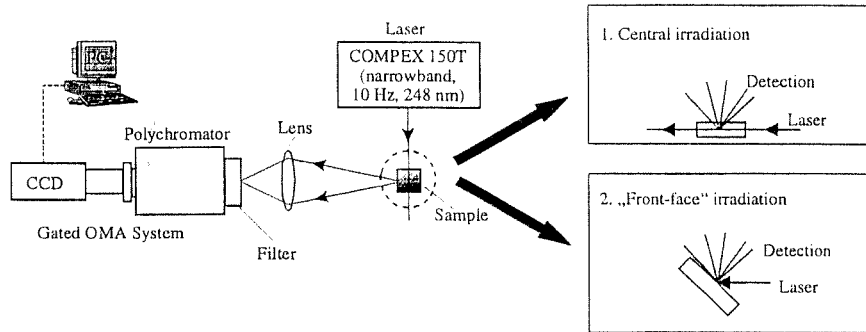


Fig. 2. Experimental set-up for pulse laser excited LIF and Raman measurements.

4. Results

4.1. LIF in OH-rich fused silica samples

The effect of pulse laser interaction with OH-rich fused silica samples is reflected by the NBOH-LIF signal at $\lambda = 650$ nm [1]. The temporal evolution of this LIF signal is shown in Fig. 3. A strong rise of the LIF signal is detected during the first 250 pulses. After approximately 2000 pulses the fluorescence has reached a steady state. The dependence of the saturated LIF signal on pulse energy is given in Fig. 4. The measured quadratic energy dependence proves that a two-photon process is responsible for the generation of the NBOH centres. Typical LIF spectra of fused silica compared with a reference sample are demonstrated in Fig. 5. The sample was investigated with spatial resolution under central irradiation. At the

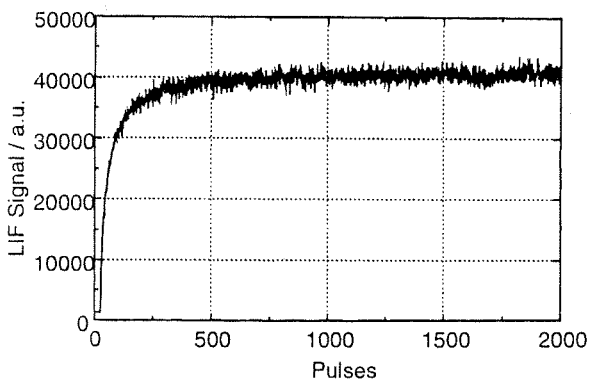


Fig. 3. Development of the LIF signal at 650 nm during KrF laser irradiation (300 mJ/cm^2 , 10 Hz).

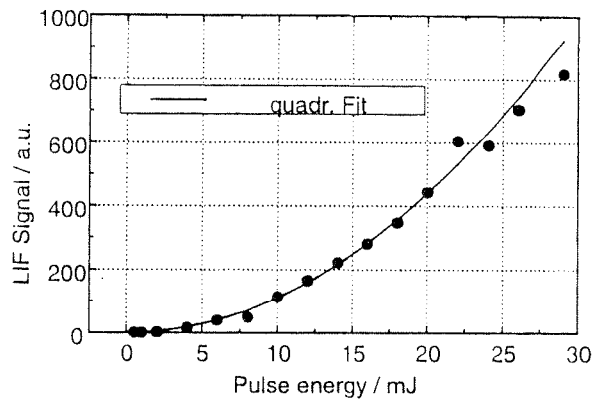


Fig. 4. Dependence of the KrF laser excited LIF signal on pulse energy (10 Hz).

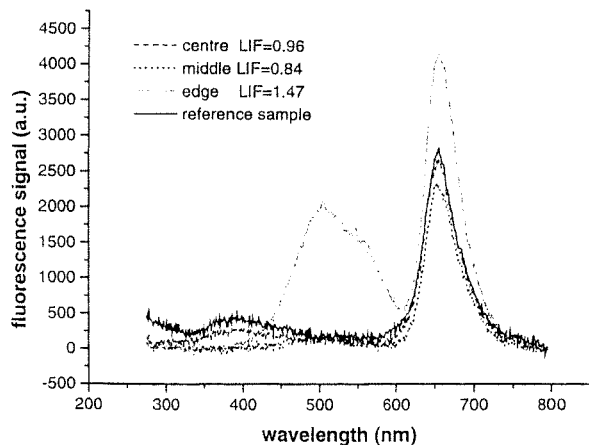


Fig. 5. Typical LIF spectra of fused silica SQ1 excited by KrF laser pulses (300 mJ/cm^2 , 10 Hz).

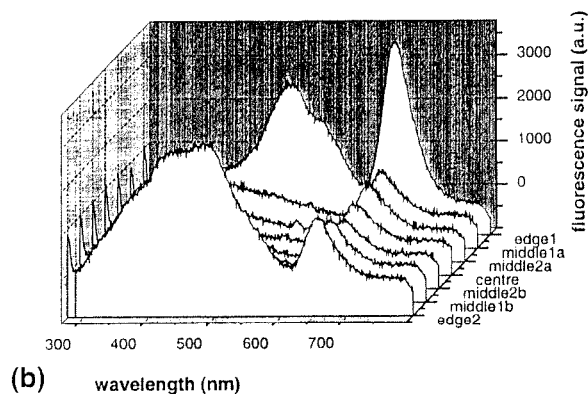
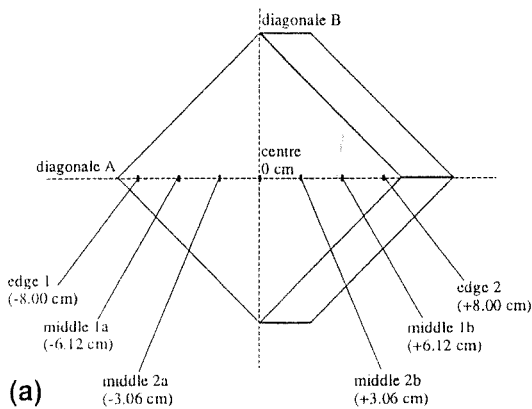


Fig. 6. LIF investigations of a 6" glass substrate. Measuring positions at substrate for mask blanks (a), LIF spectra (300 mJ/cm², 10 Hz) (b).

sample edge the LIF value rises and a green fluorescence is detected.

The investigation results of 6" substrate material for mask blanks under front-face irradiation are summarised in Fig. 6(a,b). Typical results are the low LIF values in the centre and middle positions of the substrate and the rising LIF values and the detection of the green fluorescence at the edges. The signal of the green fluorescence is found to correlate qualitatively with the initial absorption of the material.

4.2. Raman scattering in OH-rich fused silica samples

In order to provide detailed information about important species like precursors of defects,

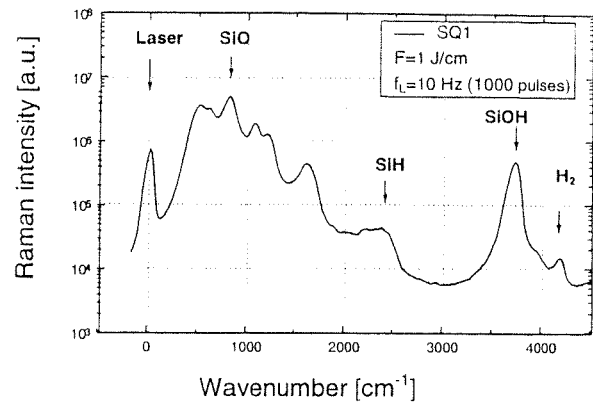
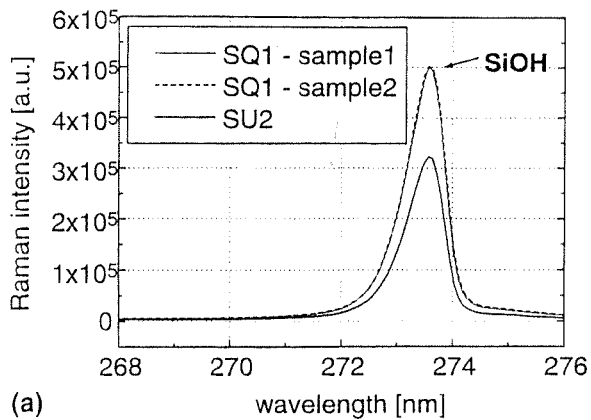


Fig. 7. Complete Raman spectrum of fused silica SQ1 excited by KrF pulse laser.

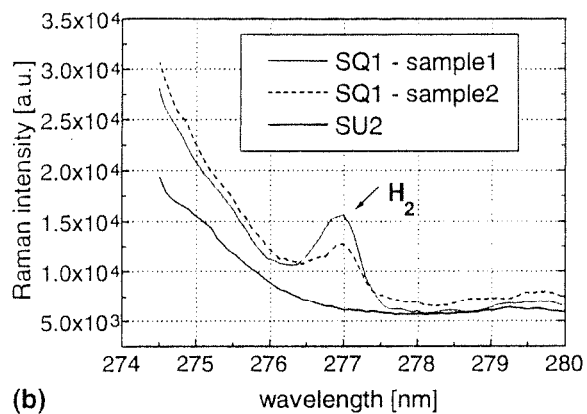
bonding irregularities and molecules (e.g. SiH, SiOH, H₂) within the glass matrix in situ Raman spectroscopic measurements have been carried out under central and front-face irradiation. Fig. 7 shows a typical Raman spectrum measured during 248 nm excimer laser irradiation. The laser signal is suppressed at least by a factor of 10⁻³. The Raman signal at 800 cm⁻¹ corresponding to the SiO vibration is used to calibrate the Raman signals in different samples [4]. In Fig. 8(a,b) zoomed regions of the Raman spectra of three fused silica samples are compared concerning the SiOH and H₂ signals. The SiOH concentration is identical in both SQ1 samples but lower in the SU2 sample. The latter did not show a detectable H₂ signal. The H₂ signal is used to calculate the H₂ concentration corresponding to a calibration with the help of H₂ loaded reference samples [5]. The H₂ concentrations of the SQ1 samples are $(4.3 \pm 0.4) \times 10^{18}$ and $(2.3 \pm 0.2) \times 10^{18}$ cm⁻³.

5. Discussion

The results of the LIF and Raman measurements of OH-rich fused silica show a relation between LIF values and H₂ content. In Fig. 9 an example is demonstrated for the glass SQ1 with different H₂ content. The LIF values clearly decrease with increasing H₂ content. Such a correlation is important to determine technological parameters for the production of laser resistant



(a)



(b)

Fig. 8. Raman spectrum – zoomed regions. SiOH-peak (a) and H₂-peak (b).

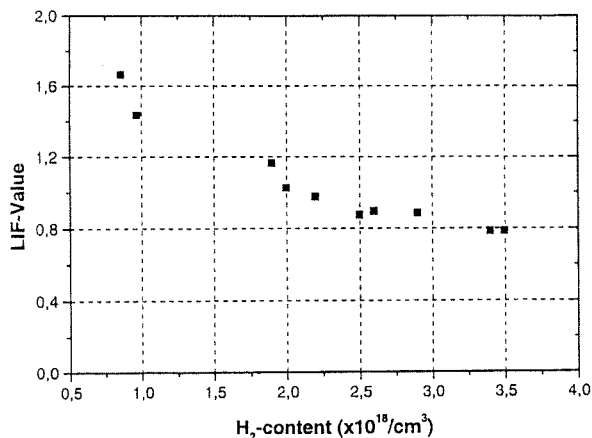
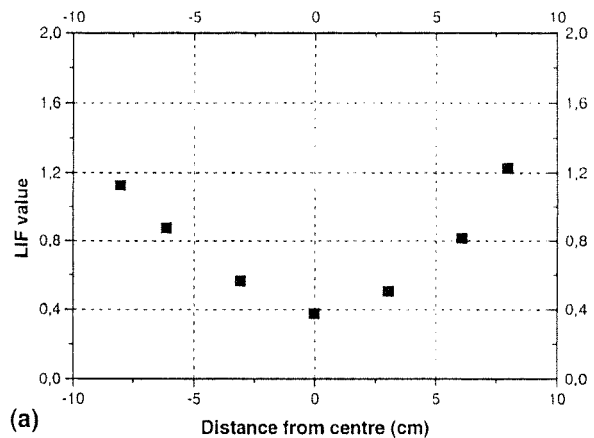
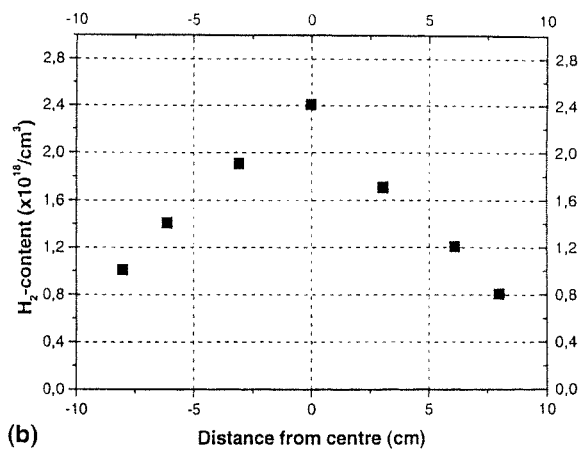


Fig. 9. Evaluation of LIF and Raman measurements, correlation between LIF values and H₂ content in SQ1.

fused silica [6]. Locally resolved LIF and Raman measurements of 6'' substrates for mask blanks (supplier: Shin Etsu) are compared in Fig. 10(a,b). It is clearly seen that in the substrate centre the LIF values are very low and the H₂ content is high. Towards the edges the LIF values increase and the H₂ concentrations decrease. The slopes of LIF and H₂ are completely inverted. From some references it is known that hydrogen is clearly an important reactant in the fused silica system [7]. In order to discuss such experimental results a model was developed and a system of rate equations is used to describe excitation and relaxation processes in OH-rich fused silica [3]. The relaxation behaviour of NBOH and E' defects is mainly influenced by diffusion limited processes probably related to the



(a)



(b)

Fig. 10. Evaluation of LIF and Raman measurements of a Shin Etsu substrate. Locally resolved LIF values (a) and locally resolved H₂ content (b).

concentration of interstitial molecular hydrogen. A comparison of Raman and transmission measurements as a function of the number of laser pulses is given in [8] and illustrates the importance of kinetic modelling to develop fast ageing procedures and predict laser stability of fused silica materials.

Acknowledgements

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