Polishing-induced Generation of Intrinsic Defects of Fused Silica

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Fused silica optics are widely used in high-power laser applications, and polishing-induced intrinsic defects have become the key reason for the degradation of optical performance. Although intrinsic defects could be removed by wet etching and other methods, they also cause the deterioration of surface roughness. Thus, it is significant to understand the generation mechanism of intrinsic defects during the polishing process. In this paper, taking E' center and non-bridging oxygen hole center (NBOHC) as examples, polishing experiments and molecular dynamics simulations were performed to analyze the influencing factor and generation mechanism. It is found that the population of intrinsic defects increases as a function of the load on the single particle. The growth rate of E' center is higher than NBOHC, which cannot be explained by the mechanism of the breakage of strained Si-O-Si bonds. Thus, a new generation mechanism was proposed based on the intermediate of overcoordinated pa irs. The reaction barrier of the generation of E' center is higher than that of NBOHC, indicating the reliability of the generation mechanism. The results provide valuable insights into the generation of intrinsic defects and guide the precision manufacturing of fused silica.

1. Introduction

Fused silica has been widely used as optical components in high-power laser systems due to its excellent chemical stability and high transmittance. To meet the growing demand for the performance of laser systems in industry and other fields, the scale and population of manufacturing-induced defects are both required to be reduced continuously. The intrinsic defects, such as the E' center and non-bridging oxygen hole center (NBOHC), have narrow band gaps, leading to higher adsorption and thus a degradation in optical performance. Although intrinsic defects could be removed by wet etching after the grinding and polishing processes, the deterioration of surface roughness and contamination is difficult to avoid. Thus, it is significant to understand the generation mechanism and influencing factors of intrinsic defects during the polishing process.

Many studies in the previous decades have identified and characterized intrinsic defects in detail by electron paramagnetic resonance (EPR), photoluminescence (PL), and optical absorption (OA). Skuja et al. [1] summarized types of intrinsic defects that had a negative impact on the performance in laser, such as E' center (≡Si·), non-bridging oxygen hole center (NBOHC, ≡Si-O·), peroxy radical (POR, ≡Si-O-O·) and et al., and thought they could be created under the stress during the manufacturing process. Li et al. [2] characterized the depth distribution of intrinsic defects of the polished surface by Photoluminescence (PL) spectra and found the population decreased gradually as the etching depth increased to 5000 nm, indicating the depth of the distribution is at least 5000 nm. Sun et al. [3] compared the population of intrinsic defects at different depths and thought the depth of polishing-induced intrinsic defects was less than 1 μm. Zhong et al. [4] also characterized the distribution of polishing-induced intrinsic defects, and found a similar trend with Li et al., while the depth was only about 250 nm. Thus, similar polishing processes resulted in dramatically different distribution, suggesting that polishing parameters and polishing environment played key roles in the generation of intrinsic defects. However, the underlying generation mechanism and influencing factors of intrinsic defects remain unclear, which makes their inhibition and optimization of parameters difficult.

In this paper, polishing experiments and molecular dynamics simulations (MD) were performed to analyze the generation mechanism of intrinsic defects. The influence of the load on a single particle on the concentration of intrinsic defects was analyzed. The results contribute to enhancing the understanding of the generation mechanism of intrinsic and guide the optimization of parameters in polishing and subsequent processes.

2. Methods

2.1 Experiments

Corning 7980 fused silica with a size of 20 mm × 20 mm × 1 mm was used as the sample. Polishing experiments were carried out on the automatic polishing machine (Kejing UNIPOL1200S, China) with an IC 1000 polishing pad, as shown in Fig. 1(a). Different sizes of particles were applied to analyze the effect of the load on a single on the generation of intrinsic defects. The polishing parameters and the composition of the polishing slurry are shown in Table 1.

The adsorption spectra were measured by UV/Vis/NIR spectrophotometer (LAMBDA 1050+, PerkinElmer, USA) to characterize the type and concentration of polishing-induced intrinsic defects. The polished surface was etched 5 μm to achieve a polishing-induced defect-free surface. The etching solution was composed of 80 wt% DI water, 15 wt% NH_4F, and 5 wt% HF, and the etching rate of the polished surface of fused silica was measured at about 60 nm/min. The samples were pre-etched 10 nm to avoid the influence of contamination before measurements.

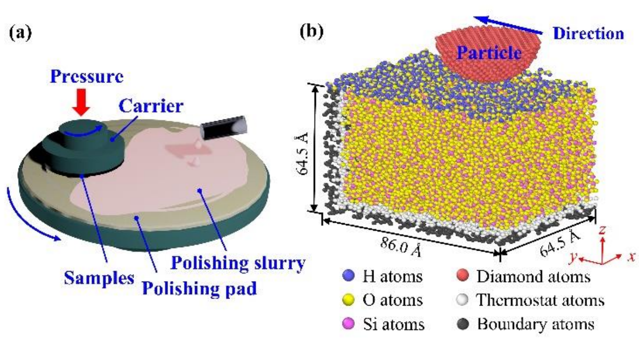

Fig. 1 The schematic diagram of (a) the macroscopic polishing process, and (b) MD model of the nanoscratch of fused silica with a single particle.

Table 1 Experimental conditions and process parameters.

Parameters	Process conditions
Particle	Al_2O_3
Particle size	50 nm, 100 nm, 250 nm
Polishing pad	IC 1000
Rotary speed	70 rpm
Pressure	50 kPa

2.2 MD Simulations

MD simulations of single-particle nanoscratch under different loads were performed to explore the polishing-induced generation mechanism of intrinsic defects and influencing factors. As shown in Fig. 1(b), MD simulations were carried out by LAMMPS software with a particle sliding against a fused silica substrate. The substrate was amorphous fused silica with a size of 64.5 Å× 86.0 Å× 64.5 Å, and the thicknesses of the boundary and thermostat layers were 4 Å. the NVT ensemble was applied with a timestep of 0.25 fs. The simplified hemisphere-shaped particle was a diamond with a radius of 20 Å. The total number of atoms in models was 26,239. The particle scratched 20 Å along the y-direction at a velocity of 10 m/s and the depth was 15 Å. The ReaxFF reactive potential for C/H/O/Si was used to describe the interaction between the particle, fused silica substrate and water [5]. It should be noted that the aim of MD simulations is to obtain the generation mechanism during the scratching of the particle, rather than the comparison of the value with experiments directly.

3. Results and Discussions

3.1 Effect of the load on the generation of intrinsic defect

The load on a single particle determines the material removal and the stress distribution during the polishing process, while its effect on the generation of intrinsic defects is unclear. Thus, Particles with different sizes were applied to change the load on a single particle to analyze its effect on the generation of intrinsic defects. Figure 2(a) presents the adsorption spectra of polished surfaces with different particle sizes. Compared with the etched surface, which is considered a surface free from polishing-induced intrinsic defects, the adsorption coefficient of polished surfaces under three conditions is higher than that of the etched surface, indicating the generation of intrinsic defects under three conditions. To further understand the type of polishing-induced intrinsic defects, the spectrum was fitted into five Gaussian peaks centered at 3.8 eV, 4.8 eV, 5.4 eV, 5.8 eV and 6.4 eV, associated with E' Center, NBOHC, POR, interstitial Cl_2 and ODC(I) et al., respectively, as shown in Fig. 2(b). Among them, the interstitial Cl_2 mainly comes from the contamination during the preparation process of fused silica, which is not the focus during the polishing process. And the peak at 6.4 eV is just partially detected, which is difficult to fit accurately. Thus, the concentration of E' Center, NBOHC and POR was calculated using Smakula's formula [6]:

$$N = 7.2 \times 10^{15} \cdot \alpha_{\max} \cdot \frac{W}{f_0} \ (\mathrm{cm}^{-3}) \tag{1}$$

where $\alpha_{\max}$ is the absorption coefficient at peak position, W is the FWHM of the absorption peak (eV), and f is the oscillator strength of corresponding defects.

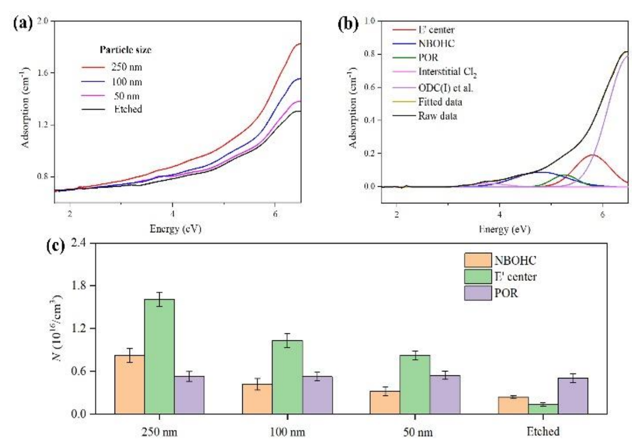

Fig. 2 (a)The adsorption spectrum of polished surface with different conditions. (b) Fitting of absorption spectrum by using multi-Gaussian functions. (c) The concentration of intrinsic defects calculated based on Eq. (1).

Fig. 2(c) shows the concentration of three intrinsic defects under different particle sizes. Compared with the etched surface, the concentration of NBOHC and E' center increases significantly with the increase of particle size, while the POR seems unchanged. It indicates that the mechanical action of particles does not cause the rise in the concentration of POR during the polishing process. To further build the relationship between the load on a single particle and the concentration of intrinsic defects, the load on a single particle is calculated based on Eq. (2) and (3):

$$F_z = \frac{E_a^*}{2}\left[\left(a_p^2 + R_p^2\right)\ln\frac{R_p+a_p}{R_p-a_p} - a_p R_p\right] \quad (2)$$

$$E_a^* = \frac{E_a}{1-v_a^2} \quad (3)$$

where F_z is the load on a single particle. E_a^* is the equivalent elastic modulus of the polishing pad. E_a (= 360 MPa) and v_a (= 0.2) are the elastic modulus and Poisson's ratio of the polishing pad. R_p is the radius of particles. a_p (= $0.98R_p$) is the radius of contact area between the polishing pad and particles, and the value was calculated based on finite element analysis. Corresponding F_z of particles with a diameter of 50 nm, 100 nm and 250 nm are 0.94 μN, 3.77 μN and 23.55 μN, respectively.

Fig. 3 shows the relationship between the load on a single particle and the variation in concentration of intrinsic defects. The concentration of the E' center and NBOHC both increase with the rise of the load on a single particle. In addition, the growth rate of E' center is much higher than that of NBOHC, indicating that they are not created in pairs. It means that the mechanism, cleavage of Si-O-Si bonds forming the E' center and NBOHC in pairs under the laser irradiation, is not applicable during the polishing process. Furthermore, when the data was fitted by the Arrhenius-type function, which describes the effect of the external load on chemical reactions, the results verified that the load on a single particle is the major of the generation of intrinsic defects during the polishing process.

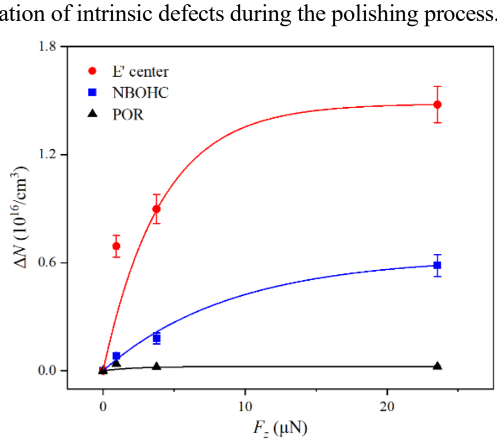

Fig. 3 The variation in the concentration of intrinsic defect as a function of the load on a single particle. The solid lines are fitting results by Arrhenius-type function.

3.2 Generation mechanism of intrinsic defects.

To reveal the generation mechanism, we tracked the generation process of E' Center and NBOHC during the nanoscratch in MD simulation, respectively, and the mechanisms were summarized as shown in Fig. 4. The path to generate E' center and NBOHC could be divided into two steps. The first is the generation of overcoordinated Si-O pairs due to the external load, and then the cleavage of original adjacent Si-O bonds causes the generation of E' center or NBOHC. When the Si-O bond linked with an intermediate of OC Si atoms is dissociated, an NBOHC defect is created, while the dissociation of the bond linked with OC O atoms leads to the generation of an E' center.

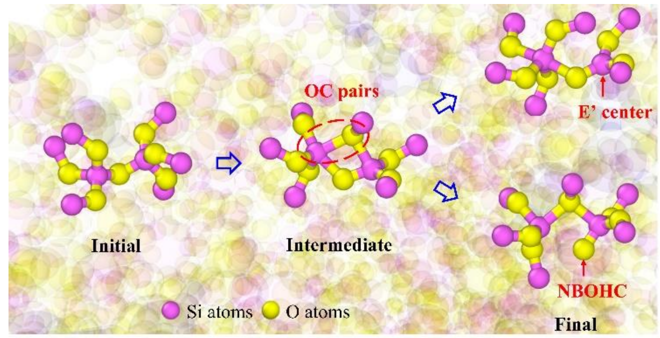

Fig. 4 The generation mechanism of E' center and NBOHC during the polishing process.

4. Conclusions

The polishing-induced generation of intrinsic defects of fused silica was analyzed by experiments and MD simulations. The effect of the load on a single particle was explored and the generation mechanism of intrinsic defects was clarified. During the polishing process, the E' center and NBOHC are the main types with increased concentration, which is dominated by the load on a single particle. As the load on a single particle rises, the concentration of them increases and follows the Arrhenius-type function. Compared with NBOHC, E' center has a higher growth rate, instead of equivalence under the laser irradiation. This is because E' center and NBOHC are generated by the formation of OC pairs and cleavage of adjacent Si-O bonds. The results provide new insights into the polishing-induced generation of intrinsic defects and contribute to optimizing the polishing processes of fused silica.

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