Improvement of laser damage thresholds of fused silica by ultrasonic-assisted hydrofluoric acid etching*

Yuan Li(李源)[1,2], Hongwei Yan(严鸿维)[2], Ke Yang(杨科)[2], Caizhen Yao(姚彩珍)[2], Zhiqiang Wang(王志强)[2], Chunyan Yan(闫春燕)[1], Xinshu Zou(邹鑫书)[2], Xiaodong Yuan(袁晓东)[2], Liming Yang(杨李茗)[3], and Xin Ju(巨新)[1,†]

[1] *University of Science and Technology Beijing, Department of Physics, Beijing* 100083, *China*
[2] *China Academy of Engineering Physics, Laser Fusion Research Center, Mianyang* 621900, *China*
[3] *Fine Optical Engineering Research Center, Chengdu* 610041, *China*

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Polished fused silica samples were etched for different durations by using hydrofluoric (HF) acid solution with HF concentrations in an ultrasonic field. Surface and subsurface polishing residues and molecular structure parameters before and after the etching process were characterized by using a fluorescence microscope and infrared (IR) spectrometer, respectively. The laser induced damage thresholds (LIDTs) of the samples were measured by using pulsed nanosecond laser with wavelength of 355 nm. The results showed that surface and subsurface polishing residues can be effectively reduced by the acid etching process, and the LIDTs of fused silica are significantly improved. The etching effects increased with the increase of the HF concentration from 5 wt.% to 40 wt.%. The amount of polishing residues decreased with the increase of the etching duration and then kept stable. Simultaneously, with the increase of the etching time, the mechanical strength and molecular structure were improved.

Keywords: HF etching, fused silica, laser induced damage threshold, infrared spectra

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1. Introduction

Fused silica optics have high theoretical laser induced damage thresholds (LIDTs) and are widely used in high power laser systems due to their excellent optical transparency and uniformity for ultraviolet (UV) spectrum. However, the optics may suffer from laser damage when irradiated by laser fluence much lower than the theoretical value, which may be due to the existence of damage precursors induced by the polishing process,[1–3] and thus limit the output abilities of the high power laser systems. In order to improve the laser damage resistance of fused silica optics, the polishing procedures have been improved. He *et al.*[4] introduced colloidal silica polishing and obtained a much higher damage threshold than ceria polishing. Meanwhile, HF etching is normally employed by researchers to remove damage precursors induced by manufacturing processes, e.g., absorbed impurities and mechanical subsurface damages.[5–7] Battersby *et al.*[8] investigated the effect of the etching depth on the LIDTs of fused silica substrates by using a wet etching process, and their results showed that the laser damage performance of fused silica was improved or maintained with increasing etching depth, which may be due to the exposure of subsurface defects. The author also suggested that the benefits of the wet etching process should be evaluated for each polishing process. Suratwala *et al.*[9] investigated the effects of various HF-based etching processes on the laser damage resistance of scratched fused silica, and found that the laser damage resistance was strongly dependent on the etching process. The etching process was also optimized to remove or prevent the presence of identified precursors in their research. Bude *et al.*[10] succeeded in reducing the damage density in silica by more than 100 times by minimizing the presence of precipitates during the chemical process.

Evidences suggested that LIDTs of fused silica optics can be improved by the etching process. However, the obtained values are still far below the theoretical one.[7,11] Most previous studies were focused on removing the damage precursors or modifying the surface morphologies of fused silica optics. While an important factor, the molecular structure parameter was seldom investigated. In this article, the surface and subsurface polishing residues, molecular structure parameters, and LIDTs of fused silica samples were investigated before and after ultrasonic-assisted HF acid etching. The dependence of the LIDTs on the polishing residues and molecular structure parameters was discussed. The mechanism of the improvement of LIDTs after the etching process was also explored.

2. Sample preparation and characterization

2.1. Sample preparation

Fused silica samples (50 mm×50 mm×10 mm; Corning 7980, Corning NY) were conventional ceria polished down to

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†Corresponding author. E-mail: jux@ustb.edu.cn

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a surface roughness of 1 nm (RMS) and used as substrates. A sample without etching was prepared for comparison purpose and nominated as sample A. The samples were first sprayed with ultrapure water and ultrasonic rinsed at 40–270 kHz, and then etched in HF solution with ultrasonic agitation of 40–270 kHz as follows: 5 wt.% HF solution, 3 μm depth removed (sample B); 40 wt.% HF solution, 3 μm depth removed (sample C); and 5 wt.% HF solution, 6 μm depth removed (sample D). The removed depth referred to the etched depth on one side of the sample, which was controlled by the etching time and estimated from the mass loss of the etched sample. After etching, the samples were sprayed with ultrapure water and ultrasonic rinsed at 40–270 kHz. The spraying, rinsing, and etching processes were carried out at room temperature and the temperatures of ultrapure water and etching solution were kept at around 25 °C. Finally, the samples were allowed to air dry in a clean room.

2.2. UV confocal fluorescence microscopy

An integrated confocal fluorescence microscope system consists of a fluorescence microscope, laser light sources, and a scan head which directs the laser on the sample and collects the emission. A computer with software was used for controlling the scan head and displaying the acquisition. An excitation beam with a wavelength of 355 nm and an objective lens with a magnification of 20× were employed and the fluorescence images were detected in the spectral band of 410–488 nm in this research.

2.3. Reflected infrared spectra

Fourier transform infrared (FT-IR) spectra were obtained by using a Nicolet 5700 spectrometer with a smart accessory. The attenuated total reflection (ATR) technique was used for FT-IR analysis, the depth of penetration into the sample was in the order of a few micrometers. The IR absorption spectra were measured in a frequency range of 400–1300 cm^{-1}, associating with the Si–O–Si stretching, bending, and rocking vibrations. All spectra were taken at room temperature with more than 200 scans at a 0.96 cm^{-1} resolution.

2.4. R-on-1 LIDTs measurement

A Q-switched Nd-YAG laser system was used to generate a laser with a wavelength of 355 nm and a pulse duration of 6.4 ns. The LIDTs tests were carried out at ambient conditions in R-on-1 mode. The beam profile was Gaussian with a $1/e^2$ area of 0.6 mm^2 at the sample plane. In the R-on-1 test, the LIDTs were obtained by ramping the laser fluence incrementally with an increase of 1 J/cm^2 each time until the damage occurred. The tested surface was the rear surface.

3. Results and discussion

3.1. Polishing residue

Photoluminescence (PL) defect is normally used by researchers to describe the polishing residue defects on the surface and subsurface of a sample.[12] Figure 1(a) is a comparison of the confocal fluorescence microscope images of the prepared samples. PL defects on the surface and subsurface are indicated by the black points. It can be observed that the black points in sample D are much less than those in the other samples. In order to quantitatively describe the PL defects, the gray values of those images were extracted and the concentration of PL defects can be calculated from the gray matrices of the images

$$C_{\text{defects}} = \frac{N_{\text{black}}}{N_{\text{total}}}, \tag{1}$$

where C_{defects} is the PL defect concentration (in units of part per million (ppm)), N_{black} refers to the count of black points, and N_{total} is the count of total pixels.

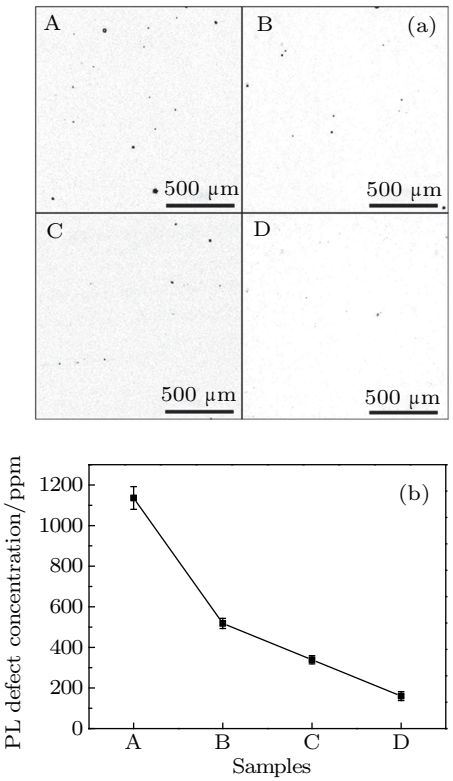


Fig. 1. (a) Confocal fluorescence microscope images and (b) PL defect concentrations of the samples. A refers to the sample without etching. B–D are samples etched by the following conditions: 5 wt.% HF, 3 μm removed; 40 wt.% HF, 3 μm removed; and 5 wt.% HF, 6 μm removed. The unit of ppm refers to part per million.

Figure 1(b) shows the comparison of the PL defect concentration of the prepared samples. The PL defect concentration was obtained from the average of five areas on each sample. The PL defect concentration of sample A is about 1137 ppm, while for etched samples B–D, their PL defect concentrations are all below 1000 ppm, much lower than that of sample A. This result indicates that the surface and subsurface

polishing residues can be effectively reduced by the ultrasonic-assisted HF acid etching process. Interestingly, for samples A, B, and D, the PL defect concentration decreases sharply with the increase of the etching depth (from 0 μm to 3 μm) and then becomes stable (from 3 μm to 6 μm) in 5 wt.% HF solution. Suratwala *et al.*[9] proposed that a large etched depth is needed for acid to penetrate and open up cracks, and thus the absorbing fracture surface can be eliminated and mass transfer rates of reaction products away from the surface can be increased. However, there are few fractured cracks in the high quality polished sample. In this case, eliminating the subsurface impurities may not need that large etched depth (∼ 30 μm). Sample C (40 wt.% HF, 3 μm etched) has a lower PL defect concentration than that of sample B (5 wt.% HF, 3 μm etched), indicating that the HF concentration might be another important factor which influences the etching efficiency during the ultrasonic-assisted acid etching process, which should be paid attention in further studies.

3.2. Surface molecular structure

Different etching processes will result in different surface molecular structures, and thus may influence the LIDTs of the treated samples. In this research, the surface molecular structures were characterized by infrared absorption spectra and shown in Fig. 2(a). These spectra typically have four peaks, corresponding to four vibrational modes of Si–O–Si bond: ν_R (rocking mode, ∼ 470 cm^{-1}), ν_B (bending vibration, ∼ 800 cm^{-1}), ν_S(TO) (transverse optical mode of asymmetric stretching vibration, ∼ 1100 cm^{-1}), and ν_S(LO) (longitudinal optical mode of asymmetric stretching vibration, ∼ 1200 cm^{-1}).[13] The wavenumbers of these peaks are derived from the central and non-central force assumption,[14,15] which change slightly at different etching conditions and can

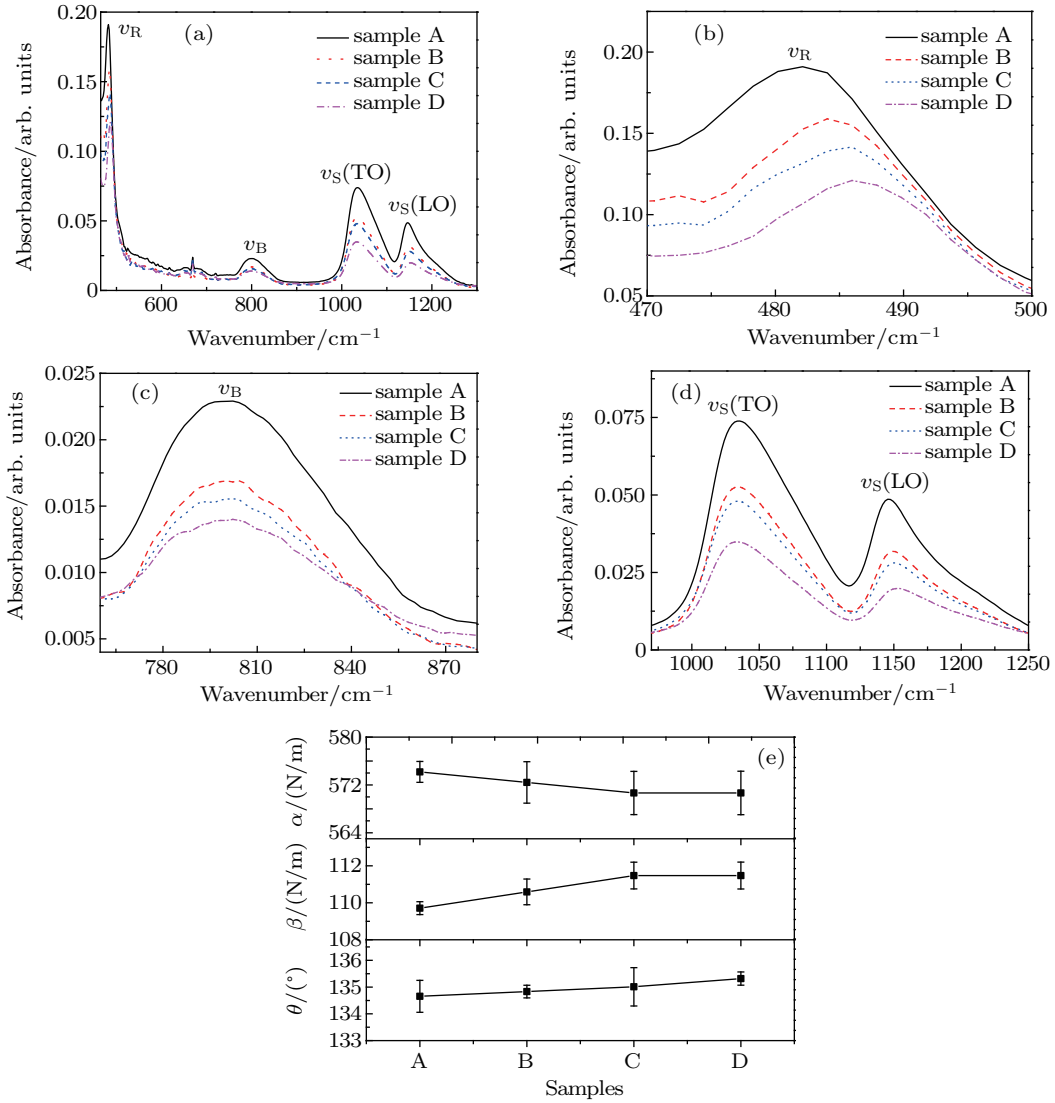


Fig. 2. (color online) Comparison of (a) infrared absorption spectra and (e) molecular structure parameters of the prepared samples. Panels (b)–(d) are blow-ups of ν_R, ν_B, and ν_S, respectively.

be expressed by the following equations:[16,17]

$$\nu_{\mathrm{R}} = \frac{1}{2\pi c}\sqrt{\frac{2\beta}{m_{\mathrm{O}}}}, \tag{2}$$

$$\nu_{\mathrm{B}} = \frac{1}{2\pi c}\sqrt{\frac{4(\alpha+2\beta)}{3m_{\mathrm{Si}}}}, \tag{3}$$

$$\nu_{\mathrm{S}} = \frac{1}{2\pi c}\sqrt{\frac{2}{m_{\mathrm{O}}}\left(\alpha\sin^2\frac{\theta}{2}+\beta\cos^2\frac{\theta}{2}\right)}, \tag{4}$$

where α is the central force constant, β is the non-central force constant, and θ is the Si–O–Si bond angle. m_{Si} and m_{O} refer to the atomic masses of silicon and oxygen, respectively, and c is the velocity of light. The force constants α and β are related to the elastic constants: α determines Young's modulus, while β determines the shear modulus.[16] The angle of Si–O–Si bond, θ, is related to the density of surface materials.[18,19]

The calculated surface molecular structure parameters are given and compared in Fig. 2(e). The estimated Si–O–Si bond angles of all samples are slightly lower than the average value of the bulk fused silica estimated from x-ray diffraction ($\sim 140^\circ$).[20,21] This discrepancy may be due to the manufacture induced polishing residues or material densification. The compression of the Si–O–Si bond angles indicates that the surface molecules are in states with higher energies, so these molecules may absorb photons and induce laser damage under the irradiation of high power pulse. Therefore, from the viewpoint of laser-induced damage, the compression of the Si–O–Si bond angles can be considered as a structural defect. The Si–O–Si bond angle increases after the etching process, and is close to that of bulk fused silica, which may be due to the exposure of bulk material. The decrease of α and increase of β indicate that the surface mechanical strength is improved by the etching process. The comparison of samples B–D indicates that both increasing the HF concentration and the surface etching depth are effective to remove the structure defects induced by polishing.

3.3. LIDTs

As shown in Fig. 3, the LIDTs of the samples are improved by the etching processes in comparison with the original surface. Sample D has the largest etched depth and possesses the highest LIDT. The LIDT of sample C is slightly higher than that of sample B with the same etching depth, indicating that high concentration HF etchant may benefit to improving the LIDT of fused silica. The dependence of LIDTs on HF concentration and etching depth is in agreement with the previous reports.[5,8] Since it is unsafe to use the etchant with HF concentration higher than 10 wt.%, the authors suggest that it is adoptable to increase the etching depth in a relative low concentration ($<$ 10 wt.%) of HF etchant to achieve a better etching effect.

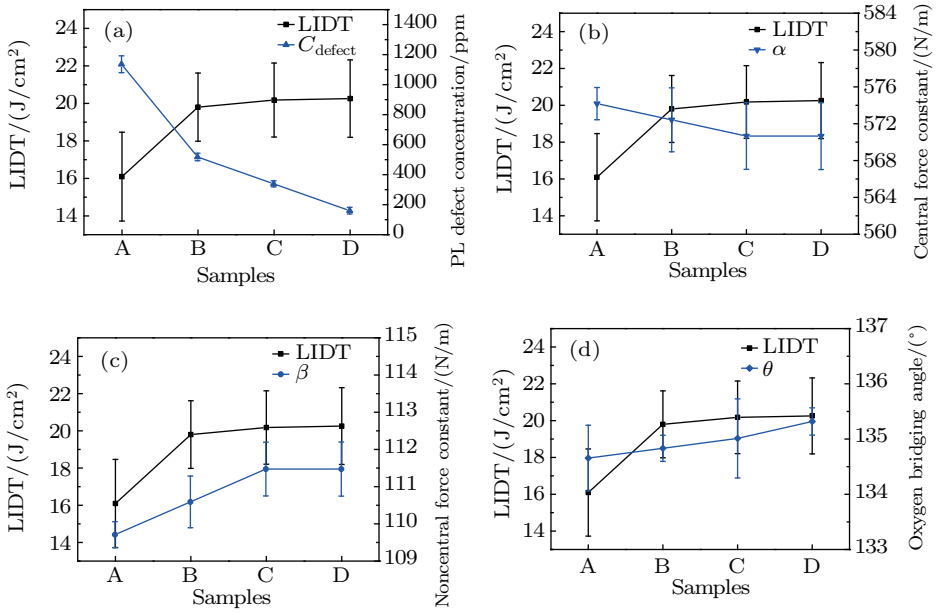


Fig. 3. (color online) The correlation between surface properties ((a) PL defect concentration and (b)–(d) surface molecular structure parameters) and LIDTs.

With the etched depths of 3 μm and 6 μm, the RMS values of the samples were kept under 1 nm, so the degradation of the surface by etching can be neglected. In order to analyze the influence of polishing residues and surface molecular structure parameters on LIDTs, the PL defect concentration C_{defect}, central force constant α, non-central force constant β, and Si–O–Si bond angle θ are also given in Figs. 3(a)–3(d), respectively. According to the results of samples A, B, and D, as the etched depth increases, the PL defects decrease while the surface molecular structure and the LIDT are improved. Com-

paring with sample A, the LIDTs of the etched samples are improved by the decrease of the PL defect concentration and the increase of the surface mechanical strength (indicated by the decrease of α in Fig. 3(b) and the increase of β in Fig. 3(c) and Si–O–Si bond angle). It is indicated that though the depth of Beilby layer is around 100 nm typically, a relative large etching depth is needed for improving the LIDTs as not only the polishing slurry residues but also the structure defects of Si–O–Si compression should be removed.

4. Conclusion

Polished fused silica samples were treated by using the ultrasonic-assisted HF etching processes. Different etching depths and HF concentrations were employed. Surface and subsurface polishing residues, surface molecular structure parameters, and laser damage performance of the etched samples were characterized and compared with those of the un-etched sample. The correlation between surface properties (polishing residues, molecular structure parameters) and laser damage thresholds of fused silica was analyzed. The results showed that the acid etching process can effectively remove polishing residues and modify the molecular structure parameters of the surface materials. The central force constant α decreased, non-central force constant β and Si–O–Si bond angle θ increased after the etching process. The LIDTs were improved by the etching, which may be due to the elimination of the polishing residues. Higher HF concentration is more effective to achieve a better etching result. However, the authors believe that increasing the etching depth with a relatively low HF concentration etchant is an economic, safe, and practical method.

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