REAXFF MOLECULAR DYNAMICS SIMULATION OF MATERIAL REMOVAL MECHANISMS DURING CMP PROCESS OF SILICA GLASS IN AQUEOUS H2O2

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ABSTRACT

Molecular dynamics simulations using Reactive Force Field (ReaxFF) are employed to study the silica glass chemical mechanical polishing (CMP) process in aqueous H2O2. The material removal mechanisms in CMP process are studied by analyzing the tribochemical process of silica glass. Results shows that the surface of silica glass is hydroxylated after the reaction with H2O2 solution. Through dehydrogenation and dehydroxylation, the Si-O-Si bridge bonds are formed between abrasive layer and silica glass surface. The chemical bonds between surface atoms and substrate atoms are broken due to the stretch of bridge bonds. The relationship between the sliding speed and the removal of atoms is also studied.

Keywords—silica glass; chemical mechanical polishing; ReaxFF; removal mechanism; speed.

INTRODUCTION

Chemical-mechanical polishing (CMP) is the only technology that can achieve global planarization of brittle-hard material at present [1], as one of important optical material, study on the material removal mechanism and surface quality in CMP process is of great significance. The material removal process occurs at micro scale in CMP process. With the development of various high precision microscopic experimental and measuring equipment (AFM, TEM), the material removal process of CMP has been studied. Katsuki et al. [2,3] studied the atomic-scale removal mechanism during Si tip scratching on Si and SiO2 surfaces in aqueous KOH, the results show that the Si-O-Si bridge bonds are formed at the interface in the slipping of Si tip and the hydrolysis leads to the removal of silicon atoms.

With the continuous development of computer technology, computer simulation technology has been one of the main ways to study the process of material processing. At present, simulation technologies such as TBQCMD and ReaxFF [1,4] has been developed and applied to MD simulations. Kubo et al [1] simulated the SiO2 CMP process with CeO2 polishing particles by TBQCMD, showing that mechanical forces introduced by CeO2 accelerated the chemical reaction. J Wen [4] studied the tribochemical wear mechanism of silicon at the Si/SiO2 interface by ReaxFF, showing the removal mechanism in atomic scale. Considering the mechanical and chemical actions, the ReaxFF method is applied to study the removal mechanism of silica glass in CMP process in this paper.

SIMULATION METHOD

ReaxFF use the bond order and polarizable charge to describe the interactions between atoms, allowing the formation and broken of bonds [5]. It divides the energy of the system into 14 parts, including bond energy, bond angle energy, van der Waals forces energy, Coulomb interaction energy and some correction terms. The basic assumption of ReaxFF is that the bond order $BO_{ij}^{'}$ is related to the distance between atoms and it can be described as follows:

$$BO_{ij}^{'} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} = \exp\left[P_{bo1}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{P_{bo2}}\right] + \exp\left[P_{bo3}\left(\frac{r_{ij}}{r_0^{\pi}}\right)^{P_{bo4}}\right] + \exp\left[P_{bo5}\left(\frac{r_{ij}}{r_0^{\sigma}}\right)^{P_{bo6}}\right] \quad (1)$$

Where σ, π and double π represent the contribution of single bond, double bond and triple bond and P_{bo1} to P_{bo6} are the parameters determined by different bond types respectively. r_0^{σ} , r_o^{π} and $r_0^{\pi\pi}$ are the optimized lengths of the σ bond, π bond and ππ bond respectively.

To simulate the CMP process of silica glass in aqueous H2O2, a model system was established with three parts: the silica glass substrate, the abrasive layer and the aqueous H2O2, as shown in Figure 1.

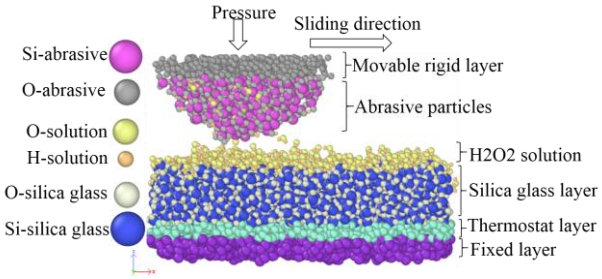


Figure 1: 3D graph of the silica glass CMP process simulation in aqueous H2O2.

During the whole simulation process, three steps are

carried out to imitate the simple CMP process: (1) reaction between the silica glass surface, aqueous H2O2 and abrasive layer for 60 picoseconds (ps); (2) vertical movement of the abrasive layer towards the substrate surface, compressing the molecules at the interface until reaching to the target pressure; (3) application of a normal pressure uniformly to the movable rigid layer along Z-axis direction and push the abrasive particle sliding on the substrate surface. The specific simulation parameters are shown in Table I.

TABLE I Specific parameters of the CMP simulations

The number of total atoms	8279
Size of the model	70×70×45Å^3
Number of H2O/H2O2	800, 50
Ensemble	NVT
Temperature (K)	300
Time step (fs)	0.25
Sliding speed (m/s)	10, 50, 100
Pressure (Gpa)	6

RESULTS AND ANALYSIS

Effect of H2O2 on the surface chemical state

After reaction between silica glass surface and aqueous H2O2, O and Si atoms on the surface of silica glass combined with H atoms and OH groups, forming hydroxyl structures (Si-OH). The break of Si-O bonds and the generation of Si-OH bonds have important significance for the CMP process of silica glass. Comparing to Si-OH bond, the energy of Si-O bond is larger, so the energy needed to break the Si-O bond during CMP process is larger. In macroscopic view, the generation of Si-OH bonds reduce the hardness of the workpiece surface and improve the processing performances.

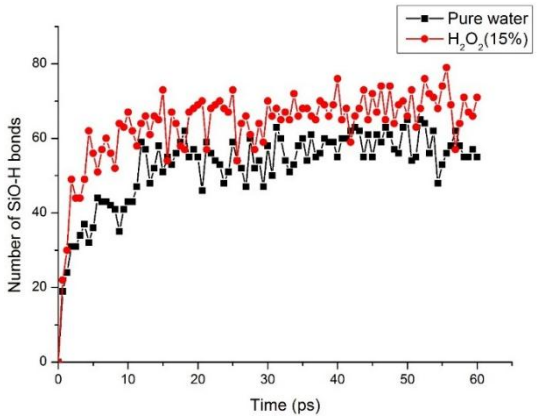
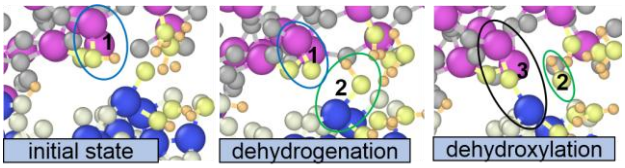


Figure 2: The number of hydroxyl group on the surface

To study the effect of the H2O2 solution on the surface chemical state of silica glass, the number of Si-OH structures formed during the reaction was counted and compared with the reaction between silica glass and pure water. As shown in Figure 2, since there are many free H atoms in H2O2 solution and they can combine with O atoms on the surface rapidly to form the Si-OH structures, the speed and of hydroxylation is faster than pure water and more Si-OH structures are formed. After fully reaction with water and H2O2, about 65 hydroxyl groups were formed in H2O2 solution while 55 hydroxyl groups were formed in pure water.

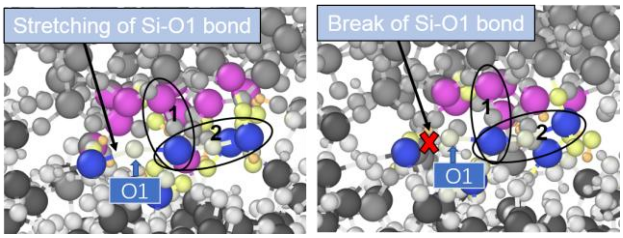
Coupling actions of chemical and mechanical

The removal of surface materials of silica glass is the result of the coupling effects of chemical and mechanical in CMP process, the mechanical force transmitted by interface Si-O-Si bridge bonds is the key of the break of the chemical bonds between surface atoms and substrate atoms. Fig. 3 shows the formation mechanism of interface bridge bond during the sliding. Process 1 in fig. 3 (a) and (b) is the dehydrogenation reaction and process 2 in (b) and (c) is the dehydroxylation reaction. The interface bridge bond 3 is formed after the two reaction above.

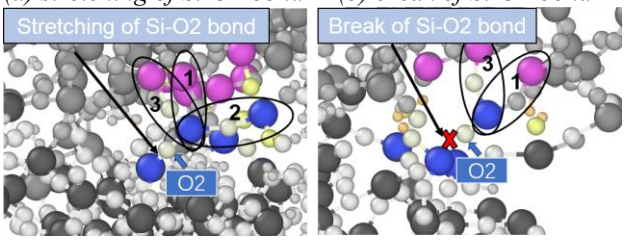


(a) (b) (c)

Figure 3: Formation mechanism of interface bridge bond



(a) stretching of Si-O1 bond (b) break of Si-O1 bond



(a) stretching of Si-O2 bond (b) break of Si-O2 bond

Figure 4: The coupling actions of chemical and mechanical

Fig. 4 shows the coupling actions of chemical and mechanical in the CMP process. As shown in Fig. 4(a), there are two bridge bonds in the interface. Bridge bond 1 was formed by dehydrogenation reaction and then re-bonding to the silicon atom on the silica glass surface. Bridge bond 2 was formed by the removed atoms. Under

the synergistic action of bridge bond 1 and bridge bond 2, the Si-O1 chemical bond in the substrate is stretched. As shown in Fig. 4(b), the Si-O1 chemical bond is broken. The O1 atom then re-bonded with the silicon atom in the abrasive particle to form a new bridge bond 3, as shown in Fig. 4(c). Those three bridge bonds move along with the abrasive particle, stretching the last chemical bond Si-O2 between the surface atom and the substrate. During this process, the bridge bond 2 is broken, but under the action of bridge bond 1 and bond 3, the last chemical bond Si-O2 is broken finally. Therefore, the removal of the silica glass surface atoms is a dynamic process, in which there are continuous formation or broken of interface bridge bonds. Under the synergistic actions of multiple bridge bonds, the atoms on the surface can be removed.

Effect of the sliding speed

Many polishing experiments [6] have proved that the material removal rate can be improved by increasing polishing speed. To investigate the effect of the polishing speed on the silica glass CMP process, the sliding speed of the abrasive layer is changed (10 m/s, 50 m/s, 100 m/s). The pressure on the interface is 6 Gpa and the other parameters remain unchanged. As shown in Fig. 5, with the increase of the sliding speed, the number of removed atoms decreases.

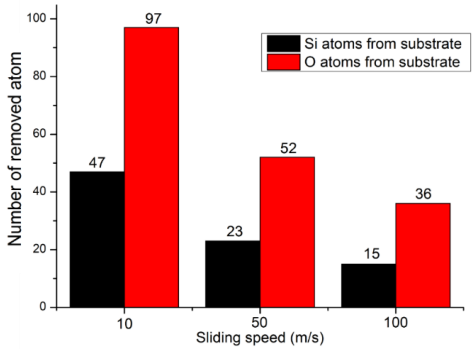


Figure 5: The number of removed atoms under different sliding speeds

From the previous analysis, we know that the number of removed atoms on the silica glass surface is related to the interface bridge bond. Figure 6 shows the relationship between the number of bridge bonds and the sliding distance at different speeds. With the increase of sliding speed, the number of bridge bonds decreases due to the decrease of contact time, which finally leads to the decrease of removed atoms. However, the material removal rate is determined by the removal amount per unit time (ps), so under the sliding speed of 10 m/s, 50 m/s and 100 m/s, the material removal rate are 0.059, 0.143, 0.188 respectively. With the increase of speed, the material removal rate increases corresponding, which is in good agreement with experiments results.

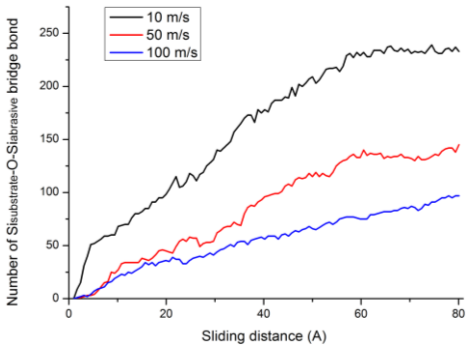


Figure 6: The number of bridge bonds formed under different sliding speeds

CONCLUSIONS

(1) After fully reacted with the H2O2 solution, the silica glass surface will be hydroxylated. Compared with pure water, the hydroxylation degree is higher and the hydroxylation speed is faster when reacted with aqueous H2O2.

(2) The interface bridge bonds are formed through dehydrogenation and dehydroxylation reactions during the sliding process. Under the synergistic actions of chemical and mechanical transmitted by bridge bonds, the surface atoms are removed.

(3) Sliding speed affects the material removal by affecting the number of bridge bonds. With the increase of speed, the number of removed atoms decrease, but the material removal rate increases.

ACKNOWLEDGEMENTS

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ReaxFF molecular dynamics simulation of material removal mechanisms during CMP process of silica glass in aqueous H2O2

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Introduction

As one of important optical materials, study on the material removal mechanism and surface quality of silica glass in CMP process is of great significance. Molecular dynamics simulation using Reactive Force Field (ReaxFF) are employed to study the silica glass chemical mechanical polishing (CMP) process in aqueous H2O2. The material removal mechanisms in CMP process are studied by analyzing the tribochemical process of silica glass. Results shows that the surface of silica glass is hydroxylated after the reaction with H2O2 solution. Through dehydrogenation and dehydroxylation, the Si-O-Si bridge bonds are formed between abrasive layer and silica glass surface. The chemical bonds between surface atoms and substrate atoms are broken due to the stretch of bridge bonds. The relationship between the sliding speed and the removal of atoms is also studied.

Methods

▪ Modelling and simulation steps

To simulate the CMP process of silica glass in aqueous H2O2, a model system was established with three parts: the silica glass substrate, the abrasive particle and the aqueous H2O2. Three steps are carried out to imitate the simple CMP process: (1)Reaction between the silica glass surface, H2O2 solution and abrasive particle for 120ps. (2)Vertical movement of the abrasive layer towards the substrate, compressing the H2O2 solution at the interface until the normal force has reached the target normal pressure. (3)Push the abrasive particle sliding along the X-axis direction at the speed of 50m/s until the abrasive particle leave the surface.

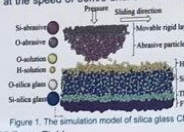

Figure 1. The simulation model of silica glass CMP process

▪ ReaxFF Force Field

The basic assumption of ReaxFF is that the bond order BOij' is related to the distance between atoms and it can be described as follows:

$$BO'_{ij} = BO^{\sigma}_{ij} + BO^{\pi}_{ij} + BO^{\pi\pi}_{ij}$$

$$= \exp[P_{bo1}(\frac{r_{ij}}{r_0^{\sigma}})^{P_{bo2}}] + \exp[P_{bo3}(\frac{r_{ij}}{r_0^{\pi}})^{P_{bo4}}] + \exp[P_{bo5}(\frac{r_{ij}}{r_0^{\pi\pi}})^{P_{bo6}}]$$

Results

▪ Coupling actions of chemical and mechanical

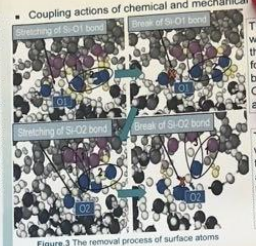

Figure.3 The removal process of surface atoms

The Si-O2 bond was stretching by the bridge bond 1, 2 and 3 and finally broken under the stretch if bridge bond 1 and 3.

The removal of the silica glass is a dynamic process, in which there are continuous formation or broken of interface bridge bonds. Under the synergistic actions of multiple bridge bonds, the atoms on the surface can be removed.

▪ Effect of the sliding speed

To investigate the effect of the polishing speed on the silica glass CMP process, the sliding speed of the abrasive layer is changed (10 m/s, 50 m/s, 100 m/s). As shown in Fig.4, with the increase of sliding speed, the number of removed atoms decreases. The number of the removed atoms is related to the interface bridge bonds. As shown in Fig.5, with the increase of sliding speed, the number of bridge bonds decreases due to the decrease of contact time, which finally leads to the decrease of removed atoms.

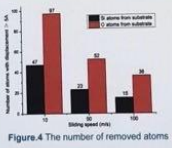

Figure.4 The number of removed atoms

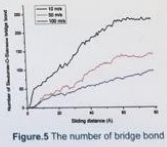

Figure.5 The number of bridge bond

The material removal rate is determined by the removal amount per unit time (ps), so under the sliding speed of 10 m/s, 50 m/s and 100 m/s, the material removal rate are 0.059, 0.143, 0.188 respectively. With the increase of speed, the material removal rate increases corresponding, which is in good agreement with experiments results.

Results

▪ Formation mechanism of interface bridge bonds

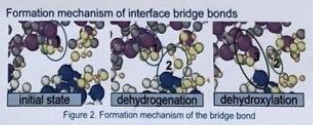

Figure 2. Formation mechanism of the bridge bond

The mechanical force transmitted by Si-O-Si bridge bonds is the key to the break of the chemical bonds between surface atoms and substrate atoms. As shown in Fig.2, through the dehydrogenation and dehydroxylation reactions, the interface bridge bond is formed

Conclusion

(1) After fully reacted with the H2O2 solution, the silica glass surface will be hydroxylated. Compared with pure water, the hydroxylation degree is higher and the hydroxylation speed is faster when reacted with aqueous H2O2.

(2) The interface bridge bonds are formed through dehydrogenation and dehydroxylation reactions during the sliding process. Under the synergistic actions of chemical and mechanical transmitted by bridge bonds, the surface atoms are removed.

(3) Sliding speed affects the material removal by affecting the number of bridge bonds. With the increase of speed, the number of removed atoms decrease, but the material removal rate increases.

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CHEMICAL MECHANICAL MATERIAL REMOVAL OF