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Atomistic mechanisms of Si chemical mechanical polishing in aqueous H_2O_2: ReaxFF reactive molecular dynamics simulations

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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.

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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

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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], SiO_2 [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 H_2O_2 (0.5 nm thick) contains 400 H_2O and 40 H_2O_2 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 300 K 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 H_2O_2 and semi-spherical silica particle were combined along the z axis to generate the final simulation model, resulting in total system dimensions of $53.76 \times 53.76 \times 70.00$ Å^3. Fig. 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.

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.

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