

Article

Mechanism of Surface Hydroxylation Acceleration and Laser-Induced Damage Threshold Reduction during Ion Beam Sputtering of Fused Silica

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Abstract: The mechanism of the combined process of ion beam sputtering (IBS) and HF acid etching on the chemical structure defects of fused silica and its laser damage resistance performance were investigated in this paper. During the removal process of surface material, the sputtering effect causes lattice atoms to flee their native space locations, and a large amount of unsaturated chemical structures are produced on the silica surface, which improves the chemical activity of Si and O atoms, accelerates the chemical reaction process between surface atoms and water molecules, increases the content of hydroxyl groups (OH⁻) in the shallow layer, and enhances the photothermal weak absorption intensity. However, the increase in hydroxyl content weakens the binding strength of silicon–oxygen bonds, destroys the spatial network structure of silica bulk, and reduces its mechanical strength, resulting in a decrease in its laser damage resistance performance. The paper reveals for the first time the mechanism by which IBS changes the structure characteristics of silica material, accelerates the surface hydroxylation process, and thereby reduces the laser damage resistance performance. This work provides technical guidance for effectively suppressing chemical structure defects on silica surfaces and improving the laser damage resistance performance of optical components under high-flux laser irradiation.

Keywords: ion beam sputtering; laser damage; hydroxyl groups; surface hydroxylation; chemical structure defect



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1. Introduction

Fused silica is widely used in the field of high-energy laser systems due to its excellent physical and optical properties [1,2]. And laser damage resistance performance has become the primary goal due to the damage and failure of optical components caused by high-flux laser irradiation. In order to improve the laser-induced damage threshold (LIDT) of fused silica, many scholars internationally are committed to researching the processing methods for obtaining the intrinsic surface of high-power optics [3–7]. With the deepening of research, researchers have gradually realized that chemical structure defects generated by pre-processing are one of the main damage precursors under higher flux (12–16 J/cm²) laser irradiation. However, relevant research is not sufficient, the generation rules are not clear, and there is also a lack of effective suppression methods. How to further improve the laser damage resistance performance of fused silica has become a hot and major scientific problem, and manufacturing research for higher flux laser irradiation is imminent.

Current research has shown that it is difficult to achieve comprehensive and effective suppression of damage precursors by a single post-treatment process [4–8]. Therefore,

exploring the theories and methods of combining multiple post-treatment processes to suppress defects has become an inevitable choice to realize the low-defect surface manufacturing of high-energy optics. Based on the high removal efficiency of HF acid etching and the low damage characteristics of IBS, our research team has explored this combined process. When IBS is used to remove a certain depth (<1000 nm) of HF acid-etched surface, it can reduce the concentration of oxygen deficiency center (ODC), non-bridging oxygen hole center (NBOHC), and OH- groups on the surface, weaken the photothermal absorption intensity, and increase the LIDT of fused silica components by 30% compared with that of the single HF acid etching method. This preliminary verification verifies the good effect of IBS in suppressing chemical structure defects [9–12]. The IBS processing technique has the advantage of modifying the surface and physical properties of many optical films [13–15]. Irradiation through ionizing radiation has been developed to bring about changes in the form of thermal absorption or oxidation in the oxide thin film's structure and physical properties.

IBS has also become one of the most promising new processing methods for suppressing chemical structural defects. However, with the emergence of new phenomena and the deepening of research, it has been gradually realized that IBS has two sides in the regulation of chemical structure defects, which can not only remove chemical structure defects generated by pre-processing but also produce sputtering damage on its intrinsic surface, but the process conditions and generation mechanism of the two-sided effect are still unclear. The regulation law of IBS on chemical structure defects is not well understood, and the research on the combination sequence and process interface conditions of the combined process is not fully studied, which cannot provide technical guidance for effectively suppressing surface chemical structure defects.

The OH- groups in fused silica are both impurity defects and chemical structure defects. They break the Si-O bonds in the silica network, reduce the chemical stability of the substrate surface, and also affect the existence of other types of structure defects, seriously reducing its laser damage resistance performance [16]. Our team has studied the evolution law of chemical structure defects on fused silica surfaces during the combined process of HF acid etching and IBS [4,8–11]. It was found that the hydroxyl content on the sputtering surface increased after being cleaned with deionized water, and the photothermal weak absorption intensity also increased while the LIDT decreased significantly. However, there is a lack of deep understanding of the mechanisms and rules of this phenomenon. In this paper, the theoretical analysis of the hydroxylation process of fused silica surfaces is carried out, and the mechanism of IBS to change the material's structural characteristics and accelerate the surface hydroxylation process is revealed. Based on the mapping relationship between surface hydroxylation and photothermal weak absorption intensity, the influence of surface hydroxylation on laser damage resistance performance is investigated, providing technical guidance for effectively suppressing chemical structure defects, forming a low-damage surface manufacturing process for optical components, and achieving the improvement of laser damage resistance performance under high-flux laser irradiation.

2. Influence of OH- Groups on Material Characteristics

During the processing of fused silica components, along with the chemical bond breakage in the silicon–oxygen tetrahedral network structure [SiO₄], a large amount of chemical structure defects will occur in the material, mainly due to oxygen deficiency and doping of other elements (such as Cl, -OH, etc.) [17]. The chemical stability of fused silica depends on the firmness of the Si-O-Si network connection structure, and the hydroxyl defects break the silicon–oxygen (Si-O) bonds, change the continuity of the network structure, and reduce its chemical stability.

The introduction of impurity ions in the SiO₂ network structure leads to breakpoints in its complete grid structure. Figure 1 shows the chemical structure defects generated by the introduction of OH- and F- ion impurities [18]. Chemical structure defects can form energy absorption points in high-flux laser irradiation and reduce the LIDT. The absorption

effect of individual defects is equivalent to that of the Ce element, which can absorb a large amount of energy from the laser photons, causing a sharp temperature increase and producing a plasma effect, resulting in surface damage. Therefore, it is necessary to strictly control the content of OH- groups inside fused silica to improve its optical uniformity and increase its LIDT under 351 nm ultraviolet laser irradiation [19].

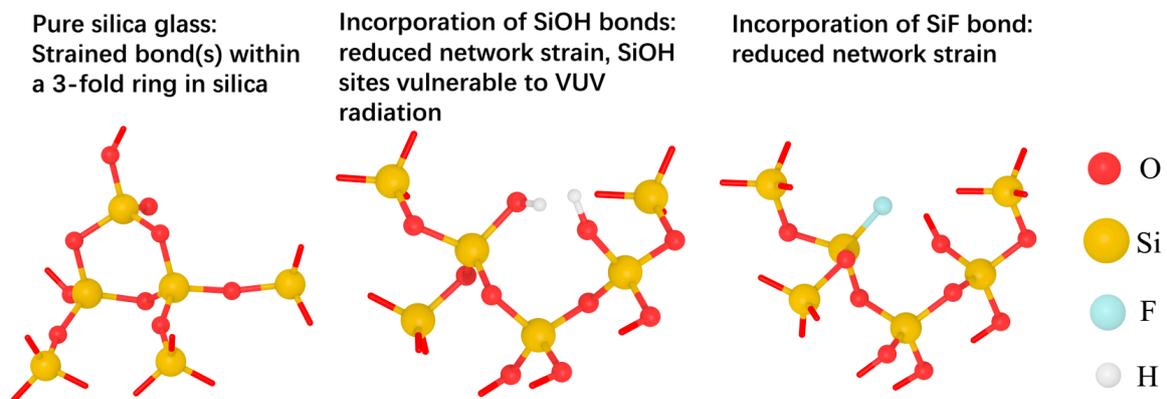


Figure 1. Chemical structure defects in fused silica due to the introduction of OH- and F- ions.

3. Experimental Method

Two Heraeus 312 fused silica samples were pre-polished by the supplier to avoid the uncertain effects of different polishing qualities. The size of the samples is 50 mm × 50 mm × 10 mm, and all samples had bright surfaces with no obvious brittle scratches. Samples 1# and 2# were first etched with a 5% HF acid solution supplemented by megasonic vibration. The etching process parameters have been optimized, and each round of operation includes 30 min of HF acid etching and 30 min of megasonic cleaning by deionized water. Then, the samples were dried with absolute alcohol. The ion beam sputtering parameters are shown in Table 1.

Table 1. Process parameters of IBS.

Beam Voltage	Beam Current	Incidence Angle	Working Pressure	Cathode Airflow	Neutralizes Airflow
900 eV	5 mA	0°	5×10^{-3} Pa	6 sccm	6 sccm

Both surfaces of Sample 1# were sputtered with the same removal depth before LIDT tests. The removal depths of the three IBS treatments were 900 nm, 1500 nm, and 2000 nm, respectively. The LIDT test is performed using an R-on-1 method, which irradiates the test point with a gradually increasing laser flux until the imaging Charge Coupled Device (CCD) can observe the damage. For the LIDT test, 10 test points are selected randomly in the corresponding area, and the average of the damage thresholds is taken as the damage threshold corresponding to the removal depth. A 3ω Nd:YAG laser was employed in the LIDT test; the pulse width is 7 ns, and the repetition rate is 1 Hz. The laser spot is close to a flat Gaussian type, and its diameter is about 1.2 mm. The laser beam is focused on the back surface of the sample. When both surfaces of Sample 2# are removed by IBS at a certain depth each time, the LIDT tests are carried out first, and then the sample is soaked in deionized water for 30 min, and then the LIDT tests are carried out again after anhydrous alcohol dehydration.

Infrared spectroscopy is the main way to study the OH- group structure characteristics of fused silica. The absorption peak in the infrared spectrum corresponds to the vibrational form of the OH- group, and the characteristic absorption peak near 3660 cm^{-1} indicates the presence of OH- groups [20]. A Bruker Vertex70 (Bruker Corporation, Ilerica, MA, USA) high-resolution Fourier transform infrared spectroscopy (FTIR) was used to measure the hydroxyl content after different surface treatment methods.

The photothermal weak absorption technology is used to detect and evaluate the surface absorption characteristics of fused silica. The photothermal weak absorption detection system is provided by Hefei Zhichang Optoelectronic Technology Co., Ltd. (Hefei, China), and the product type is PTS-2000-RT-C.

4. Experimental Results and Analysis

4.1. Damage Performance Test

The results of the damage performance test corresponding to different IBS removal depths are shown in Table 2. A phenomenon beyond existing knowledge is that the damage threshold of the sputtered surfaces after ultrasonic cleaning is significantly lower than that of the surfaces that have only been sputtered, and the damage threshold test results are reduced by 21%, 23%, and 14%, respectively. Additionally, the damage threshold of the IBS surface after ultrasonic cleaning is almost all lower than that of the HF acid-etched surfaces.

Table 2. Results of LIDT tests.

Surface Treatment Process	LIDT of Non-Megasonic Cleaning (J/cm ²)	LIDT of Megasonic Cleaning (J/cm ²)	Change Amplitude
HF etching 120 min	8.11 ± 0.32		
IBS removal 900 nm	10.38 ± 0.28	8.17 ± 0.31	−21%
IBS removal 1500 nm	8.25 ± 0.34	6.36 ± 0.23	−23%
IBS removal 2000 nm	8.27 ± 0.24	7.08 ± 0.19	−14.5%

The experimental results give us a thought: What is the reason for the significant reduction in the damage threshold by about 20% after the sputtered surface is cleaned with deionized water? Revealing the mechanism of this change plays an important role in in-depth research on the influence of IBS on optical material characteristics and its laser damage resistance performance, which then optimizes the IBS process and provides technical guidance for the optimization of combined process parameters.

4.2. Measurement of OH- Groups

As shown in Figure 2, fused silica samples, after different processes, show strong absorption peaks at 3660 cm^{−1}. When the silica surface is removed by IBS at 600 nm and 1000 nm, respectively, the hydroxyl absorption peak intensity decreases to a certain extent compared with that of the HF-etched surface. After a removal depth of 1000 nm, the sample was immersed in deionized water for 30 min, then dried with high-pressure nitrogen gas and immediately measured by infrared spectroscopy. Figure 2 shows that the intensity of the hydroxyl absorption peak is significantly enhanced after water immersion, even stronger than that of the HF-etched surface.

The hydroxyl content is calculated as follows [16]:

$$C = 96.5 \times (1/d) \lg(I_0/I) \quad (1)$$

where C is the hydroxyl content of the sample, ppm (10^{-6}). d is the sample thickness, cm. I_0 is the distance from the baseline to the zero line at wavelength 2.73 μm , mm. I is the distance from the absorption peak to the zero line at wavelength 2.73 μm , mm. Based on the infrared spectral transmittance curve shown in Figure 2, the hydroxyl content is 93.2 ppm with a removal depth of 1000 nm and 110.0 ppm after being cleaned by deionized water, in which the hydroxyl content increased by 18%. It should be noted that the calculation of hydroxyl content is greatly affected by the thickness of the sample, and the transmittance of the hydroxyl peak increases as the thickness increases. Therefore, the change rate in hydroxyl content here is only used as a reference to characterize the degree of surface hydroxylation.

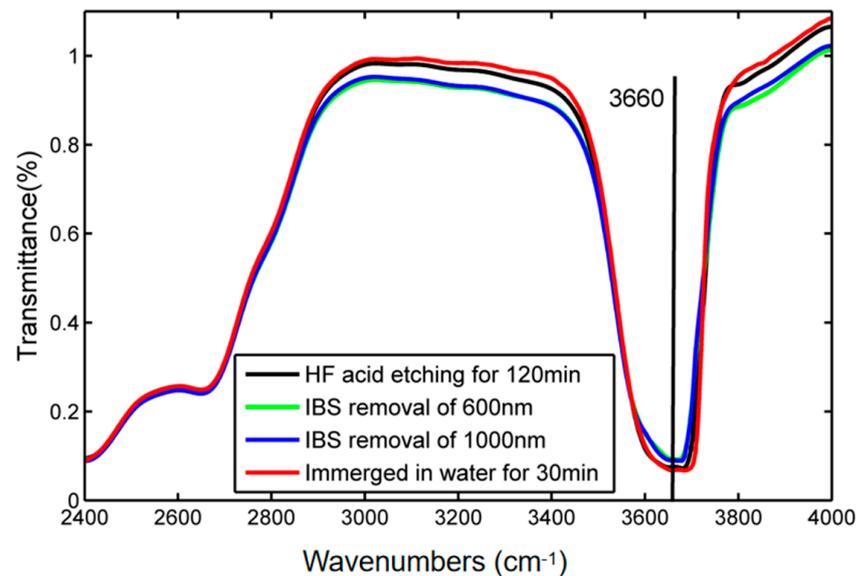


Figure 2. Infrared spectra with different treatment processes.

4.3. Relationship between Surface Hydroxylation and Photothermal Weak Absorption Effects

The absorption loss of high-energy optics has become a very important parameter to evaluate their performance. As a non-destructive detection technology, the photothermal weak absorption detection technology can detect the absorption loss accurately, quickly, and in real-time [21]. If there are damaged precursors on the surface, the photothermal absorption peak of the corresponding intensity will appear on the detection chart, and the smaller the photothermal absorption signal obtained, the weaker the absorption loss. In this paper, the photothermal weak absorption detection technology is used to detect and evaluate the absorption characteristics of the IBS surface. The changes in photothermal weak absorption intensity of three marking points on fused silica surfaces before and after immersion were tested, and the size of each area was $3 \text{ mm} \times 3 \text{ mm}$. Figure 3 shows the change curves of photothermal weak absorption intensity corresponding to the three marked areas on the sample surface.

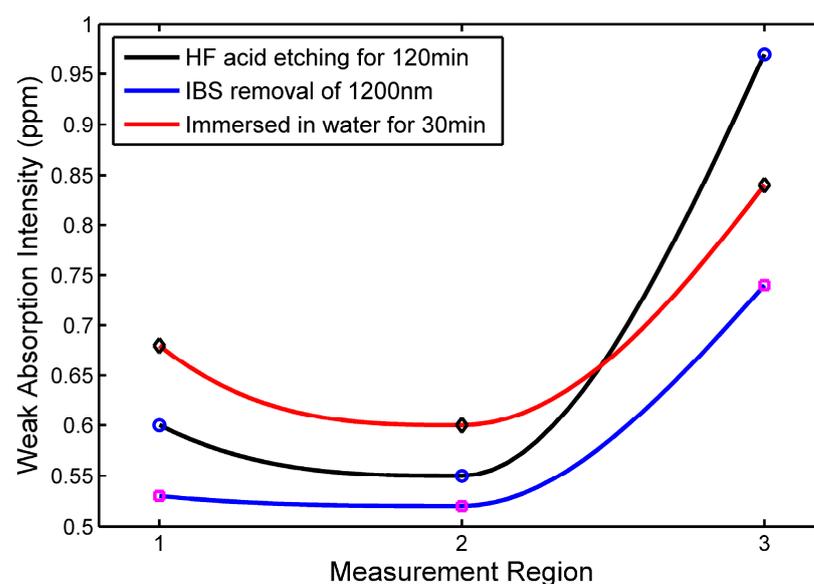


Figure 3. Changes in weak absorption intensity during different surface treatments.

It is obvious from Figure 3 that the photothermal weak absorption intensity of the IBS surface is significantly enhanced after deionized water immersion, indicating that a chemical reaction has occurred after the sputtered surface is immersed in deionized water, resulting in a change in the surface material properties.

Previous studies have shown that when the IBS removal depth is greater than 1000 nm, ion sputtering damage will occur in the shallow layer of fused silica [9]. Although the overall photothermal weak absorption intensity of the HF acid-etched surface can be reduced by IBS, the structure damage on the shallow surface caused by sputtering accelerates the change in material characteristics, which further improves the photothermal weak absorption intensity of the corresponding area after immersion.

5. Discussion: Mechanism of Surface Hydroxylation of Fused Silica

The surface energy is saturated due to the intermolecular force symmetry of the atoms inside the solid. However, the atoms on the solid surface are at a higher energy level due to the unbalanced intermolecular force, which makes the solid surface have a higher reactivity. Molecular dynamics simulations were used in Ref. [20] to show that the band gap on the silica surface is significantly smaller than that of the bulk structure (Figure 4), indicating that surface atoms are more likely to have chemical reactions with external atoms than the bulk atoms.

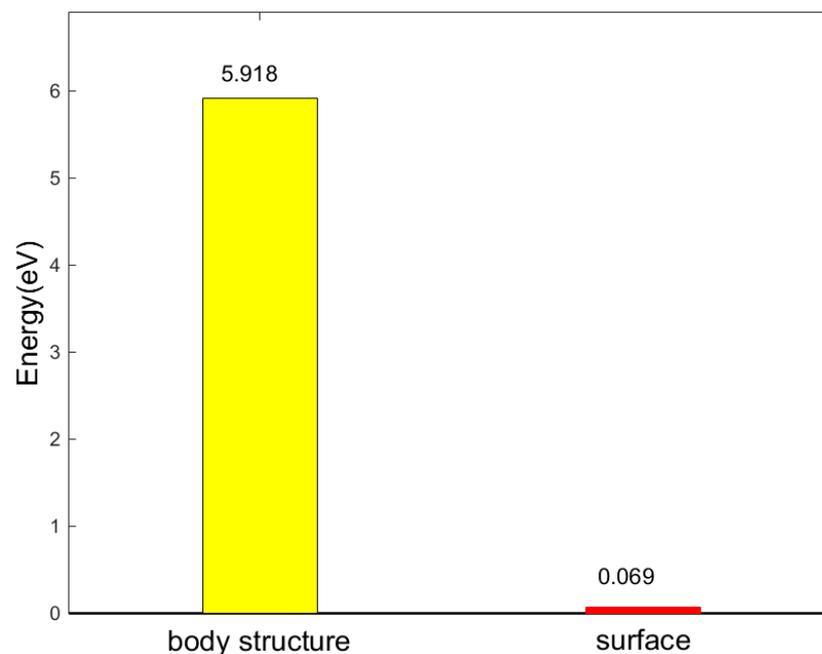


Figure 4. The band gap between the body structure and the surface of fused silica.

On the other hand, the waviness of microscopic fluctuations on the solid surface is mainly manifested in the form of lattice defects, vacancies, and dislocations at the atomic scale. The chemical state of surface atoms is also different due to the different structural forms of atoms at different surface defect locations. The silicate glass surface composed of $[\text{SiO}_4]$ mainly contains unsaturated structures such as non-bonded oxygen, tri-bonded silicon, and cyclic silicon, as shown in Figure 5.

During the sputtering process, many atoms leave their lattice position under the bombardment of incident ions, resulting in the fracture of chemical bonds or the formation of new chemical bonds on surface atoms, which will cause chemical structure defects such as lattice defects, vacancies, and dislocations, making the chemical bonding state of surface atoms significantly different from that of the internal bulk atoms. The asymmetry of the chemical bond energy of the surrounding atoms and the existence of multiple unbound electrons in the outer layer of the atoms lead to the enhancement of the physical properties

and chemical activity of surface atoms. The chemical properties of fused silica are very stable and water-soluble. However, there are many unsaturated structures on the surface after IBS treatment, which has a strong adsorption capacity for polar molecules.

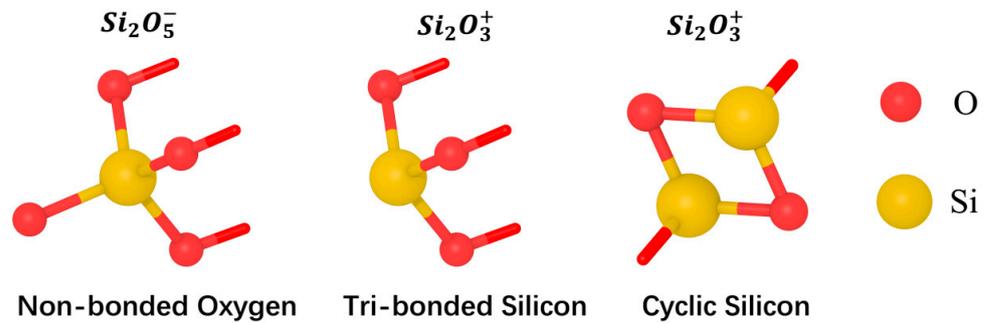
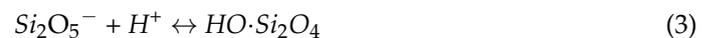


Figure 5. Schematic diagram of the unsaturated structure on the silica surface.

Michalske et al. [22] found that the broken or unbroken Si-O-Si bonds can undergo electrophilic or nucleophilic reactions with water molecules to weaken the Si-O bond strength so that the silica structure is continuously destroyed to form a surface adsorption layer of OH- groups. Water plays an extremely important role in the SiO₂ medium, and the water molecules can penetrate into the SiO₂ molecule under hydrostatic force at room temperature to break the Si-O bond, making it change into a Si-OH bond with lower bond energy. The diffusion of water molecules causes surface hydroxylation of SiO₂ molecules, thus forming a soft layer of Si(OH)₄, which can be expressed as:



Cook [23] believed that the hydroxylation generated by the chemical reaction between siloxane (Si-O-Si) and water is mainly determined by the chemical properties of the processed surface. When the IBS surface of fused silica is immersed in water, the polar water molecules easily adsorb with surface atoms and hydroxylate these surface atoms, thus forming a layer of Si(OH)_n structure on the silica surface so that the Si atoms on the surface form a relatively stable structure. Due to the presence of H⁺ and OH⁻ ions in aqueous solutions, the two ions chemically interact with different types of unsaturated structures on the surface, respectively. Leed et al. [24] found that the surface hydroxylation process is that H⁺ reacts with non-bonded oxygen in an aqueous solution, while OH⁻ reacts with unsaturated silicon to form OH- groups. The whole action process can be expressed as follows:



Generally speaking, the more unsaturated the bonding structure, the stronger its adsorption capacity for water molecules, thus the stronger its surface hydroxylation ability, and correspondingly, the higher the number of OH- groups formed on its surface. Due to the limitation of the bonding ability of Si atoms, the number of OH- groups of a single Si atom after hydroxylation is not more than 3. Bassett et al. [25] found that the average area density of OH- groups on the traditional polished fused silica surface after water cleaning is 4–6/nm².

After the surface hydroxylation process, the binding force between surface atoms will be relatively weakened due to the introduction of OH- groups, and the binding energy of surface atoms after surface hydroxylation can be expressed as [26]:

$$E_{as} = E_{bs} - (1/2)kTn_{OH} \quad (5)$$

where E_{as} is the binding energy of surface atoms after surface hydroxylation; E_{bs} is the binding energy of surface atoms before surface hydroxylation; n_{OH} is the number of OH-groups generated by a single Si atom ($n_{OH} = 1, 2, 3$); k is the Boltzmann constant, and T is the ambient temperature. The more OH- groups adsorbed during the surface hydroxylation process, the more severe the weakening of the atomic binding energy of the surface layer, resulting in a reduction in surface mechanical strength. The hydroxylation process on the silica surface destroys the original spatial network structure of the silica bulk, thereby reducing its mechanical strength [16].

The strong hydroxyl characteristic peak of fused silica samples treated by HF acid etching is mainly due to the acid etching process occurring in a water environment. Once the freshly etched surface is exposed, it is easy to have surface hydroxylation with the surrounding water molecules, resulting in the formation of hydroxyl on the silica surface. After the removal of 1000 nm by ion sputtering, the hydroxylation layer on the surface was removed, resulting in a decrease in the characteristic hydroxyl peak intensity. When the ion-sputtered surface is completely immersed in deionized water, the chemical activity of surface atoms is enhanced by ion sputtering, which improves the probability of reaction between the unsaturated structure of the silica surface and water molecules, resulting in a further increase in surface hydroxyl content. This is the reason for the enhancement of the characteristic hydroxyl peak after immersion in deionized water. In addition, the characteristic hydroxyl peak intensity of the IBS surface after immersion in deionized water for 30 min is stronger than that of HF acid etching for 120 min, indicating that ion sputtering increases the unsaturated structure, enhances the activity of Si and O, and thus makes the surface hydroxylation reaction easier to occur.

Due to the corrosive effect of OH- ions on the silica surface, chemical adsorption will occur and destroy the original spatial network structure of the silica bulk, resulting in a reduction in mechanical strength and a decrease in laser damage resistance performance. Therefore, the ion sputtering surface should be strictly avoided from contact with the water environment to avoid a decrease in the laser damage threshold caused by surface hydroxylation.

6. Conclusions

During the material removal process of IBS, due to the ion sputtering effect, the lattice atoms are separated from their native space locations, and a large number of unsaturated structures are formed, which improves the chemical activity of Si and O atoms, accelerates the chemical reaction process between surface atoms and water molecules on the sputtered surface, increases the OH- groups content in the shallow layer, and enhances the photothermal weak absorption effect. However, an increase in OH- groups reduces the bonding strength of Si-O, destroys the spatial network structure of silica bulk, and reduces its chemical stability and surface mechanical strength, resulting in a decrease in its laser damage resistance performance. Therefore, the IBS surface should be strictly prevented from contact with the water environment in order to avoid surface hydroxylation during the combined process of HF acid etching and IBS cleaning, so as to avoid a reduction in the laser damage threshold caused by surface hydroxylation. This paper reveals for the first time the mechanism of IBS to change the structure characteristics of silica material, accelerate the surface hydroxylation process, and thereby reduce the laser damage resistance performance. This work provides a theoretical basis for the combination sequence and process interface conditions of the combined process and also provides technical guidance for effectively suppressing chemical structure defects on silica surfaces and improving the laser damage resistance performance of optical components under high-flux laser irradiation.

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