



Research Article

Correlation between Photoluminescence Properties of Surface Defects and Laser-Induced Damage Threshold of Fused Silica

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Laser-induced damage threshold is the main limitation for fused silica optics in high-power laser applications. The existence of various defects near the surface is the key factor for the degradation of the threshold. In this work, the photoluminescence spectra at different regions of the damaged and recovered fused silica samples are recorded to analyze the correlation between photoluminescence of surface defects and laser-induced damage threshold. The experimental data concluded the inverse proportional correlation between fluorescence and laser-induced damage threshold value. The weak photoluminescence is the guarantee of the high laser-induced damage threshold, and then the higher local Si nanocluster concentration corresponds with the higher laser-induced damage threshold value for the fused silica optics after CO₂ laser treatment. The investigation reveals that photoluminescence measurement can be employed to check the quality of pristine fused silica and evaluate the tendency of the laser-induced damage threshold value. The current results are helpful for understanding the evolution of interaction from CO₂ laser treatment and fused silica optics and can provide the guide of process technology for the high quality of fused silica optics.

1. Introduction

Fused silica optics is widely used in high-power laser facilities such as inertial confinement fusion (ICF) due to its high transparency and excellent thermal and chemical stabilities. However, there exist some intrinsic defects and many kinds of flaws on the surface associated with the fabrication process of fused silica optics. These defects could absorb ultraviolet laser and cause the initial laser damage [1] and then further degrade the laser-induced damage threshold (LIDT) of fused silica optics. Some approaches, such as ion beam etching [2, 3], chemical etching [1, 4], and CO₂ laser treatment [5, 6], have been employed to mitigate the initial damage sites. Among these methods, CO₂ laser treatment is one important method to repair the initial damage site by heating effect. Some investigations demonstrated that the LIDT may return to the normal level or higher after CO₂ laser treatment [7, 8]. Although there have

been some reports on the optical and mechanical effects of CO₂ laser treatment for scratches and laser-induced damage sites on the surface of fused silica, as well as the physical model of the secondary treatment or annealing process to eliminate residual stress [9, 10], there is no report about the evolution of defects on the fused silica surface during this process.

Some works revealed that the intrinsic defects and laser-induced structural defects in fused silica optics include the E'-center [11], which comprised an unpaired electron of single silicon bonded to just three oxygens, oxygen-deficiency center (ODC) [12], nonbridging oxygen hole center (NBOHC) [13], peroxy radical (POR) [14], and Si nanocluster [15]. The presence of defects in the silica matrix can dramatically change its structural, electrical, and optical properties. So, photoluminescence (PL) spectra are one significant tool to understand the evolution of the defects in the fused silica optics during high-power laser irradiation.

According to PL analysis, the electron structural information of various defect species and the distribution of defects on the surface should be obtained for fused silica optics.

Some groups investigated the luminescence properties of the defects in fused silica in the past few decades. Demos et al. assigned the luminescent bands around 400 nm and 650 nm to ODC and NBOHC defects [16], separately. The other emission bands in the range from 450 nm to 600 nm are attributed to the combination of the self-trapped exciton (STE). Švrček et al. concluded that the emission band of the Si nanocluster can be in a wide range around 700 nm. The concentration of various defects in the laser-induced initial damage site would increase dramatically compared with the pristine area. The initial damage site will probably expand exponentially due to higher defect density as reported [17–19].

In this paper, PL properties of defects near the surface for the laser damage site and CO₂ laser treatment site are systematically investigated. The correlation between the distribution of different defects and LIDT in the same site is analyzed.

2. Experimental

The experiments were conducted on UV-grade Corning 7980 fused silica samples with 40 mm square and a thickness of 4 mm. They were firstly etched in the buffered hydrofluoric (HF) acid solutions and then cleaned by deionized water.

Laser-induced damage sites were generated on the output surface of pristine samples by using a triple-frequency Nd:YAG laser (Saga) which delivers a pulse width of 6.3 ns at 355 nm with a diameter of 800 μm at $1/e^2$. The diameter of the damage area is about 250 μm .

The CO₂ laser of the repairing treatment is a commercial radio frequency power excited CO₂ laser (Coherent GEM-100L), with a maximum output power of 100 watt and power stability of $\pm 3\%$.

The photoluminescence spectra were recorded by using a spectrometer (LabRAM HR800, Jobin Yvon) with a confocal microscope and a multichannel air-cooled CCD detector. The excitation sources were an Ar ion laser ($\lambda_0 = 514.5$ nm; source power: 20 mW) and He-Cd laser ($\lambda_0 = 325$ nm; source power: 40 mW). All spectra were recorded at room temperature.

Laser-induced damage threshold is obtained by the R-on-1 testing mode. The schematic diagram of the measurement setup is shown in Figure 1. On each selected site, the laser fluence was progressively increasing, until the first damage occurred. For each set of parameters, a series of sites were selected and analyzed, and the results given in this work are based on a statistical analysis on the fused silica samples.

3. Results and Discussion

Figure 2(a) shows the photoluminescence spectra at the pristine region and the damaged region of the fused silica sample with the excitation of 325 nm laser. The

corresponding decomposition peaks are displayed in Figures 2(b) and 2(c), respectively. The shoulder peak around 400 nm is from ODC defects. The broad emission bands centered at 490 nm and 580 nm can be definitely ascribed to the transition from the laser-induced STE [12, 13]. The peaks around 650 nm and 750 nm are assigned to the luminescence bands of NBOHC and Si nanocluster defects, respectively. The weak emission indicates the low concentration for these defects in the clear pristine sample. These defects in pristine fused silica optics can have a high absorption for the UV laser and become an initial laser damage site according to existing reports [1, 11, 12]. In other words, the low defects' density can guarantee the high LIDT value. The contribution from the NBOHC and Si nanocluster is hardly observable for the pristine region, but the obvious peaks occur for the two defects in the damaged region as seen in Figure 2.

Figure 3 compares the photoluminescence spectra of the pristine region, ion beam etching-treated region, and the edge region of the laser-induced damage site with the excitation of a 514.5 nm laser. The sharp peaks at 526 nm, 536 nm, and 543 nm are the response to Raman modes for Si-O-Si, fourfold rings, and threefold rings in fused silica, respectively [11].

The broad weak fluorescence of curve #2 in Figure 3 for the pristine region is similar to that in Figure 2 with 325 nm excitation. Ion beam etching process can smooth the surface of the optics and mitigate a part of the existing surface defects. The microscopic image of the etching region is shown in Figure 3(c). It is smoother and has higher uniformity compared with the pristine region.

Except for Raman peaks, no emission bands can be detected for the ion beam etching-treated sites as seen in curve #3 of Figure 3(a). This verified that the ion beam etching process can remove the flaws localized on the surface and enhance the LIDT value.

The strong luminescent band centered at 580 nm is quite prominent as shown in curve #1 of Figure 3(a) for the edge region of the laser-induced damage area. It indicates that the laser-induced damage process generates a higher concentration of defects. In general, the type and relative concentration of defects depend on the peak position and intensity of PL spectra, respectively. As the description given above, the laser-induced self-trapped excitons dominate the emission around 580 nm. These defects could result in the damage of fused silica under ultrahigh power running of the UV laser due to the strong absorption. Investigating the influence on the LIDT from these defects, the values of LIDT at different sites are measured by the R-on-1 testing mode [20]. The LIDT, the type, and the relative concentration of defects for different regions are given in Table 1. The LIDT values for the pristine surface and ion beam-treated region are 13.9 J/cm² and 17.2 J/cm², separately. The low LIDT value of 4 J/cm² is the response to the edge region of the laser-induced damage site. The results from Table 1 reveal that the PL intensity is inversely proportional to the LIDT value of the fused silica optics. Further comparing the contribution from different defects for the pristine region and damaged region, the laser-induced STEs

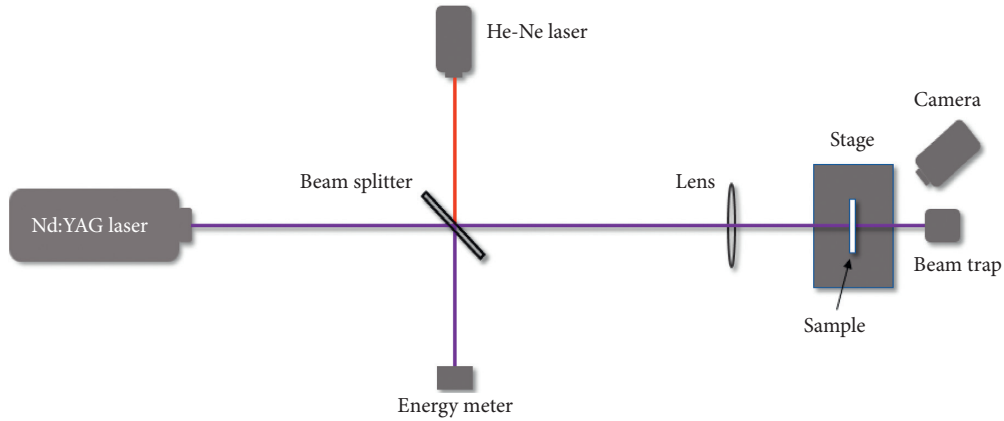


FIGURE 1: Schematic diagram of the laser-induced damage threshold measurement. The setup consists of a single-longitudinal-mode Nd:YAG laser at 355 nm, a He-Ne laser collimating light source, a beam splitter, a focusing lens, an energy meter, and a two-dimensional stage.

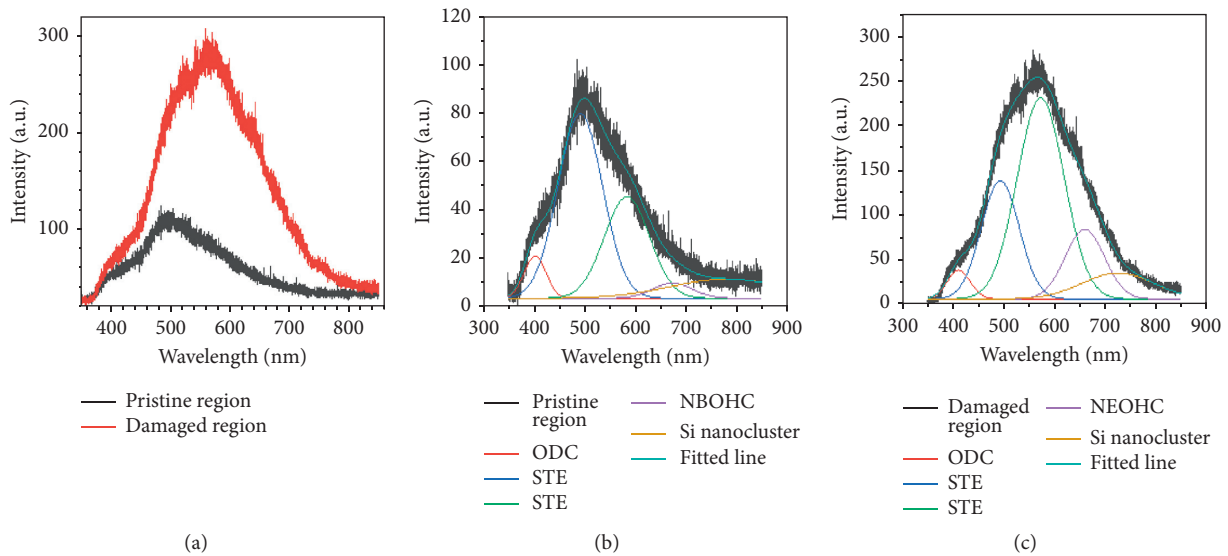


FIGURE 2: (a) PL spectra of the pristine region and damaged region of the fused silica sample with 325 nm excitation. The decomposition peaks for (b) the pristine region and (c) the damaged region.

dominate the damaged threshold value. These results indicate that the PL can be employed to check the quality of pristine fused silica and evaluate the possible LIDT value based on the confirmed reference standard sample.

CO₂ laser treatment is the most effective method for fused silica materials to mitigate the defects on the surface. Figure 4(a) shows the optical microscopy image of the CO₂ laser treatment site. The PL spectra of three different regions are shown in Figure 4(b). This laser-induced damage site has been overtreated by the CO₂ laser, and the ablation trace can be observed in its edge region. The PL spectrum for the edge region has relative high intensity around 500 nm from the laser-induced STE and the shoulder at 400 nm from the ODC according to the previous reports [13, 14]. The measured LIDT value in this region is 4.5 J/cm², and it supports the same inverse proportional correlation between PL band intensity centered at 500 nm and the LIDT.

In spite of the weak fluorescence for center regions 1 and 2, a new luminescence band centered at 750 nm obviously

occurs. This band is ascribed to the Si nanoclusters. The fabrication process and Si-implanted *a*-SiO₂ after 1100°C annealing can generate the nanoclusters [21]. These inducing paths are all related to the CO₂ laser heating process. The intensity at center region 1 is higher due to near the center and bathing in higher temperature during the laser irradiation. These results are quite helpful to understand the mechanism of defects' evolution of the CO₂ laser treatment process. It should also be noticed that the LIDT value in center region 1 of the CO₂ laser-treated site is 19.2 J/cm² higher than 17 J/cm² for center region 2 as shown in Figure 5. This indicates that CO₂ laser-treated fused silica optics can run under higher fluence compared to the pristine fused silica optics.

Combining Table 1 with Figures 4 and 5, we can conclude that the weak photoluminescence can be taken as the criterion of the high LIDT value; furthermore, the higher nanocluster contribution protects the damage of fused silica under higher laser power running. In fused silica materials,

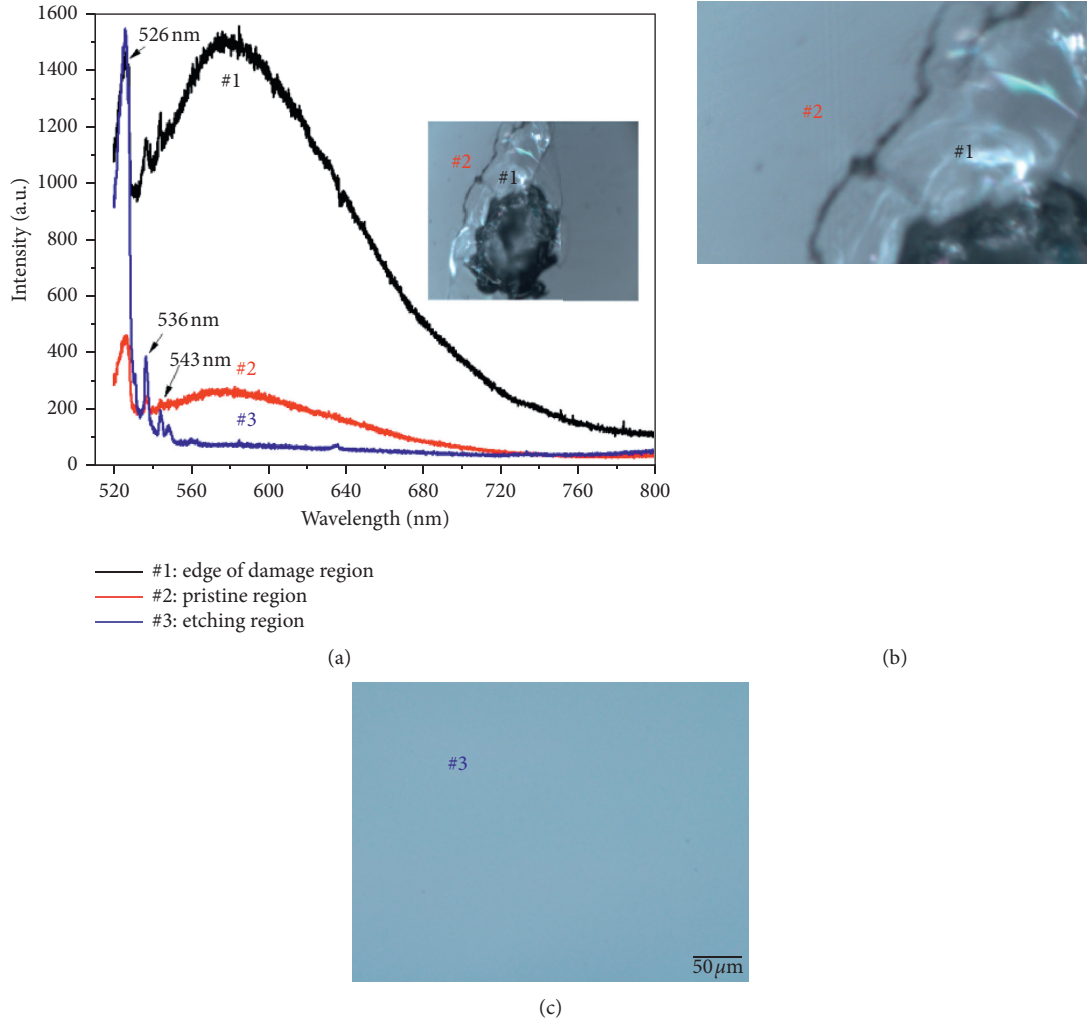


FIGURE 3: (a) PL spectra of the fused silica sample with 514.5 nm excitation. Curve #1: pristine region, curve #2: the edge region of the laser-induced damaged site, and curve #3: the ion beam etching-treated region. The inset is the microscopic image of the selected damage site. (b) The magnification of the inset. (c) The microscopic image of the etching region.

TABLE 1: LIDT and relative fluorescence intensity of several types of defects in different regions.

| Measured region | Pristine region | Ion beam-treated region | Edge region of the damaged site |
|-----------------|------------------------|-------------------------|---------------------------------|
| LIDT | 13.9 J/cm ² | 17.2 J/cm ² | 4.0 J/cm ² |
| ODC | 5.8 (2.3) | Undetectable | 3.5 |
| STE | 80.4 (32.2) | Undetectable | 72.7 |
| NBOHC | 3.8 (1.5) | Undetectable | 14.4 |
| Si nanoclusters | 10.0 (4.0) | Undetectable | 9.4 |

The PL intensity is normalized. The intensity of the pristine region possesses 40% of the intensity for the damaged site. The value in the bracket for the pristine region is the relative ratio to the PL intensity of the damaged region.

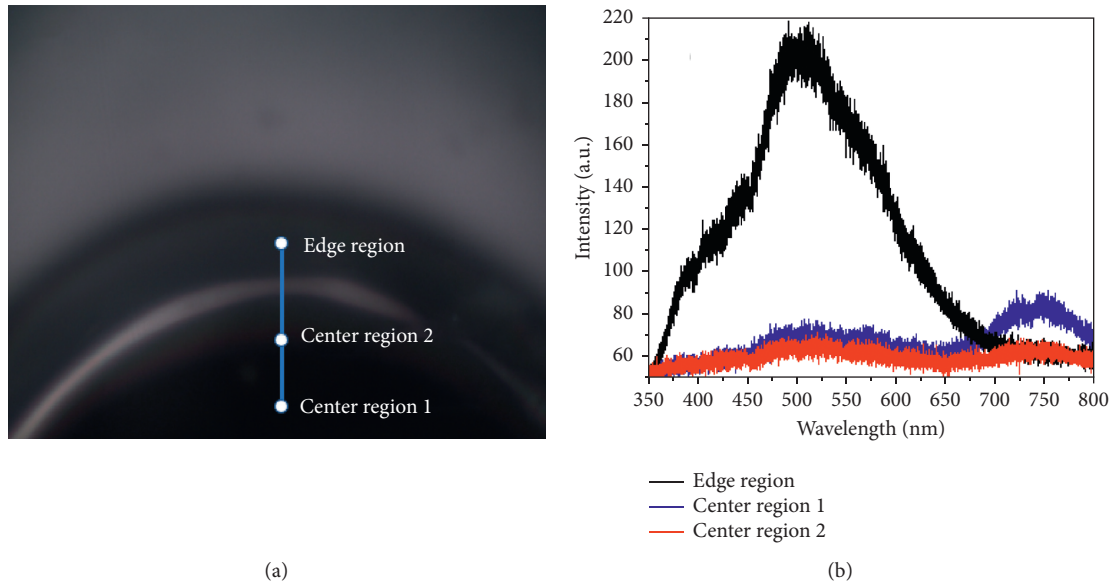


FIGURE 4: (a) Optical microscopy images of the CO₂ laser treatment site. (b) PL spectra of different regions under 325 nm excitation.

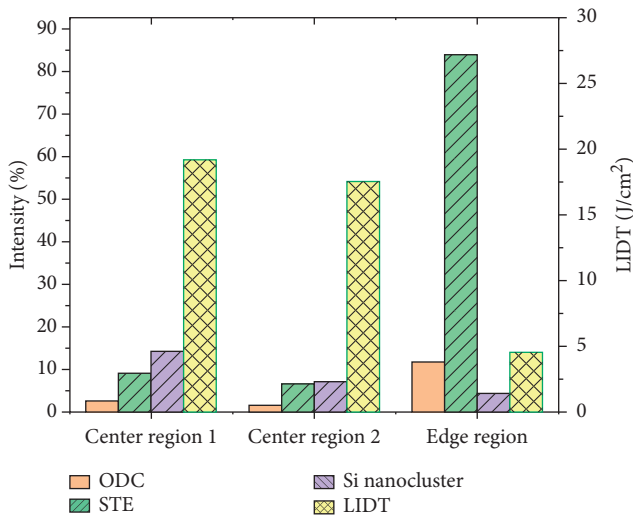


FIGURE 5: Luminescent intensities of defects and LIDT values for different regions in Figure 4. Each photoluminescence spectrum area is normalized to that at the edge region.

the self-trapped exciton is known to be correlated with the absorption precursor according to the existing reports; this is consistent with the results shown in Figure 5. The relationship between the LIDT and Si nanocluster needs to be studied further.

4. Conclusions

PL technique combined with the laser-induced damage threshold measurement is employed to investigate the distribution of the defects on the surface of the fused silica sample. The inverse proportional correlation between fluorescence and LIDT value is built according to the

experimental results. The weak photoluminescence and the higher Si nanocluster concentration can enhance the LIDT value for the fused silica optics after CO₂ laser treatment. The investigation reveals that the fluorescence can be employed to check the quality of pristine fused silica and evaluate the possible laser-induced damage threshold value. The wide emission from the ODC and self-trapped excitons dominates the low LIDT value. The current results are helpful for understanding the evolution of action from CO₂ laser treatment and fused silica optics.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

Qiao Chen and He Wang are the coauthors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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