Atomistic mechanisms of Si chemical mechanical polishing in aqueous
H₂O₂: ReaxFF reactive molecular dynamics simulations

Jialin Wen¹, Tianbao Ma¹, Weiwei Zhang², Adri C.T. van Duin², Xinchun
Lu^{1*}

¹State Key Laboratory of Tribology, Tsinghua University, Beijing 100084,
China

²Department of Mechanical and Nuclear Engineering, Pennsylvania State
University, University Park, Pennsylvania 16802, United States

Corresponding Author

*Phone: +861062797362. E-mail: xclu@tsinghua.edu.cn.

Abstract

ReaxFF reactive molecular dynamics simulations are employed to study the process of the silica abrasive particle sliding on the Si (100) substrate in the aqueous H_2O_2 in order to clarify the atomistic mechanisms of the Si chemical mechanical polishing (CMP) process. Our results reveal that the mechanical sliding effects induced chemical reactions at the abrasive particle and Si substrate interface dominate the CMP process and lead to the removal of Si atoms. Before the abrasive particle and Si substrate surface interact mechanically, aqueous H_2O_2 can make the Si substrate more oxidized. Once they contact with each other, they are connected by the interfacial Si-O-Si bridge bonds due to the chemical reactions at the interface. Under the mechanical sliding effects, the Si-Si and Si-O bonds on the Si substrate can be mechanically strained to be broken, leading to the removal of Si atoms from the Si substrate. Compared with the CMP process in pure H_2O , the CMP process in the aqueous H_2O_2 leads to more oxidized substrate and the removal of more Si atoms, demonstrating the significant role of H_2O_2 as an oxidizer. Besides, the friction force is higher than that in the pure H_2O case due to the stronger interfacial covalent bonds formation and breaking. Our results may shed light on the removal mechanism of Si atoms in the CMP process at the atomic level and provide an effective method to help design the components of the CMP slurry.

Keywords

Silicon, Chemical mechanical polishing, H_2O_2 , ReaxFF, Molecular dynamics simulation

1. Introduction

Si chemical mechanical polishing (CMP) process is of significant importance for the semiconductor industry because it is an essential and effective method to produce a defect free and flat enough surface for further manufacturing process of microelectronic devices including the semiconductor chips. During the Si CMP process, both mechanical effects and chemical reactions are involved as a result of comprehensive interactions between silicon wafer, abrasive particles, pad and slurry. Mechanical effects can be accelerated by chemical effects, and the latter can be induced by mechanical friction effects [1]. There are various abrasive particles, such as Si_3N_4 [1], SiO_2 [2–6], Al_2O_3 [7–9], CeO_2 [9–11] and others [10]. These particles can interact with the wafer surface through repeated indentation, impact, rolling as well as sliding effects, in which the sliding effect plays the most important role in Si material removal process. The widely used slurry contains hydrogen peroxide (H_2O_2), which is contamination free as well as of high oxidizing ability, acts as the silicon oxidizer during the process and can speed the removal

process of Si material. Besides, aqueous H_2O_2 can also be used to clean the Si surface [12]. With the development of the semiconductor industry, CMP needs to overcome the increased wafer size, the need to achieve the sub-nano level roughness as well as avoid the surface damages, which have almost reached the limit for surface manufacturing. Therefore, understanding the CMP mechanism is very important in the development of semiconductor industry.

Si CMP mechanisms have been widely investigated using the CMP experimental methods [2–9,13–15], AFM experiments [16–19] as well as molecular simulation methods [20–26]. During the CMP process, pressure and velocity parameters are the two most important mechanical parameters that dominate the Si CMP process. The most widely used relationship between the material removal rate (MRR) and these two parameters is the Preston equation, which shows that the removal rate of surface material is proportional to the contact pressure and relative sliding speed between material surfaces and the polishing pad. According to the experiments, both higher pressure and higher velocity can lead to higher Si MRR [4,7]. In addition, the chemical effects of H_2O_2 have also been extensively investigated [5,6,9,10]. H_2O_2 plays a very important role during the Si CMP process, the concentration of H_2O_2 can affect the Si micro surface roughness as well as its contact angle [5], thus determining the material removal process of Si [27] and leading to the difference of Si

MRR [9]. Besides, H_2O_2 can also affect the properties of the abrasive particles [10], which directly interact with the Si surface and influence the surface quality.

In order to further understand the Si CMP mechanism, we should not only focus on the macroscale, but also on the microscale and atomic level. Based on the infrared spectroscopy of Si surfaces after the CMP process, it has been proposed that the Si removal mechanism at the atomic level is a result of interplay of surface oxidation by slurry oxidizers and passivation by hydrogen [13–15]. Besides, the AFM experiments are used to study the wear behavior between Si and SiO_2 in the aqueous environment, so as to clarify the mechanisms during the Si CMP process in which the silica abrasive particle is used in the polishing slurry [16–18,28–31]. The AFM experiment results indicate that the removal of Si material at the atomic level involves the formation of the Si-O-Si bridge bonds at the Si and SiO_2 interface, and the oxidation of the Si-Si bonds at the Si surface as well as the breaking or dissociation of these bonds under the mechanical sliding effects and water chemical effects.

Although these CMP experiments at the macroscale can determine the process parameters that affect the CMP processes, they cannot clearly illustrate the CMP mechanisms because they are unable to obtain the details of chemical reactions and mechanical effects in this process. Even though experimental inspection of Si surface morphologies and AFM

experiments may provide atomic details for the Si CMP process, they cannot provide the dynamic process of CMP, thus unable to fully illustrate the mechanisms in this process. In order to reveal the chemical reactions and mechanical effects in this dynamic process, molecular simulation may be effective. Classical molecular dynamics (MD) simulations based on empirical force fields have been used to investigate the Si CMP process to illustrate the mechanical sliding [20,21,25], impact[22–24] and rolling[26] effects of abrasive particles on the Si atoms removal process. However, they only considered the mechanical effects during the CMP process, and cannot simulate the chemical reactions which are not negligible for this process. Therefore, methods that can simulate both chemical reactions and mechanical effects at the same time need to be employed in order to study the Si CMP process. In principle, *ab initio* methods based on quantum mechanics (QM), can be used to simulate the chemical reactions with satisfying accuracy. However, the high computational cost restricts their use to short-time and small-system simulations, making it impractical to simulate the dynamic evolution of a system such as the wear process under a contact load [32]. It is remarkable that recently methods that can simulate both the chemical reactions and mechanical effects have been developed. The tight-binding quantum chemical MD (TB-QCMD) has been successfully applied to study the CMP processes of Si [33], Cu [34,35], SiO₂ [36] and GaN [37].

Besides, MD methods based on the reactive force fields, such as the reactive empirical bond order (REBO) method [38] and the reactive force field (ReaxFF) method [39] are also promising for simulating chemical reactions and mechanical effects in the CMP process.

In this work, we use ReaxFF reactive force field MD simulations to study the sliding process of a silica abrasive particle on the Si (100) substrate in the aqueous H_2O_2 so as to illustrate the Si CMP mechanisms. The next section describes the computational details including the simulation model details and computational setup. The subsequent section describes the MD simulation results and finally we give the conclusions.

2. Computational methods

2.1. Model construction

In order to simulate the Si CMP process in aqueous H_2O_2 environment, a model system was constructed with three parts: The Si (100) substrate, the aqueous H_2O_2 and a silica particle. The model was prepared as follows: (1) The Si (100) substrate that contains 2352 Si atoms, was prepared using the NVT simulation, where the temperature was set to 300 K and controlled using the Berendsen heat bath [40] with a damping constant of 25 fs until a minimum potential energy had been achieved via the rearrangement of the surface atoms. Then 964 H_2O molecules were

used to interact with the Si (100) substrate surface using the NVT simulation under 300 K, as is similar to our previous work [41]. With these two steps, the initial Si (100) substrate surface which contains 2352 Si, 266 O and 319 H was generated. (2) The aqueous H₂O₂ (0.5 nm thick) contains 400 H₂O and 40 H₂O₂ molecules was equilibrated with the NVT simulation. (3) The silica particle with the radius of 20 Å, was cleaved from the amorphous silica structure which was produced from a melting quench process of a bulk α -quartz silica crystal similar to the previous work [42]. Then the surface of the silica particle was annealed to remove the edge effects by using the NVT simulation in which the particle was raised to 2000 K (below the silica melting temperature) and then lowered to 300K so as to reach the minimum potential energy via the rearrangement of the surface atoms, as is similar to the process used by Russo et al. [43] In order to lower the computational cost, a semi-spherical silica particle was cleaved from the sphere particle, which was then terminated by hydroxyl as processed in the work performed by Kawaguchi et al. [35] The semi-spherical silica particle contains 351 Si, 777 O and 145 H atoms.

After the above procedure, the Si (100) substrate, aqueous H₂O₂ and semi-spherical silica particle were combined along the z axis to generate the final simulation model, resulting in total system dimensions of 53.76 $\times$ 53.76 $\times$ 70.00 Å³. Figure 1 illustrates the detailed model, which

contains 7 layers: (1) rigid layer of the bottom Si substrate atoms which is constrained to be stationary in the entire simulations, (2) thermostat layer of Si substrate and (3) thermostat layer of silica particle, which are used to control the system temperature to be constant, (4) free Si substrate layer and (5) free silica particle layer with atoms allowed to move dynamically in the simulations, (6) aqueous H_2O_2 at the interface between Si substrate and silica particle surfaces, (7) rigid layer of the amorphous silica, which is laterally movable.

Figure 1. Schematic of the model for ReaxFF reactive MD simulations of Si CMP in the aqueous H_2O_2 .

2.2. Simulation setup

Based on the relationships between bond order and bond distance as well as between bond energy and bond order, ReaxFF reactive force field [39,44] can lead to the proper formation and dissociation of bonds, and is therefore able to simulate reactive systems containing a large number of atoms, which cannot be achieved using classical MD methods. Since the parameters of the force field are derived from quantum chemical calculations on bond dissociation, MD simulations based on the reactive force field can deal with a relatively larger chemical reaction system with a longer time scale, at the same time, ensure the accuracy of chemical reaction. The detailed description of the ReaxFF method is given by Chenoweth et al.[44] ReaxFF has already been successfully applied to study various processes, such as metal / metal oxide interaction with water [42,45,46], friction processes [47–49]. Besides, this method can be easily extended to any systems containing any compounds.

The ReaxFF force field used in the present MD simulations is developed based on the combination of the Si/Ge/H force field [50] with the water force field [51], and has been successfully used in our previous study [41]. All simulations were performed by LAMMPS code [52,53], using the NVE ensemble with a time step of 0.25 fs. Periodic boundary conditions were applied in both x and y directions. Before the sliding wear process, the system was relaxed at 1 K for 100 ps, and then the temperature was slowly increased to 300K at the rate of 10 K/ps. Six

steps were carried out to imitate the sliding wear process during the whole CMP process: (1) Reaction between the silicon substrate and aqueous H_2O_2 for 100 ps. (2) vertical movement of the silica particle towards the silicon substrate surface, compressing the water molecules at the interface until the target normal force has reached the normal load to be applied to the silica, (3) application of a normal load uniformly to the top rigid layer of silica along the z-axis direction, (4) equilibration of the compressed system for 100 ps, (5) sliding of silica laterally along the x-axis direction at the constant speed of 10 m/s for the distance of 50 Å along the substrate surface, and (6) interface separation by moving the silica particle away from the Si surface at a speed of 10 m/s for 300 ps. The temperature was controlled to be 300 K using Langevin thermostat with a damping constant of 100 fs during these processes. Ovito [54] was used to produce the snapshot pictures of all simulations.

3. Results and discussion

3.1. Reaction between Si substrate surface and pure water as well as aqueous H_2O_2 .

The initial Si substrate surface before the sliding process is presented in Figure 2. The surface is terminated by H_2O , OH and H, which is consistent with the experimental results [55–62]. The H termination can form two types of structures, the monohydride structure and the dihydride structure, as observed with high-resolution infrared spectroscopy [56].

Besides, the Si surface can also be oxidized and form Si-O-Si bonds, as proved by both the experimental and theoretical studies [63–65]. In addition, there exist HSi-O-Si-H and HSi-SiH dimers on the Si substrate surface, which is in agreement with both the experimental and theoretical analysis using surface infrared adsorption spectroscopy and density functional theory (DFT) calculations [63].

Figure 2. Top view of initial Si substrate surface configuration.

In order to illustrate the role of H₂O₂ during the CMP process, we compared the Si CMP process in pure water with that in aqueous H₂O₂. In the pure water condition, the solution contains 482 H₂O molecules,

making the O atoms in both processes comparable. Before the sliding wear process, both H_2O and H_2O_2 can interact with the initial Si substrate surface and O atoms from these two kinds of molecules diffuse into the Si substrate. As demonstrated in Figure 3, under the pure water and aqueous H_2O_2 conditions, almost no O atoms from H_2O or H_2O_2 diffuse into the substrate at the temperature of 1 K. When temperature increase to 300K, both H_2O and H_2O_2 interact with the initial Si substrate surface and O atoms from these two species diffuse into the substrate. There are more O atoms on the substrate under the aqueous H_2O_2 condition, demonstrating that aqueous H_2O_2 can make the Si substrate surface more oxidized.

Figure 3. Number of O atoms on the Si substrate during the interaction with pure water and aqueous H_2O_2 , respectively, from the temperature of

1 K to 300 K.

3.2. Si atom removal process.

After the reaction process between the substrate and solution, the silica abrasive particle moves towards the Si substrate surface until the normal load reaches the target value of 1 GPa, and then slides along Si substrate. After the sliding and separation processes, some Si atoms which originally belong to the silicon substrate are removed from the Si substrate surface, as shown in Figure 4a. Besides, some Si atoms from the silica particle stay on the substrate surface, demonstrating the wear of the particle during the CMP process, which is consistent with the results of AFM experiments conducted by Katsuki et al. [16–18]. Only Si atoms in the system are shown in Figure 4b to clearly show the wear of Si atoms from both the substrate and the particle.

Figure 4. The CMP system after the sliding wear and separation processes in the aqueous H_2O_2 . (a) All atoms of the system are displayed. (b) Only Si atoms are shown for clarity, some Si atoms from the substrate are taken away by the silica particle, while some Si atoms from the silica particle remain on the substrate (Si atoms in the black solid circles).

In order to illustrate the Si atom removal mechanism, we tracked the removal process of the Si atoms on the substrate. As discussed previously, the Si atoms on the substrate surface connect to the substrate through the Si-Si bonds or the Si-O-Si bonds due to the oxidation effects of both H_2O and H_2O_2 before the sliding process. Figure 5 illustrates the removal of Si^1 atom from the Si substrate. Before the sliding wear process, the Si^1 atom belongs to the substrate and bonds to two Si atoms (Si^2 and Si^3) as well as two H atoms (Figure 5a). During the sliding process, the $\text{Si}^1\text{-O}^5\text{-Si}^4$ interfacial bridge bond is formed, as a result, the particle and substrate surfaces are connected with each other (Figure 5b). As the sliding process of the particle surface along the substrate surface continues, the $\text{Si}^2\text{-Si}^1$ bond (Figure 5c) and the $\text{Si}^3\text{-Si}^1$ bond (Figure 5d) are stretched to be broken, leading to the removal of Si^1 atom from its original site.

Figure 5. Breaking of Si-Si bonds that leads to the removal of the Si¹ atom during the sliding wear process. (a) Before the sliding wear process, Si¹ atom is bonded to two nearest Si atoms (Si² and Si³) and two H atoms. (b) Formation of the Si⁴-O⁵-Si¹ interfacial bridge bond. (c) Breaking of Si¹-Si² bond. (3) Breaking of Si¹-Si³ bond, which leads to the removal of Si¹ from its original site.

Apart from the breaking of Si-Si bond that leads to the removal of Si atoms, the breaking of Si-O bond can also lead to the removal of Si atoms

from the substrate. As shown in Figure 6, Si⁸ initially belongs to the substrate with the Si⁶-O⁷-Si⁸ bond (Figure 6a). During the sliding process, the Si⁸-O⁹-Si¹⁰ interfacial bridge bond is formed at the interface between particle and substrate (Figure 6b). With the stretch of Si⁶-O⁷-Si⁸ bond (Figure 6c), the Si⁶-O⁷ bond is broken, leading to the removal of Si⁸ atom from its original site (Figure 6d). During this process, we found that one H atom bonds to the O⁷ in the Si⁶-O⁷-Si⁸ bond, which has also been observed in our previous work [41] and has also been proved to assist the breaking of such Si-O-Si bonds from the DFT calculations [47].

Figure 6. Si-O bond breaking that leads to the removal of the Si⁸ atom during the sliding wear process. (a) Before the sliding wear process, Si⁸

atom belongs to the substrate through the $\text{Si}^6\text{-O}^7\text{-Si}^8$ bond. (b) Formation the $\text{Si}^8\text{-O}^9\text{-Si}^{10}$ interfacial bridge bond. (c) Stretch of the $\text{Si}^6\text{-O}^7\text{-Si}^8$ bond. (3) Breaking of $\text{Si}^6\text{-O}^7$ bond, which leads to the removal of Si8 from its original site.

During our simulation, it is found that the Si atoms of the silica particle can also be removed in the interaction process, demonstrating the wear of the silica particle (Figure 4b). Figure 7 shows the detail of the Si^A atom removal process from the silica particle. When the silica particle gets close to the substrate (Figure 7a), the interfacial $\text{Si}^A\text{-O}^B\text{-Si}^C$ bridge bond is formed at the interface (Figure 7b). As the particle slides on the substrate, this bridge bond is stretched (Figure 7c), inducing the breaking of the $\text{Si}^C\text{-O}^B$ bond (Figure 7d). With the sliding process goes on, the $\text{Si}^A\text{-O}^D\text{-Si}^E$ bond of the silica particle is stretched to be broken (Figure 7e), leading to the final removal of Si^A from the particle (Figure 7f).

Figure 7. Snapshots of the wear process of the Si^{A} atom from the silica particle. (a) Configuration of the substrate and particle interface. (b) Formation of the interfacial $\text{Si}^{\text{A}}\text{-O}^{\text{B}}\text{-Si}^{\text{C}}$ bridge bond. (c) Stretch of the $\text{Si}^{\text{A}}\text{-O}^{\text{B}}\text{-Si}^{\text{C}}$ bond during the sliding process. (d) Breaking of the interfacial $\text{Si}^{\text{A}}\text{-O}^{\text{B}}\text{-Si}^{\text{C}}$ bridge bond. (e) Stretch of the $\text{Si}^{\text{A}}\text{-O}^{\text{D}}\text{-Si}^{\text{E}}$ bond of the silica particle. (f) Breaking of the $\text{Si}^{\text{A}}\text{-O}^{\text{D}}\text{-Si}^{\text{E}}$ bond and finally Si^{A} is removed from the silica particle.

The substrate surface structure after the CMP process is important because it is usually used to evaluate the effects of the whole CMP process. Thus we are also interested in what happens on the Si substrate surface after the CMP process. In order to clearly illustrate the difference between the substrate surfaces before and after the CMP process, we

colored the Si atoms that are removed after the CMP process as green, and the Si atoms that are the nearest neighbor of these Si atoms before the CMP process as dark blue, as shown in Figure 8. By comparing the surfaces before (Figure 8a) and after (Figure 8b) the CMP process, we can see clearly that after the CMP process, some of the nearest neighbor Si atoms connect with each other directly, forming the Si-Si bond (shown in the red circles in Figure 8b), while some bonded to O to form the Si-O-Si bonds (shown in the green circles in Figure 8b) on the substrate. In addition, some of them connect to other Si atoms on the substrate to form the Si-Si bonds (yellow circles in Figure 8b) and Si-O-Si bonds (black circles in Figure 8b). Besides, the substrate surface after the CMP process is similar that of the initial substrate surface as shown in Figure 2.

Figure 8. Comparison of the substrate surfaces before (a) and after (b) the CMP process in the aqueous H_2O_2 . The green atoms are Si atoms that

are removed after the CMP process and the dark blue atoms are their nearest Si atoms.

3.3. Comparison of Si CMP process in pure H₂O and aqueous H₂O₂ conditions.

In order to compare the difference of Si removal process under these two conditions (aqueous H₂O₂ and pure H₂O), we adopt the same method as used in our previous work [41] to analyze the products after the simulation process for recognition of the removed Si atoms. As shown in Figure 9 for the initial Si substrate (only the Si atoms are shown), the green atoms are the original sites of the removed Si atoms after the CMP processes in aqueous H₂O₂ condition (Figure 9a) and pure H₂O condition (Figure 9b) under the same pressure of 1.0 GPa, respectively. It is obvious that more Si atoms are removed in the aqueous H₂O₂ (24 Si atoms removed) than the pure H₂O (only 10 Si atoms removed). Besides, we also found that the wear of silica particle under the aqueous H₂O₂ condition (9 Si atoms removed) is more severe than that under the pure H₂O condition (7 Si atoms removed).

Figure 9. Configuration of the substrate before the CMP process (only Si atoms are shown), the green atoms are removed after the CMP processes in aqueous H₂O₂ (a) and pure water (b) conditions.

To characterize the wear degree of the substrate during the wear process, we calculated the displacement of Si atoms as $d = \sqrt{(x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2}$, in which d is the displacement of an atom, (x_0, y_0, z_0) is its initial coordinate, (x, y, z) is its position during the CMP process. Since in the Si single crystal structure, the Si-Si bond has the length of around 3.0 Å in its single crystal structure, as also can be concluded from the RDF of Si-Si (Figure 10a). We thus use the criterion that $d > 3.0$ Å to characterize the wear degree of the substrate. As shown in Figure 10b, during the initial 120 ps, no Si atoms has the displacement larger than 3.0 Å, while the number of that kind of Si atoms keeps increasing after that, indicating the continuously worn of the substrate. Besides, in the same sliding period, more Si atoms have the displacement larger than 3.0 Å in the aqueous H₂O₂ condition than that in

the pure H₂O condition, and finally leads to the removal of more Si atoms from the substrate. The wear process of Si atoms from the substrate during the CMP in aqueous H₂O₂ and pure H₂O can be seen in the supplementary videos S1 and S2.

Figure 10. (a) Si-Si RDF in single crystal structure. (b) Number of Si atoms whose displacement is larger than 3.0 Å during the sliding wear process under the aqueous H₂O₂ and pure H₂O conditions, respectively.

Figure 11 shows the interfacial friction force and relative potential energy (RPE) of the system during the sliding wear process under the aqueous H₂O₂ and pure H₂O conditions, respectively. There is no significant difference of the friction force during the initial 150 ps, while after that period of time, the friction force under the aqueous H₂O₂ condition is higher than that under the pure H₂O condition. This corresponds to the variation of the number of Si atoms with the displacement larger than 3.0 Å as shown in Figure 10. From the results of

the work conducted by Yue et al. [48], it is known that the number of interfacial covalent bonds formed at the sliding interface governs the interfacial friction force, thus we expect that more covalent bonds are formed under the aqueous H_2O_2 condition. The fluctuation of the friction force corresponds to the formation and breaking of interfacial covalent bonds. For the RPE, it does not change too much during the first half sliding process and then gradually decrease. Similar to the friction force, the RPE also fluctuates due to the interfacial bonds formation and breaking, as well as thermal activation and relaxation of the intermediate species formed at the interface [49].

Figure 11. Friction force and relative potential energy of the system during the sliding wear process under the aqueous H_2O_2 and pure H_2O

conditions, respectively.

4. Conclusion

In this work, we employed ReaxFF molecular dynamics simulations to study the CMP process of Si (100) surface in the aqueous H_2O_2 with the SiO_2 abrasive particle. In the Si CMP process, the interfacial Si-O-Si bridge bonds are formed to connect the Si substrate and abrasive silica particle surfaces. During the sliding process, the mechanical sliding effect may cause the stretch of the interfacial bridge bonds and the breaking of the Si-Si and Si-O bonds on the Si substrate, which leads to the removal of Si atoms. This demonstrates the mechanically sliding process induced chemical reactions at the interface which is difficult to be captured experimentally. In addition, the Si-O bonds on the silica particle can also dissociate under the mechanically sliding effects, leading to the removal of Si atoms from the silica particle, demonstrating the wear of the silica particle.

From the comparison of the CMP processes under the pure H_2O and aqueous H_2O_2 conditions, we found that in the aqueous H_2O_2 condition, the substrate is more oxidized than that in the pure water condition, leading to the formation of more interfacial Si-O-Si bridge bonds at the interface. As a result, more Si atoms from the substrate as well as from the silica particle are removed from its original site. Besides, the

interfacial friction force is higher for the aqueous H_2O_2 condition, which leads to a higher shear force at the substrate and particle interface.

This study has successfully modeled the dynamic process of Si CMP, incorporating both chemical effects of aqueous H_2O_2 and mechanical sliding effects of the abrasive SiO_2 particle. Based on the present results, we have also clarified the slurry chemistry and mechanical induced chemical reactions which lead to the removal of Si materials at the CMP process at the atomic level. Therefore, this study may shed light on the design of the components of the polishing slurry, which is significant for the final Si surface quality.

Supporting information

S1 – Displacement of Si atoms on the substrate during the CMP process in aqueous H_2O_2 . Red colored atoms are the atoms with the displacement larger than 3.0 Å.

S2 – Displacement of Si atoms on the substrate during the CMP process in pure H_2O . Red colored atoms are the atoms with the displacement larger than 3.0 Å.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grants 91323302, 51375010, 51335005). Simulations were carried out on the “Explorer 100” cluster system of Tsinghua National

References

- [1] H. Liang, F. Kaufman, R. Sevilla, S. Anjur, 211 (1997) 271–279.
- [2] B. Mullany, G. Byrne, J. Mater. Process. Technol. 132 (2003) 28–34.
- [3] Y. Liu, K. Zhang, F. Wang, W. Di, Microelectron. Eng. 66 (2003) 438–444.
- [4] M. Forsberg, Microelectron. Eng. 77 (2005) 319–326.
- [5] H. Wang, Z. Song, W. Liu, H. Kong, Microelectron. Eng. 88 (2011) 1010–1015.
- [6] J. Li, Y. Liu, Y. Dai, D. Yue, X. Lu, J. Luo, Sci. China Technol. Sci. 56 (2013) 2847–2853.
- [7] I. Zarudi, B.S. Han, J. Mater. Process. Technol. 140 (2003) 641–645.
- [8] E. Estragnat, G. Tang, H. Liang, S. Jahanmir, P. Pei, J.M. Martin, J. Electron. Mater. 33 (2004) 334–339.
- [9] Y.G. Wang, L.C. Zhang, A. Biddut, Wear. 270 (2011) 312–316.
- [10] R. Manivannan, S. Ramanathan, Appl. Surf. Sci. 255 (2009) 3764–3768.
- [11] Z. Zhang, L. Yu, W. Liu, Z. Song, Appl. Surf. Sci. 256 (2010) 3856–3861.

- [12] R.C. Henderson, J. Electrochem. Soc. 119 (1972) 772–775.
- [13] G.J. Pietsch, G.S. Higashi, Y.J. Chabal, Appl. Phys. Lett. 64 (1994) 3115–3117.
- [14] G.J. Pietsch, Y.J. Chabal, G.S. Higashi, J. Appl. Phys. 78 (1995) 1650–1658.
- [15] G.J. Pietsch, Y.J. Chabal, G.S. Higashi, Surf. Sci. 331–333 (1995) 395–401.
- [16] F. Katsuki, K. Kamei, A. Saguchi, W. Takahashi, J. Watanabe, J. Electrochem. Soc. 147 (2000) 2328.
- [17] F. Katsuki, A. Saguchi, W. Takahashi, J. Watanabe, Jpn. J. Appl. Phys. 41 (2002) 4919–4923.
- [18] F. Katsuki, J. Mater. Res. 24 (2009) 173–178.
- [19] R. Imoto, F. Stevens, S.C. Langford, J.T. Dickinson, Appl. Phys. A. 94 (2009) 35–43.
- [20] X. Han, Appl. Surf. Sci. 253 (2007) 6211–6216.
- [21] X. Han, Y. Hu, S. Yu, Appl. Phys. A. 95 (2009) 899–905.
- [22] R. Chen, J. Luo, D. Guo, X. Lu, J. Appl. Phys. 104 (2008) 104907.
- [23] R. Chen, J. Luo, D. Guo, H. Lei, J. Appl. Phys. 108 (2010) 73521.
- [24] R. Chen, M. Liang, J. Luo, H. Lei, D. Guo, X. Hu, Appl. Surf. Sci. 258 (2011) 1756–1761.
- [25] L. Si, D. Guo, J. Luo, X. Lu, J. Appl. Phys. 107 (2010) 1–8.
- [26] L. Si, D. Guo, J. Luo, X. Lu, G. Xie, J. Appl. Phys. 109 (2011)

- 84335.
- [27] J. Yu, L. Qian, B. Yu, Z. Zhou, J. Appl. Phys. 108 (2010) 1–10.
- [28] J. Yu, S.H. Kim, B. Yu, L. Qian, Z. Zhou, ACS Appl. Mater. Interfaces. 4 (2012) 1585–1593.
- [29] J. Yu, L. Chen, L. Qian, D. Song, Y. Cai, Appl. Surf. Sci. 265 (2013) 192–200.
- [30] X. Wang, S.H. Kim, C. Chen, L. Chen, H. He, L. Qian, Appl. Mater. Interfaces. 7 (2015) 14785–14792.
- [31] L. Chen, H. He, X. Wang, S.H. Kim, L. Qian, Langmuir. 31 (2015) 149–156.
- [32] A.L. Barnette, D.B. Asay, D. Kim, B.D. Guyer, H. Lim, M.J. Janik, S.H. Kim, Langmuir. 25 (2009) 13052–13061.
- [33] T. Yokosuka, H. Kurokawa, S. Takami, M. Kubo, A. Miyamoto, A. Imamura, Jpn. J. Appl. Phys. 41 (2002) 2410–2413.
- [34] T. Yokosuka, K. Sasata, H. Kurokawa, S. Takami, M. Kubo, A. Imamura, A. Miyamoto, Jpn. J. Appl. Phys. 42 (2003) 1897–1902.
- [35] K. Kawaguchi, H. Ito, T. Kuwahara, Y. Higuchi, N. Ozawa, M. Kubo, ACS Appl. Mater. Interfaces. 8 (2016) 11830–11841.
- [36] A. Rajendran, Y. Takahashi, M. Koyama, M. Kubo, A. Miyamoto, Appl. Surf. Sci. 244 (2005) 34–38.
- [37] K. Kawaguchi, T. Aizawa, Y. Higuchi, N. Ozawa, M. Kubo, Int. Conf. Planarization/CMP Technol. (2014) 39–41.

- [38] D.W. Brenner, O. a Shenderova, J. a Harrison, S.J. Stuart, B. Ni, S.B. Sinnott, J. Phys. Condens. Matter. 14 (2002) 783–802.
- [39] A.C.T. Van Duin, S. Dasgupta, F. Lorant, W.A. Goddard, J. Phys. Chem. A. 105 (2001) 9396–9409.
- [40] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, Phys. 81 (1984) 3684–3690.
- [41] J. Wen, T. Ma, W. Zhang, G. Psifogiannakis, A.C.T. van Duin, L. Chen, L. Qian, Y. Hu, X. Lu, Appl. Surf. Sci. 390 (2016) 216–223.
- [42] J.C. Fogarty, H.M. Aktulga, A.Y. Grama, A.C.T. van Duin, S. A. Pandit, J. Chem. Phys. 132 (2010) 174704.
- [43] M.F. Russo, R. Li, M. Mench, A.C.T. van Duin, Int. J. Hydrogen Energy. 36 (2011) 5828–5835.
- [44] K. Chenoweth, A.C.T. van Duin, W. A. Goddard, J. Phys. Chem. A. 112 (2008) 1040–1053.
- [45] O. Assowe, O. Politano, V. Vignal, P. Arnoux, B. Diawara, O. Verners, A.C.T. van Duin, J. Phys. Chem. A. 116 (2012) 11796–805.
- [46] M. Raju, S.Y. Kim, A.C.T. Van Duin, K.A. Fichthorn, J. Phys. Chem. C. 117 (2013) 10558–10572.
- [47] D.C. Yue, T.B. Ma, Y.Z. Hu, J. Yeon, A.C.T. van Duin, H. Wang, J. Luo, J. Phys. Chem. C. 117 (2013) 25604–25614.
- [48] D.C. Yue, T.B. Ma, Y.Z. Hu, J. Yeon, A.C.T. van Duin, H. Wang, J.

- Luo, Langmuir. 31 (2015) 1429–1436.
- [49] J. Yeon, A.C.T. van Duin, S.H. Kim, Langmuir. 32 (2016) 1018–1026.
- [50] G. Psrofogiannakis, A.C.T. van Duin, Surf. Sci. 646 (2015) 253–260.
- [51] A.C.T. van Duin, C. Zou, K. Joshi, V. Bryantsev, W. a Goddard, Comput. Catal., 14 (2014). 223–243.
- [52] S. Plimpton, J. Comput. Phys. 117 (1995) 1–19.
- [53] H.M. Aktulga, J.C. Fogarty, S.A. Pandit, A.Y. Grama, Parallel Comput. 38 (2012) 245–259.
- [54] A. Stukowski, Model. Simul. Mater. Sci. Eng. 18 (2009) 15012.
- [55] H. Ibach, H. Wagner, D. Bruchmann, Solid State Commun. 42 (1982) 457–459.
- [56] Y.J. Chabal, Phys. Rev. B. 29 (1984) 3677–3680.
- [57] X.L. Zhou, C.R. Flores, J.M. White, Appl. Surf. Sci. 62 (1992) 223–237.
- [58] M. Chander, Y. Li, J. Patrin, J. Weaver, Phys. Rev. B. 48 (1993) 2493–2499.
- [59] R. Konečný, D. Doren, J. Chem. Phys. 106 (1997) 2426–2435.
- [60] S.Y. Yu, H. Kim, J.Y. Koo, Phys. Rev. Lett. 100 (2008) 1–4.
- [61] S.Y. Yu, Y.S. Kim, H. Kim, J.Y. Koo, J. Phys. Chem. C. 115 (2011) 24800–24803.

- [62] D. Liu, L. Li, Y. Gao, C. Wang, J. Jiang, Y. Xiong, *Angew. Chemie* - Int. Ed. 54 (2015) 2980–2985.
- [63] M. Weldon, B. Stefanov, K. Raghavachari, Y. Chabal, *Phys. Rev. Lett.* 79 (1997) 2851–2854.
- [64] B.B. Stefanov, K. Raghavachari, *Appl. Phys. Lett.* 73 (1998) 824–826.
- [65] C. Gondek, M. Lippold, I. Röver, K. Bohmhammel, E. Kroke, J. *Phys. Chem. C.* 118 (2014) 2044–2051.