

## Inorganic Chemistry

## Investigation of the Chemical Residuals on the Fused Silica during Chemical Mechanical Polishing

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Chemical residuals on fused silica after chemical mechanical polishing with silica and ceria have been analyzed. The surface of fused silica terminates with silanol after being polished with silica abrasives but ends up with Ce–O–Si in a ceria-based slurry under the CMP environment. The silanol firstly synthesizes on a

fused silica surface polished with ceria, but then further reacts with hydroxyl cerium groups scattering in the slurry forming Ce–O–Si. It also reveals that polishing fused silica with silica abrasives is an alternative way giving an ultra smooth surface.

## 1. Introduction

Fused silica (FS), composing from silicon dioxide in a structure of an amorphous state, gets a broad spectrum of employment in scientific and industrial fields, covering laser systems, astronomical telescopes, semiconductor industry, luminescence and optical communication, owing to its exceptional physical, chemical and mechanical properties. Nearly applications mentioned above require a high-quality subsurface and surface.<sup>[1–3]</sup>

Chemical mechanical polishing (CMP) has been broadly used to produce an ultra-smooth surface.<sup>[4–6]</sup> And the planarization process of glass has been reported by various researchers, but mechanical and chemical defects recognized as the most influential crux incurred during post-processing and polishing renders its comprehensive utilization.<sup>[7,8]</sup>

Generally speaking, abrasive particles, classified into free abrasive and fixed-abrasive polishing accordance with the fact whether those particles are freely moved or fastened with the polishing pad in the process of planarization, play a crucial rule in surface smoothing. Free abrasive polishing relates to using scattered abrasives blended with chemical additives and deionized H<sub>2</sub>O to smooth glass surface and is recognized as a rather intricate process to foretell the removal of material definitely as the free abrasive moving stochastically.<sup>[9,10]</sup> Among those free abrasives, ceria and silica are the most widely used as polishing abrasive particles in CMP process. Worth mentioning that, the widespread use of ceria abrasives are the most effective abrasives in smoothing fused silica, but cerium

contamination and subsurface damages arrive inevitable, it is now well confirmed that they are a cause of highly absorptive pollution on the polished surface, which hinder optical elements application seriously. So here we employed silica as abrasives for planarization fused silica.<sup>[11,13]</sup>

Nevertheless, the basic mechanism of the chemical mechanical planarization of fused silica is still abstruse even several approaches to this issue just rely on the fact that silicate glasses hydrate on exposure to aqueous environments and induce a near-surface hydrolyzed layer with lower mechanical properties, higher water-solubility, and higher chemical activity.<sup>[14–16]</sup>

The purpose of this study was to reveal the characteristics arising when fused silica is polished with ceria and silica abrasives during chemical mechanical polishing to establish the mechanism of this process.

## 2. Experimental

Here commercial SiO<sub>2</sub> and CeO<sub>2</sub> slurry whose pH value are around 10 were employed. The SiO<sub>2</sub> slurry purchased from NALCO Co., Ltd and the average particle size of is around 80 nm. The CeO<sub>2</sub> abrasives whose average size is about 20 nm purchased from Nano Materials Technology Pte Ltd. And the polishing conditions were given in Figure 1. After CMP, the

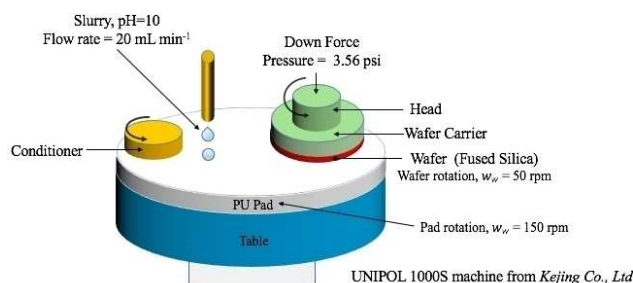
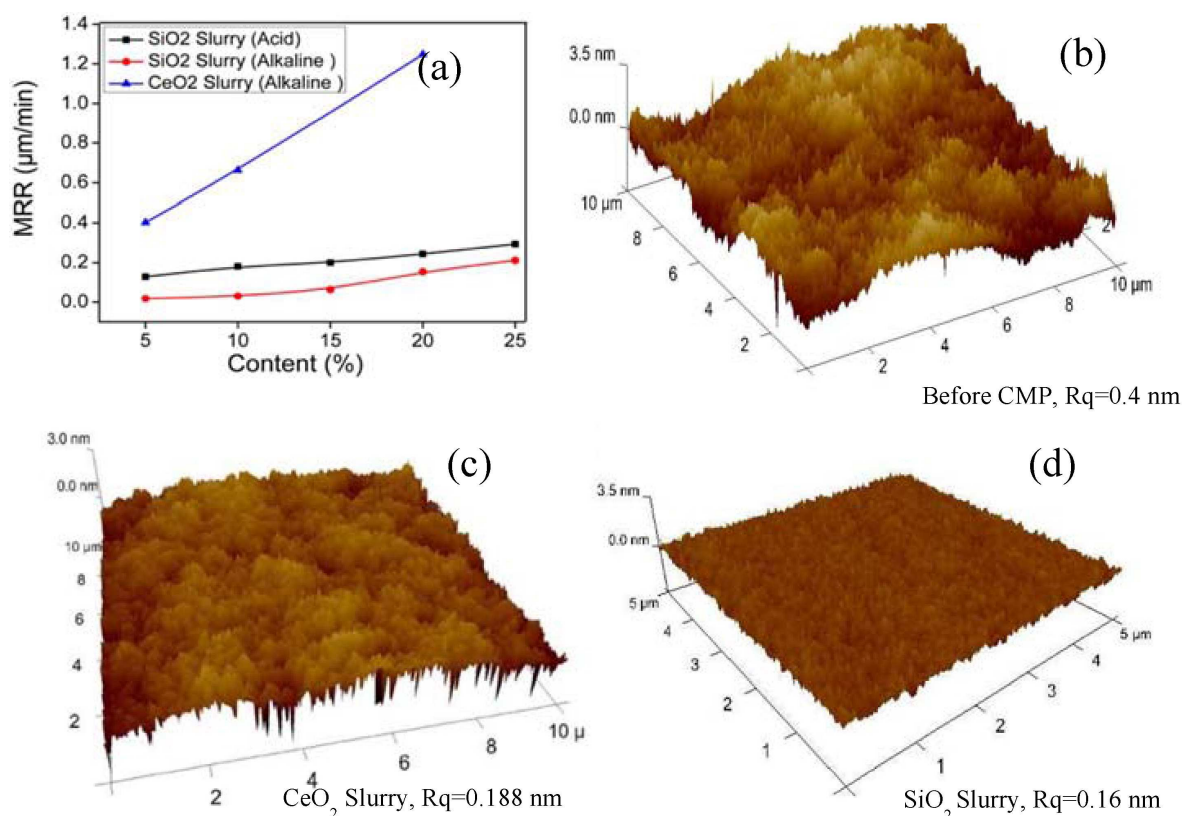


Figure 1. The CMP process and the polishing conditions.

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**Figure 2.** The effect of abrasives on polishing performance of FS. (a) The MRR and (c) (d) surface roughness of fused silica under different CMP conditions; (b) Surface roughness of fused silica before CMP

wafers were cleaned with lab-made detergents and deionized H<sub>2</sub>O and then dried after exposure to clear nitrogen wind for analyses so as to obtain a smooth fused silica surface without residuals. As for the fused silica surface polished under a CMP system by deliberately breaking the balance of physical and chemical function, only deionized H<sub>2</sub>O was used to wash away impurities that physically adsorb on the surface of fused silica.

AFM images usually used to identify the chemical residuals remained on the polished surface and seldom indicate the surface morphology for the properties of a soft material. Here, the surface information of SiO<sub>2</sub> polished / CeO<sub>2</sub> polished FS samples was examined with a commercial atomic force microscope (AFM) (Dimension Icon from Bruker Co., Ltd) in the mode of Force Volume (FV) in the air at room temperature. In an FV experiment, we indent the tip perpendicularly at each spot of a normal matrix in the selected area, which yields the local mechanical response at every point probed, to get a force curve (FC). And an en bloc of the recorded FC built a morphology, hence producing a 1:1 accordance between the map of the residuals' mechanical properties and the morphology. For all measurements, we kept the total vertical ramp length at 1  $\mu\text{m}$ , selecting a maximum force about 40 nN and vertical approaching velocity at 20  $\mu\text{m}/\text{s}$ . We conducted experiments with 64\*64 lateral resolution (4096 points) using a pyramid probe with tip radius 20 nm were obtained for each FC. A series of 2–3 FV measurements were carried in various

macroscopic positions to enhance the statistical reliability of the experiments.<sup>[17]</sup>

The new born chemical residuals on fused silica surface were detected by a Fourier transform infrared (FTIR) spectrometer using an ART FTIR spectrometer HYPARION from Bruker, Germany at room temperature. Spectra were recorded from 600 to 4000  $\text{cm}^{-1}$  using a DLaTGS detector. Spectra were collected at a resolution of 4  $\text{cm}^{-1}$  and at an average of 32 scans per sample.

Thermo-gravimetric (TG) of STA-449 F3 as well as X-ray photoelectron spectroscopy (XPS) with the spectrometer (MICROLAB 350, Thermo Fisher) with AlKa X-ray ( $h\nu = 1486.6 \text{ eV}$ ). A two-stage TGA program was used on 12 mg fused silica samples with and without polishing. In the first stage, the samples were held at 80 °C for ten minutes under a flow of 50 standard cubic centimeters per minute (SCCM) of nitrogen to kick off any loosely bound moisture. During the second stage, the temperature increased from 80 °C to 500 °C at a rate of 10 °C/min. The nitrogen gas flow was 50 SCCM.

### 3. Results and discussion

The original FS surface exhibits roughly as shown in Figure 2 and requires to be polished to achieve a defects-free surface. We employed commercial silica and ceria abrasives to smooth the original FS. Compared with a silica-based slurry, using ceria

abrasives to smooth FS yields much faster material removal rate but coarser surface, in spite of a fact that the FS surface roughness polished with ceria-based slurry decreases from 0.4 nm to 0.188 nm. There are however more chemical residuals staying on its surface, resulting in statistically lower laser-induced damage threshold and dissatisfying the demand of applications.<sup>[18]</sup> Thus, applying SiO<sub>2</sub> abrasives to polish FS is an alternate approach.

A thick layer of chemical residuals, which have a lighter color in AFM figures on both polished FS surfaces after CMP with SiO<sub>2</sub> and CeO<sub>2</sub> abrasives, was obtained to reveal the formation and removal regulation of those residuals is a dynamic process by undermining the balance of chemical etching and mechanical friction during chemical mechanical polishing, which means that we weaken mechanical role and the removing speed of residuals on the polished FS surface was slower than the formation rate of products produced by chemical etching, resulted in much more superfluous chemical residuals remaining on the surface of polished FS. And those residuals also give rise to increase in surface roughness. Figure 3 shows AFM images of FS with residual chemical products on surface. (a) (b) is the surface roughness of polished fused silica with SiO<sub>2</sub> nano-particles and CeO<sub>2</sub> nano-abrasives, respectively. There are more chemical residuals remained on the FS surface polished with CeO<sub>2</sub> nano-particles under the same CMP environment, indicating that the chemical function between FS and CeO<sub>2</sub> is stronger than that happened between FS and SiO<sub>2</sub>. A chemical reaction between abrasives and FS plays a significant role in the polishing quality and efficiency concerning the CMP process. Furthermore, the logarithmic Young's moduli values, which were calculated by data analysis carried out in a Matlab environment with an approach sufficiently described by Galluzzi et al, were used to build the mechanical map of these polished FS samples as shown in Fig. 3(c) (e) and 3(d) (f) respectively (A pyramid probe with tip radius 20 nm results in  $77.71 \pm 19.86$  GPa and  $45.33 \pm 4.52$  GPa for the FS polished with SiO<sub>2</sub> and CeO<sub>2</sub>, respectively). For the FS polished with CeO<sub>2</sub> granule, more chemical interaction happened between FS and CeO<sub>2</sub>, yields a higher surface roughness which leads to a decrease in Young's modulus distribution values, indicated a lower force is required to indent the sample surface. Quantitative analysis using histograms of Young's modulus values in log-normal scale with a Gaussian distribution fit.

To describe the dependence of abrasive on FS during the CMP process, we employed solid state FTIR to analyze the near-surface residual layer on the polished FS, as shown in Figure 4.

Before FS planarization, we don't perceive any structural information on silicon atoms. While the structure of Si-OH, Si-O, and Si-O-Si are observed after planarization. The absorption bands at 1170, 972 and 779 cm<sup>-1</sup> can be assigned to the Si-O-Si antisymmetric stretching, the bending modes of Si-OH and Si-O symmetric stretching, respectively.<sup>[19-21]</sup> Furthermore, compared with the FS surface polished with SiO<sub>2</sub> nanoparticles, much more Si-OH presents on that surface polished with CeO<sub>2</sub>. Iler once reported that the Si-O-Si bonds on the surface of silica react with H<sub>2</sub>O, forming the solute

species silanol (Si(OH)<sub>4</sub>).<sup>[22]</sup> Diagram of the hydration process of the Si(OH)<sub>4</sub> and H<sub>2</sub>O shows in Figure 5. As for its amphoteric character, CeO<sub>2</sub> holds a good affinity towards the oxide, which named as the chemical tooth, promoting in tearing the chemical bonds on the surface of silica, and forming more Si-OH groups in a humid environment,<sup>[14]</sup> resulting in the intensity of the peak related to the Si-OH evidently enhance. All the above observations show that the surface of FS is apt to transpire a hydrolysis reaction under CMP circumstances reckless of the abrasive particles. The possible mechanism of CMP on FS using ceria and silica is depicted in Figure 6.

To quantitatively analyze Si(OH)<sub>4</sub> groups on the polished fused silica, we reckon the amount of the -OH groups per unit area ( $N_{OH}/\text{nm}^2$ ) in virtue of the thermogravimetric weight loss according to the method proposed by Mueller.<sup>[23]</sup>

$$N_{OH}/\text{nm}^2 = \frac{2 \times (W_{T1} - W_{T2}) \times Na}{SSA \times M_{H2O}}$$

Here,  $W_{Ti}$  is the weight of polished FS at the temperature  $T_i$ ,  $M_{H2O}$  is the molecular weight of water, and  $Na$  is the Avogadro's constant.

Figure 7 shows the TG results of fused silica polished with SiO<sub>2</sub> and CeO<sub>2</sub> nano-abrasive particles between 100°C and 600°C under an N<sub>2</sub> atmosphere. The weight loss from 100°C to 120°C is attributed to the removal of the physically adsorbed H<sub>2</sub>O. A condensation reaction of -OH groups on the polished FS surface happens in the temperature range from 120°C to 500°C. The -OH density on the polished FS surface is counted according to the TG weight loss results and Eq (1). It's estimated the FS polished with ceria and silica have values of 0.241 and 0.110 OH/nm<sup>2</sup>, respectively, indicating a relatively higher amount of Si(OH)<sub>4</sub> groups on the FS surface polished with CeO<sub>2</sub>, which support the results discussed above.

Regarding the ultimate structure of SiO<sub>2</sub> when removed through the CMP process, various mechanisms were proposed. In the light of the one put forward by Cook and Kelsall, cerium hydroxide groups (Ce<sub>2</sub>O<sub>3</sub>) in the form of =Ce-OH produced on the surface of ceria in a humid media, react with surface sites Si-OH, generating Ce-O-Si bonds and subsequently releasing silanol into the slurry, and removing SiO<sub>2</sub> in the form of Si(OH)<sub>4</sub> other than in the form of Si-O-Ce.<sup>[14,24]</sup> But here we get different results founded on the FTIR analysis. It is Si-OH other than the structure of Si-O-Ce that remains on the polished FS surface. Or more likely, both Si-OH and Si-O-Ce generate on the surface of FS during the CMP process using a ceria-based slurry, and the latter form would be removed by the mechanical friction. To verify this consequence, we employed XPS to characterize the chemical state of CeO<sub>2</sub> abrasives and chemical bonding information between FS and abrasives. Figure 8 indicates the XPS spectra obtained on ceria abrasives after polishing FS.

Distribution of the XPS peaks indicates the presence of ceria in mixed oxidation states (Ce<sup>3+</sup> and Ce<sup>4+</sup>). The Ce 3d XPS spectrum shows three peaks at the binding energy of 887.5, 897.9 and 898.3 eV, which relate to ceria in the 4+ oxidation state.<sup>[25,26]</sup> The feature observed at 880.4 eV can be associated to Ce<sup>3+</sup>,<sup>[25]</sup> showing the presence of oxygen vacancy center in



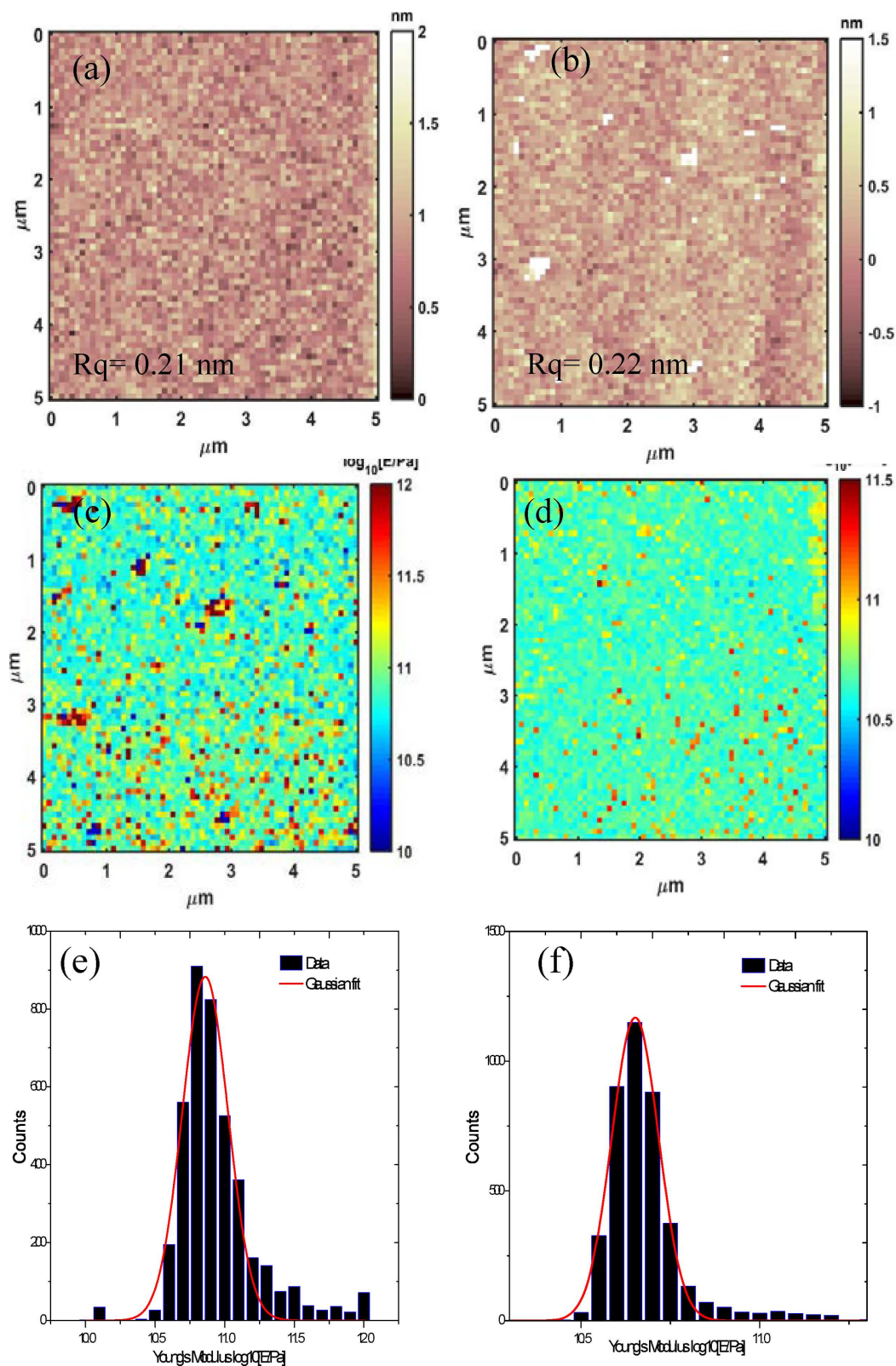


Figure 3. AFM images of FS with residual chemical products on surface.

the  $\text{CeO}_2$ . Sabia proposed that the  $\text{Ce}^{3+}$  species on the surface of  $\text{CeO}_2$  abrasives facilitate the reaction between silicon dioxide

and ceria abrasives during the CMP process.<sup>[27]</sup> Seo et al reported that the  $\text{Ce}^{3+}$  ions on the particle surface catalyze  $\text{H}_2\text{O}$

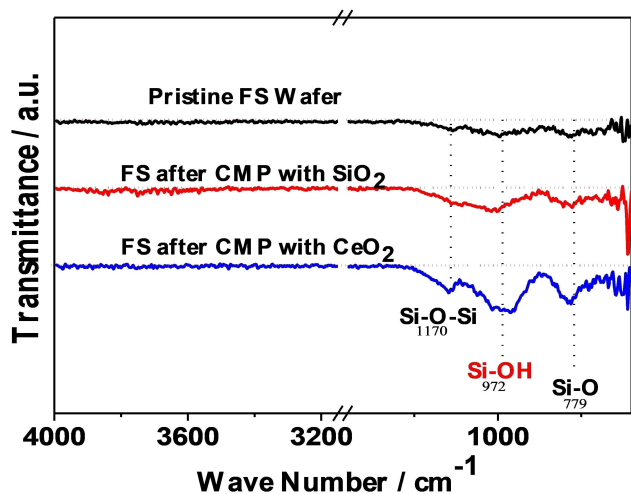


Figure 4. FT-IR spectra of the FS polished with CeO<sub>2</sub> and SiO<sub>2</sub> nano-abrasives.

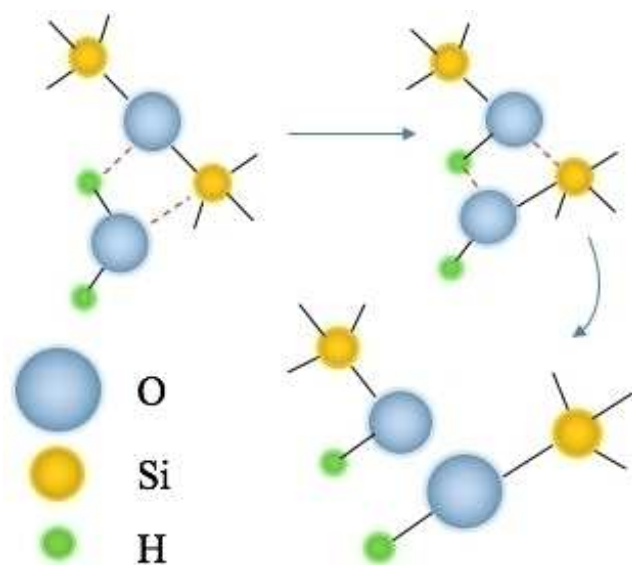


Figure 5. Diagram of the hydration process of the Si(OH)<sub>4</sub> and H<sub>2</sub>O.

dissociation to form –OH groups,<sup>[28]</sup> which play an influential role in numerous interactions at the solid/aqueous interface, including generating Ce–O–Si bonds with silicate ions.<sup>[14,29]</sup>

We additionally investigated the chemical bonding characteristics of FS and ceria abrasives. Figure 9 shows the O 1s spectra for polished FS with silica and ceria. The features observed at 532.5 eV is designated to oxygen atoms in the fused silica. Compared to the FS polished with silica, a shoulder peak at 528.8–529 eV ascribes to lattice O<sup>2-</sup> in Si–O–Ce.

#### 4. Conclusions

By using AFM, FTIR, TG, and XPS, a hydrolyzed layer has been confirmed on both FS surfaces polished with ceria and silica abrasives after lowering the role of the mechanical friction. The Si–O–Si bond on the FS surfaces is apt to react with water firstly

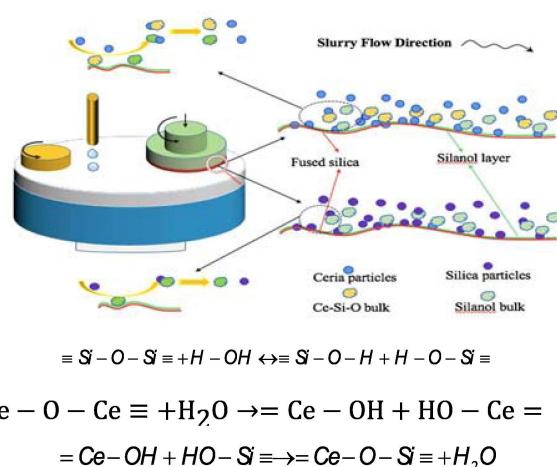


Figure 6. The possible mechanism of CMP on FS using CeO<sub>2</sub> and SiO<sub>2</sub> abrasives.

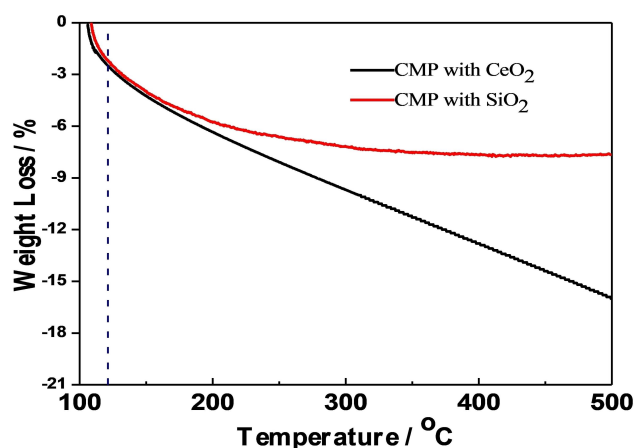


Figure 7. TG graphs of polished FS scanned at a heating rate of 10°C/min under an N<sub>2</sub> environment.

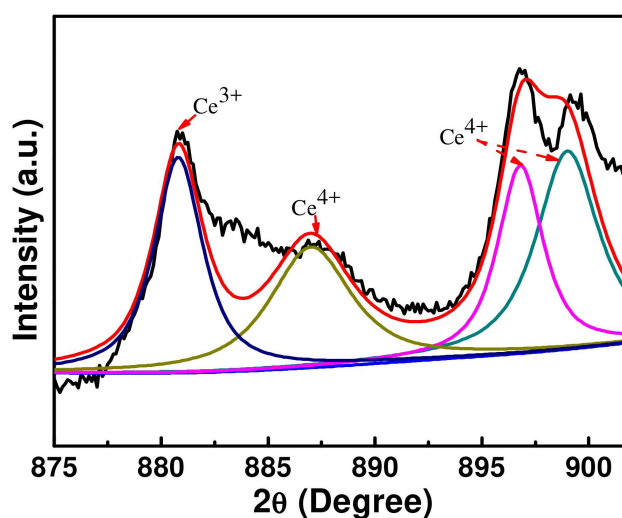


Figure 8. Ce 3d XPS spectra of polished FS by ceria abrasives.

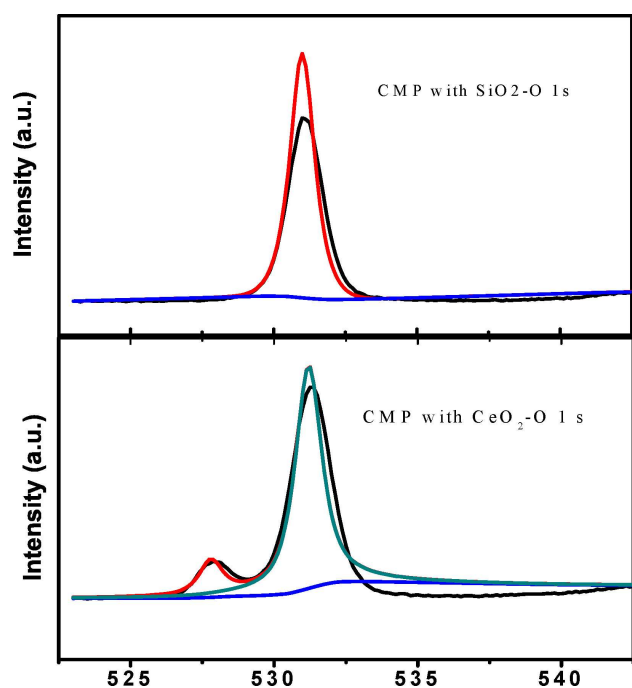


Figure 9. Comparison of O 1s XPS spectra of polished FS (a) with Silica, (b) with Ceria abrasives.

forming a silanol layer under CMP conditions, then removed by both abrasives. It is noteworthy that the silanol layer on the FS surface polished with ceria further react with hydroxylated ceria groups in slurry forming Si–O–Ce, releasing Si(OH)<sub>4</sub> into a slurry, and part of which removed by mechanical function. Ce<sup>3+</sup> stabilized by oxygen vacancy center on the ceria abrasives surface plays an essential role in speeding up the interface chemical reaction between FS and ceria abrasives. Furthermore, smoothing fused silica via CMP with silica abrasives is an alternative process.

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## Conflict of Interest

The authors declare no conflict of interest.

Keywords: Fused silica · Chemical Mechanical Polishing · Chemical Products · Material Removal Mechanism

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