

Defect-free surface of quartz glass polished in elastic mode by chemical impact reaction

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Abstract: Removal of brittle materials in the brittle or ductile mode inevitably causes damaged or strained surface layers containing cracks, scratches or dislocations. Within elastic deformation, the arrangement of each atom can be recovered back to its original position without any defects introduced. Based on surface hydroxylation and chemisorption theory, material removal mechanism of quartz glass in the elastic mode is analyzed to obtain defect-free surface. Elastic contact condition between nanoparticle and quartz glass surface is confirmed from the Hertz contact theory model. Atoms on the quartz glass surface are removed by chemical bond generated by impact reaction in the elastic mode, so no defects are generated without mechanical process. Experiment was conducted on a numerically controlled system for nanoparticle jet polishing, and one flat quartz glass was polished in the elastic mode. Results show that scratches on the sample surface are completely removed away with no mechanical defects introduced, and micro-roughness (R_a) is decreased from 1.23 nm to 0.47 nm. Functional group Ce—O—Si on ceria nanoparticles after polishing was detected directly and indirectly by FTIR, XRD and XPS spectra analysis from which the chemical impact reaction is validated.

Key words: defect-free surface; chemical impact reaction; nanoparticle jet polishing; elastic mode

1 Introduction

Laser induced damage threshold of the optical element is a key index in intense laser radiation system. However, the actual threshold of quartz glass is about one fiftieth of the intrinsic threshold [1–2]. The defect induced in machining process called damaged layer is the main reason that causes decline of laser induced damage threshold [3]. For device application, it is essential to prepare a defect-free quartz glass because the surface condition determines the quality and activity. In general, the brittle material will undergo elastic deformation, plastic flow or brittle fracture at a large process force in the traditional mechanical surface-preparation technique [4–5]. In the range of the corresponding cutting depth, the material is removed in the brittle mode or ductile mode in traditional process, in which damaged or strained surface layer containing cracks, plastic flow or dislocations cannot be avoided. Although no crack remains on the surface after machining in ductile mode, machining strains and scratches remain on the surface, which will also lead to damaged layer and decrease the surface quality. Within elastic deformation, the arrangement of each atom can be recovered back to its original position. So, if we can

remove the material in its elastic region, defect-free surface is possible to be obtained [6]. The critical problem is how to remove materials in the elastic mode. It has been discovered that certain nanoparticles such as SiO₂ or CeO₂ will chemically contact to glass surface when they impact with each other, and atoms can be removed from the workpiece surface when particles are transported to separate [7–8]. Therefore, if we can control chemical impact reaction occurred in the elastic mode with smaller contact force, the damaged layer will be avoided.

In this work, material removal mechanism of quartz glass is analyzed based on surface hydroxylation effect and chemisorption theory. Surface impact model is established based on fluid dynamic simulation, while the contact model is confirmed by the Hertz contact theory. Finally, polishing experiment is carried out on a numerically controlled nanoparticle jet polishing system on a quartz sample to verify the eliminating capability of plastic scratches.

2 Material removal mechanism

Material is removed by chemical impact reaction in the elastic mode in the machining process. Nanoparticles chemically contact to workpiece surface when they

Foundation item: Projects(51305450, 51275521) supported by the National Natural Science Foundation of China

Received date: 2013–07–29; **Accepted date:** 2013–11–15

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impact on the surface, and atoms can be removed from workpiece surface when particles are transported to separate. Nanoparticle jet polishing employs colliding and shearing actions between nanoparticles and workpiece. Brittle material removal usually takes place in three modes: elastic mode, plastic mode or brittle mode. In chemical impact reaction removal process, nanoparticles are very small, and their general velocities are very slow. The kinetic energy of nanoparticles is not large enough, so we can easily control material removal in the elastic mode without any mechanical defects.

2.1 Surface hydroxylation

Inverse gas chromatography experiments indicate that there are lots of reactive sites and defects on workpiece surface [9]. Surface chemical activity and many other characters have great reliance on surface defect types [10]. There mainly exist no bridging oxygen and unsaturated bond silicon atoms on quartz glass surface, as shown in Fig. 1(a). These structures are all unsaturated coordinate and have strong surface electrostatic field to exert a significant attraction on polar molecules such as water [9, 11]. These unsaturated coordinate structures are called active surface sites. Under certain activation energy, the active surface sites can be easily hydroxylated as $[\text{SiOH}]_n$ groups with the surface formed as siloxane network, as shown in Fig. 1(b) [12].

When active surface sites are completely hydroxylated, the hydroxy oxygen atoms have high electro negativity, so valence electrons at the region between surface layer and second layer are captured by interface oxygen atoms [13]. After being hydroxylated, the top surface atom is bonded with binding energy as [14]

$$E_a^{\text{surface}} = E_b^{\text{surface}} - \frac{1}{2}kTn_{\text{OH}} \quad (1)$$

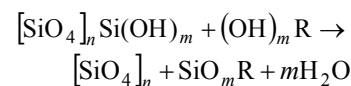
where E_b^{surface} and E_a^{surface} are surface atom bonding energy before and after being hydroxylated, respectively, n_{OH} is the number of hydroxyl, T is the Kelvin temperature, and k is the Boltzmann constant. From this equation, we know the more the hydroxyls are

hydroxylated, the faster the bonding energy is weakened.

2.2 Chemisorption

Nanoparticle has very large specific area and strong absorption ability with superfluous unsaturated chemical bonds, and hydroxyls are easily established on the surface in moist environment [13, 15]. The nanoparticle and workpiece surface are all covered with hydroxyl, and when these two surfaces approach each other with the distance about 3–5 nm, hydrogen bond is easily established for the high electro negativity of oxygen atoms in the hydroxyl called physical adsorption, the point *a* shown in Fig. 2. However, hydrogen bond is not strong enough to pull the surface atoms out. When nanoparticles overcome the energy barrier under certain impact activation, nanoparticle surface atoms will chemically contact to workpiece surface atoms to form covalent bond with surface distance about 0.4–1 nm called chemisorption, the point *b* shown in Fig. 2 [16]. The covalent bond is strong enough to pull the surface atoms out. However, interaction between the two surfaces is so weak that it can be neglected when surface distance is farther than the point *c* shown in Fig. 2. Therefore, once being pulled out from the workpiece surface, the atom can be easily removed.

Therefore, with impact and shearing actions between nanoparticles and workpiece, the following chemical impact reaction will exist [11]:



In this chemical reaction, R represents nanoparticle atoms, m is the number of hydroxyl of a single quartz glass surface silicon atom being hydroxylated ($1 \leq m \leq 3$). Surface silicon atoms are removed with chemical impact reaction under flow shearing action shown in Fig. 3 [17].

3 Impact contact model

When nanoparticle slurry is ejected on the workpiece surface, the flow will be deflected to form a streamlines parallel to the workpiece surface, as

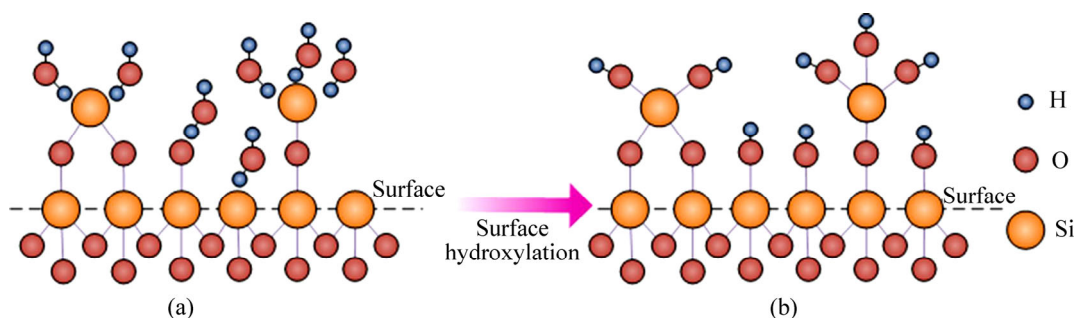


Fig. 1 Quartz glass surface structure: (a) Initial surface; (b) After hydroxylation

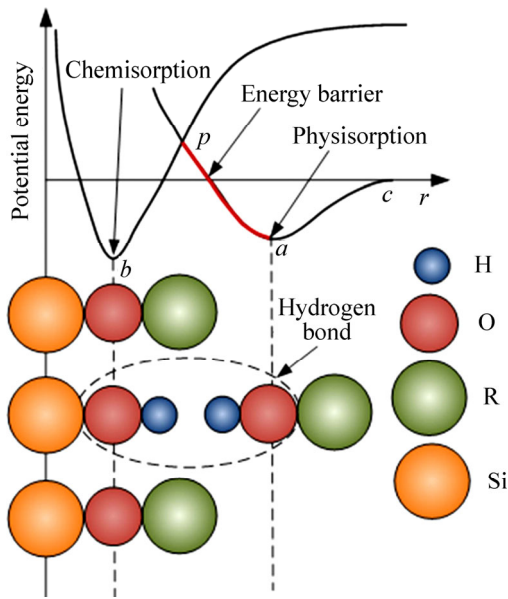


Fig. 2 Interaction between nanoparticle surface and quartz glass surface (R represents nanoparticle atom)

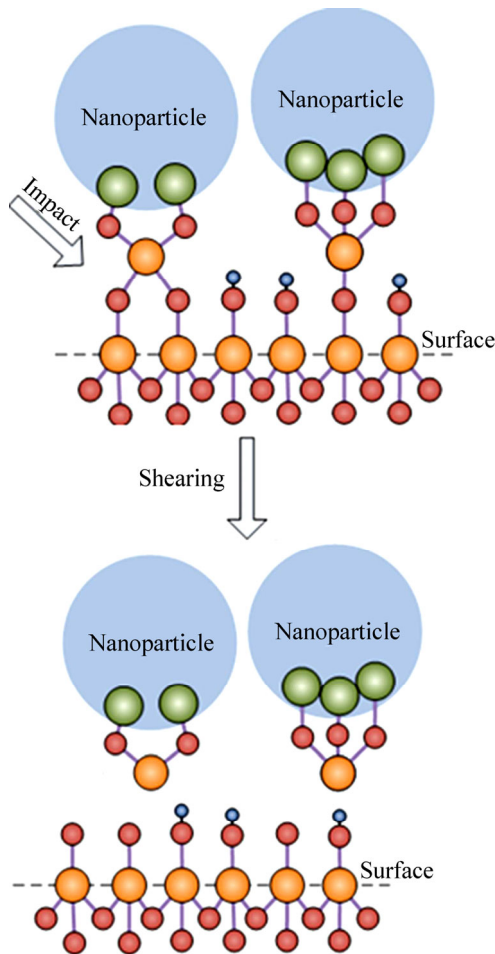


Fig. 3 Material removal process by chemical impact reaction

illustrated in Fig. 4 [18]. The bend is a circular arc with a radius of R_b which can be assumed to be approximately equal to radius of the jet in vertical impact [16]. When the nanoparticle obliquely impacts on the workpiece

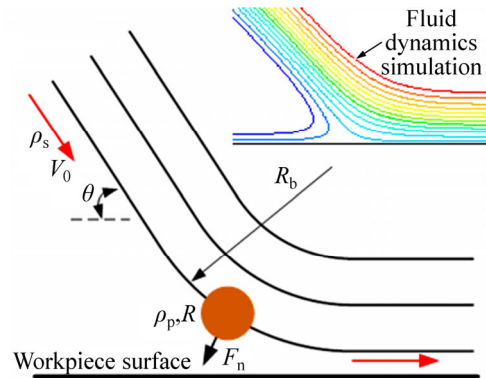


Fig. 4 Schematic of slurry streamlines and impact force acting on nanoparticle

surface, the bend radius R_b can be approximately given as

$$R_b = R_j / \sin \theta \tag{2}$$

where R_j is radius of the jet and θ denotes the oblique impact angle shown in Fig. 4. The flow speed is assumed to be a constant and equal to the jet speed V_0 . When nanoparticles move through the bend region of the flow field, the nanoparticles will be impacted on the workpiece surface under the centrifugal force F_n . From Newton’s law of motion in the slurry, it can be written as [19]

$$F_n = \frac{4}{3} \pi R^3 (\rho_p - \rho_s) \frac{V_0^2}{R_b} \tag{3}$$

As shown in Fig. 4, ρ_s is the density of polishing slurry, R denotes the diameter of the nanoparticle and ρ_p is the density of the nanoparticle. From Eqs. (2) and (3), we can obtain the impact force between the nanoparticles and workpiece surface in the polishing process.

Based on the Hertz contact theory, the maximum normal elastic contact force between the particle and the workpiece surface can be expressed as [20]

$$F_{ne} = \frac{9}{16} \left(\frac{r}{E} \right)^2 (\pi k H)^3 \tag{4}$$

where E and H are the hardness and elastic modulus of the workpiece, r denotes the radius of the particle, and k represents the mean contact pressure factor and generally equals 0.4. If the normal impact force of the particle is smaller than the maximum elastic contact force, only elastic deformation will occur on the workpiece surface.

4 Experimental procedures

Chemical impact reaction polishing experiment was conducted on a nanoparticle jet polishing system on an ultra-precision numerically-controlled optical polishing machine. Polishing slurry is a mixture of deionized water

and CeO₂ nanoparticles with average diameter of 100 nm. The quartz glass sample was submerged in the slurry to promote surface hydroxylation process and avoid spattering-out of fluid. In this work, a streamlined cylinder nozzle head (H.IKEUCHI & Co. Ltd.) was employed to transport the nanoparticle to process the surface, and Table 1 gives the process parameters and conditions. The raster polishing path was chosen as the scanning mode, and the scanning step size was 0.01 mm with the feed rate of 200 mm/min.

Table 1 Process parameters and conditions

Parameter of condition	Value or description
Workpiece	Quartz glass
Nanoparticle	CeO ₂
Diameter of particles/nm	100
Density of particles/(g·cm ⁻³)	7.132
Density of slurry/(g·cm ⁻³)	1.3
Diameter of nozzle/mm	0.5
Induced angle/(°)	45
Velocity of fluid/(m·s ⁻¹)	30

5 Results and discussion

Sample surface was measured by atomic force microscopy (AFM) operated in the tapping mode with measure area of 10 μm×10 μm. Figure 5 shows the AFM images of quartz glass surface before and after polishing. Before polishing process, the plastic scratch marks can be clearly seen in Fig. 5(a). Almost all the plastic scratches and pits on the surface are removed away after polishing, and the processed surface becomes much smoother, as shown in Fig. 5(b).

Figure 6 shows the micro-roughness of preprocessed and processed surface, which was obtained by ZYGO New Views with vertical resolution of 0.1 nm. The measurement results show the micro-roughness (*R_a*) decreases from 1.23 nm to 0.47 nm and the peak-to-valley (PV) reduces from 22 nm to 10.8 nm after polishing. Plastic scratch marks are completely cleared during the polishing process.

The average diameter of CeO₂ nanoparticle is about 100 nm analyzed by Zetasizer Nan Zs. The hardness and elastic modulus are 7.0 GPa and 71.4 GPa for quartz glass, respectively, so according to Eq. (4), the maximum elastic contact force for the nanoparticle is 1.9×10^{-7} N in the polishing experiment. On the other hand, from Eqs. (2) and (3), we can know that the impact force is about 5.5×10^{-12} N under the process parameters shown in Table 1. By comparison, we can conclude that the nanoparticle jet polishing is confined in the elastic zone in the experiment, for the impact force is much smaller

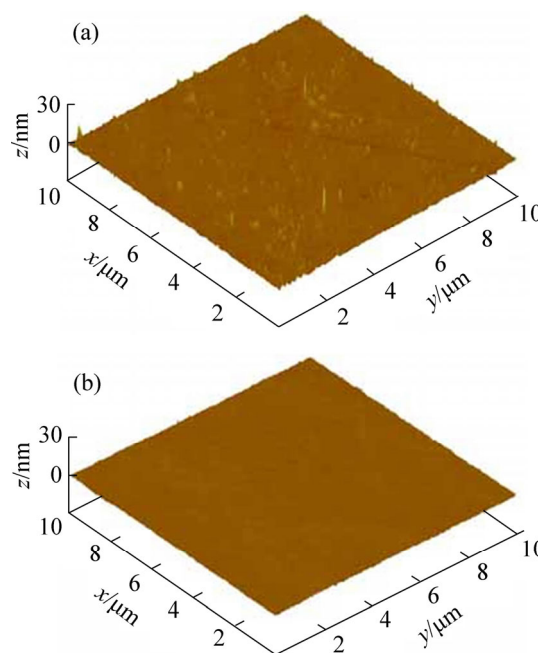


Fig. 5 Surface AFM images of quartz glass: (a) Before polishing; (b) After polishing

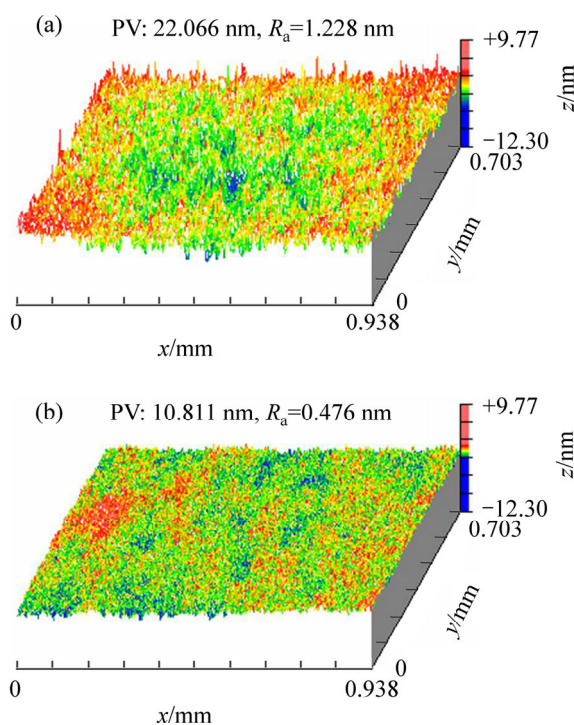


Fig. 6 Surface micro-roughness of quartz glass: (a) Before polishing; (b) After polishing

than the maximum elastic contact force. Convex atoms on workpiece surface are more coordinate unsaturated than the concave atoms, so the numbers of hydroxyls and chemical bonds with nanoparticle are larger. From Eqs. (1) and (3), we can conclude that the convex atoms' removal rate is larger than that of the concave atoms and thus after polishing the surface becomes much smoother.

After being placed at the room temperature for

about 12 h, the polishing slurry on the top of container was taken out with the pipette. The polishing slurry before and after polishing was distilled to get ceria nanoparticle samples for Fourier transforms infrared (FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) spectra analysis. FTIR spectroscopy was used to detect the functional groups presented on the surface of ceria nanoparticles before and after polishing. Sample for FTIR measurement was mixed carefully with dried KBr solid, and the solid mixture was made into pallets using a 13 mm die under certain hydraulic pressure. Previous work shows that peak of 852 cm^{-1} appearing on the spectra of polished ceria nanoparticles suggests the presence of Ce—O—Si groups on the surface of ceria nanoparticles after polishing [17]. On the basis of the observation, we can conclude that silicon atoms on the quartz glass are chemically bonded to surface of ceria nanoparticles through impact reaction with —OH groups illustrated in Fig. 3.

The other method used for structure characterization was XRD. Figure 7 shows the XRD patterns for quartz glass and ceria nanoparticles before and after polishing. There are only characteristic diffraction peak of ceria with cubic fluorite structure, and the quartz glass with amorphous structure can not be detected. By comparison, the diffraction peak intensities of ceria nanoparticles under different orientation indexes are reduced greatly after polishing, which suggests that the crystalline degree of ceria nanoparticle is reduced. It is implied in the chemical impact reaction that the silicon atoms are introduced on the ceria nanoparticle surface with a form of Si—O—Ce, which results in the decrease of the diffractive intensity around ceria attributed to substitution of Si atoms at the site originally occupied by the Ce atoms causing lattice changes.

X-ray photoelectron spectroscopy (XPS) was used to detect the chemical composition and elements chemical state of the ceria nanoparticles before and after

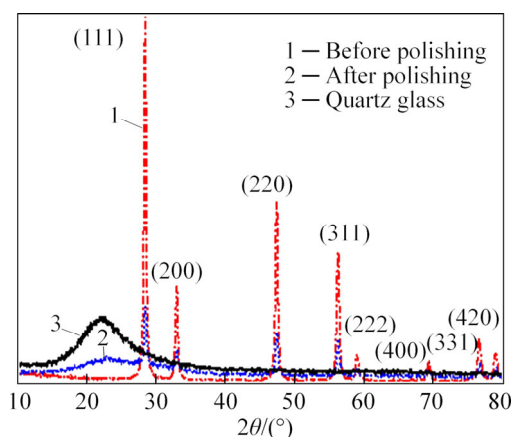


Fig. 7 XRD patterns of quartz glass and ceria nanoparticle before and after polishing

polishing. Both of ceria nanoparticles give peaks of elements Ce, O and C, while added peaks of elements Cu, Na and Si appear on the surface of the ceria particles after polishing, as shown in Fig. 8(a). Table 2 gives the element composition on the surface of ceria nanoparticles before and after polishing. By comparison, we can see that only elements Ce, O and C appear on the nanoparticle surface before polishing and elements Cu, Na and Si are introduced on the surface after polishing. The appearance of elements Cu and Na is mainly caused by oxidation of copper alloy pump body by nanoparticles, while the introduction of element Si indicates that the surfaces of ceria nanoparticles chemically react with the quartz glass.

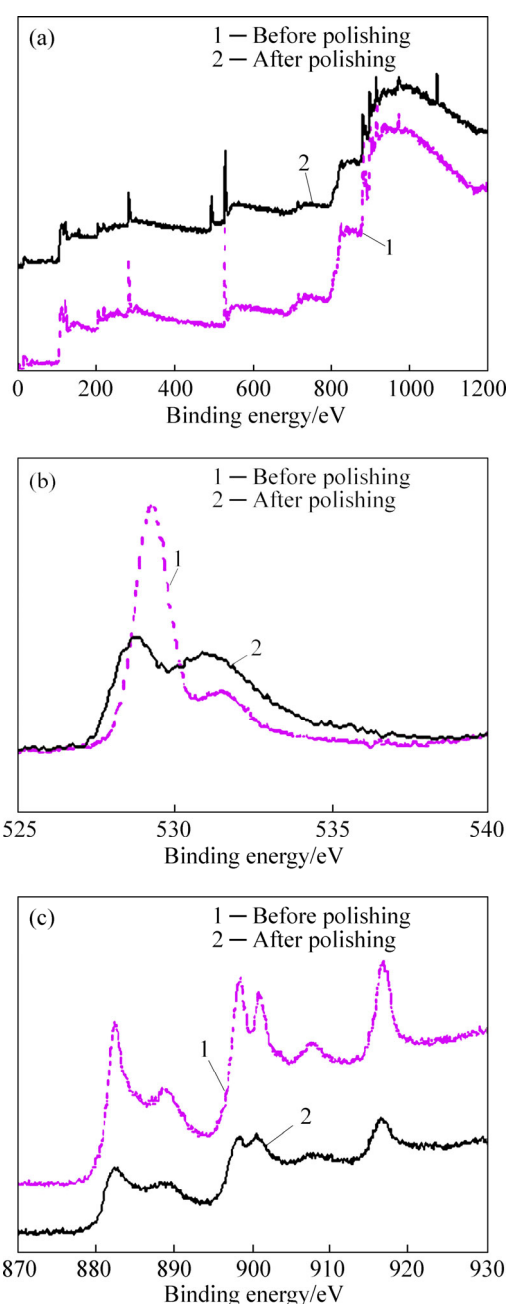


Fig. 8 XPS spectra of ceria nanoparticles before and after polishing: (a) Wide range; (b) O 1s; (c) Ce 3d

Table 2 Element compositions of ceria nanoparticles before and after polishing (mass fraction, %)

Status	Ce	O	C	Si	Cu	Na
Before polishing	28.48	64.31	7.21	0	0	0
After polishing	13.61	62.83	7.82	0.96	1.93	12.24

Bonding energy can be slightly changed by the element's chemical state [15]. From Fig. 8(b), we can see a main peak of bonding energy of 529.27 eV, corresponding to the oxygen in CeO₂ structure. Meanwhile, a shoulder is also identified at higher bonding energy of 531.38 eV, due to the formation of hydroxyl groups (—OH) on the nanoparticle surface resulted from the interaction with the water. This shoulder is almost the same after polishing, while the main peak is attenuated and shifted from 529.27 eV to 528.68 eV. This means that electron cloudy density around O atom has changed. As can be seen from Fig. 2 and Fig. 3, the —OH groups on the ceria nanoparticles are reactive sites for the reaction with siloxane (—Si—OH) of quartz glass. The variation from Ce—OH to Ce—O—Si after polishing may account for the change of the electron cloudy density around O atom since the electronegativity of element Si (1.8) is lower than that of the element of H (2.1) [21]. The reduction of O can be attributed to reaction with the elements Cu and Na. With surface hydroxylation, the initial form Ce—OH can be changed to Ce—O—Si—OH, so the number of —OH is almost the same after polishing. Figure 8(c) shows that bonding energy of Ce 3d is also shifted from 882.28 eV to 881.68 eV after polishing. This also indicates that Ce—O—Si bonds have been formed, which results in the change of electro cloud density around Ce atom for the difference electronegativity between elements Si and H.

The above results illustrate that the Ce—O—Si bonds have been formed during the polishing process. From above analysis, the material removal is caused by the chemical impact reaction in the elastic mode without any defects introduced. From Fig. 1, we know that the hydroxyl number of convex Si atoms on the glass surface after hydroxylation is usually more than that of other surface atoms. In Fig. 3, the convex atoms are much easier to be removed according to Eq. (1), so the processed surface becomes much smoother after polishing.

6 Conclusions

1) By combining surface hydroxylation and chemisorption theory, material removal mechanism of quartz glass in the elastic mode is analyzed.

2) Based on fluid dynamic simulation, the impact force on the workpiece is determined by the impact contact model established in nanoparticle jet polishing system. Elastic contact condition between nanoparticle and workpiece surface is confirmed by Hertz contact theory model.

3) After polishing, functional groups Ce—O—Si are detected on the nanoparticles by FTIR, XRD and XPS spectra analysis, which indicates that impact chemical reaction occurs during polishing process.

4) Polishing experiment results demonstrate the feasibility of removing the brittle material in the elastic mode by chemical impact reaction with no defects. This polishing method will have wide application in improving the laser induced damage threshold of the optical element.

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(Edited by YANG Bing)