Chemical Mechanical Polishing Mechanism of Silicon Nitride Surface: Effect of Tribochemical Oxidation

Hitomi Takahashi[1], and Satoyuki Nomura[2]
[1] Hitachi, Ltd., hitomi.takahashi.ne@hitachi.com
[2] Showa Denko Materials Co., Ltd., nomura.satoyuki.xikir@showadenko.com

ABSTRACT

In this presentation, we reported the chemical mechanical polishing (CMP) mechanisms of silicon nitride surface by ceria abrasive grains. We performed two simulations using first-principles molecular dynamics (FPMD) simulations which are high accuracy methods. First, surface conditions of silicon nitride under friction in CMP slurry were investigated. From the simulation results, surface oxidation by adsorption of a water molecule onto the silicon nitride surface was observed, and then a Si-N bond was broken with generating an ammonia molecule. It means that there are several kinds of silicon nitride surface from a new surface to a oxidized surface during the CMP process. Thus we performed the second simulations to study the effect of surface oxidation of silicon nitride on polishing behavior. Results clearly indicated that CMP was accelerated on a oxidized surface. It suggested that surface oxidation was the key reaction for controlling polishing rates of silicon nitride.

BACKGROUND

CMP is the process of smoothing wafer surfaces by the combination of mechanical friction and chemical reaction using a slurry. Abrasive grains and additives contained in the slurry react with wafer surfaces, and these chemical reactions accelerate polishing. Materials of the slurry have been designed to suit various targets and customer needs. It is expected that understanding CMP mechanism improves an efficiency of materials design of CMP slurry because materials of abrasive grains and additives affect the chemical reactivity, resulting in change of polishing rates. However, CMP is a complex phenomenon including chemical reactions and mechanical frictions. This is why it was difficult to unveil CMP phenomena and to design the slurry.

On the other hand, molecular simulations such as density functional theory (DFT) and molecular dynamics (MD) simulations have applied to unveil “tribochemical” phenomena in recent years. They are powerful tools for visualizing both mechanical friction and chemical reactions. In the case of CMP, chemical reactions under friction have been clarified by molecular simulations [1-4].

In our previous presentation [5-6], we reported the CMP mechanism of ceria/silica interface by first-principles molecular dynamics (FPMD) simulations. FPMD simulations are high accuracy methods, which enable to perform non-empirical simulation for tribochemical reactions. FPMD simulations revealed that a Si-O bond scission (surface removal) occurred following the formation of Ce-O-Si bonds in the CMP elementary reactions. In this study, we focused on the CMP mechanism of silicon nitride surface, which is widely used as a etch stop layer. Y. Z. Hu *et al*. performed experimental analysis on CMP mechanism of silicon nitride surface[7]. Based on the results, they proposed that surface of silicon nitride was polished after the surface was oxidized by the reaction between water and silicon nitride. However, CMP elementary reactions have not been verified yet at atomic levels. Therefore, we investigated the CMP mechanism of silicon nitride/ceria interface at atomic levels by FPMD simulations in order to improve an efficiency of developing the slurry.

METHODOLOGY

All calculations were performed with the pseudopotential/plane-wave calculation code in the “Quantum Espresso” package [8]. We used the density functional theory (DFT) - based FPMD method for investigating the dynamics of silicon nitride surfaces in the slurry and chemical reactions at the interface between a ceria abrasive grain and silicon nitride. Static DFT calculations were used to analyze chemical reactions observed in FPMD simulations. In all calculations, we used a generalized gradient approximation in terms of Perdew-Burke-Ernzerhof exchange correlation functionals [9] and ultrasoft pseudo potentials [10]. The cut-off energy was set at 40 Ry. In FPMD simulations, the fictitious electron mass of 400.0 a.u. and a integration time of 10 a.u. (0.24189 fs) were used. The motions of the electrons and atoms were calculated with the Verlet algorithm [11] in the NVT ensemble, keeping the temperature at 300.0 K. The details of the simulation models are described in the results and discussion section.

RESULTS AND DISCUSSION

1. Surface conditions of silicon nitride under friction in CMP slurry

First, we investigated the dynamics of the silicon nitride surface in order to understand the surface conditions of silicon nitride under friction in the slurry. Fig. 1 shows the simulation model. β-Si_3N_4(0001) surface terminated with amino groups was used as a new surface of silicon nitride. 50 water molecules were sandwiched between two Si_3N_4 plates. The Si_3N_4 plates were slid under pressure to consider the friction effect. The external load and shear force were 420 and 82 pN/atom, respectively. Note that the friction between two Si_3N_4 plates do not occur during actual CMP processes. Two Si_3N_4 plates was used in order to increase the surface area of silicon nitride contact with water. This enables us to visualize the surface conditions of silicon nitride more easily in a limited simulation time. The reaction between a ceria abrasive grain and a silicon nitride surface in order to model the actual CMP processes will be discussed in the next section.

Fig. 2 (a) shows the structure in the final step of the simulation. Two NH_4^+ ions were liberated in the water phase. Si-O-Si bridge bonds and Si-OH bonds were newly formed at the Si_3N_4 surface. These results mean that surface oxidation of Si_3N_4 and generation of NH_4^+ ions were occurred under friction. Among these chemical reactions, the formation of the Si-O-Si bridge bond and the generation of a NH_4^+ ion were analyzed in detail. The analysis for the formation of a Si-OH bond was omitted in this paper because a Si-O-Si bridge bond and a Si-OH bond were found to occur by the same mechanism as a result of the additional analysis.

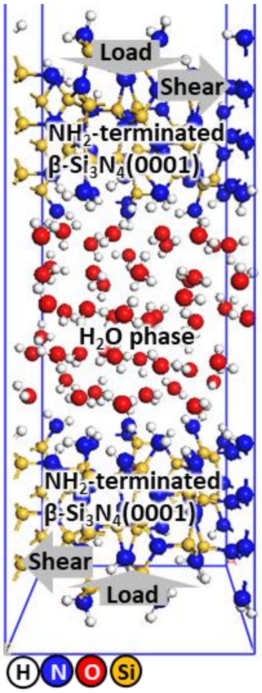

Fig. 1 Simulation model including H_2O molecules sandwiched between two β-Si_3N_4(0001) surfaces.

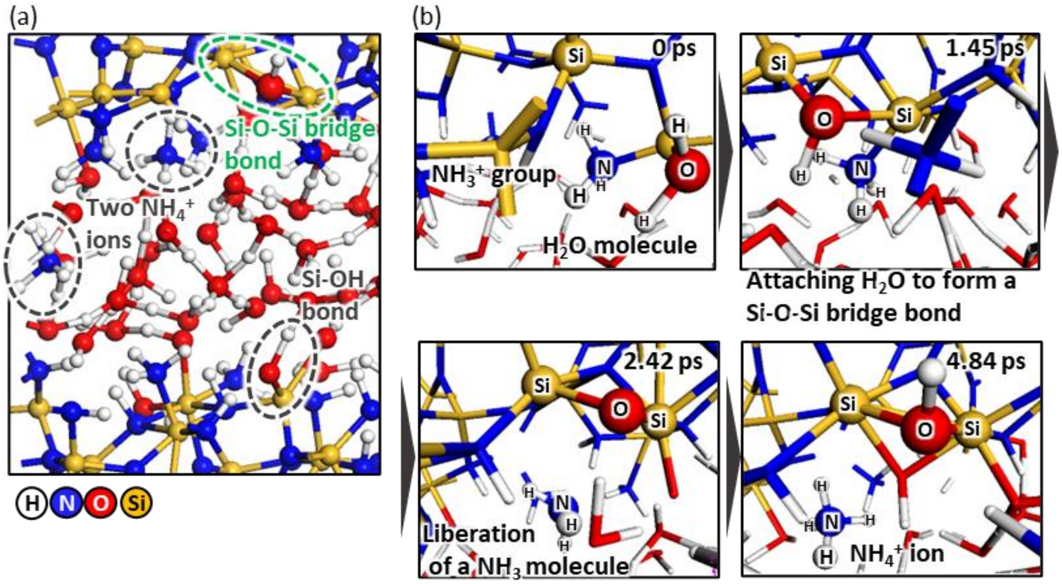

Fig. 2 (a) The final structure of the FPMD simulation. (b) Tribochemical reaction dynamics of a Si-O-Si bridge bond formation at the Si_3N_4 surface.

Fig. 2 (b) shows the snapshots of the Si-O-Si bond formation process. At the initial stage (0 pico-second), a proton was transferred from a water molecule to an amino group on Si_3N_4 surface to form a NH_3^+ group. The remaining OH^- ion then reacted with silicon atoms to form a Si-O-Si bridge bond at 1.45 ps. Instead, the firstly formed NH_3^+ group was liberated from the surface and diffused into the water phase at 2.42 ps. This ammonia molecule finally changed to a NH_4^+ ion by receiving a proton from a water molecule. This result indicated that the surface oxidation of silicon nitride was tribochemically oxidized by the following process. First, a water molecule reacted with the silicon nitride surface forming a Si-O-Si bridge bond, then the Si-N bond was broken with generating an ammonia molecule.

2. Effect of surface oxidation of silicon nitride on polishing rate

We clarified that surface oxidation of silicon nitride occurred under friction in the slurry. This means that there are several kinds of silicon nitride surfaces from a new surface to a oxidized surface during the CMP process. Thus three types of silicon nitride surfaces changing the degree of oxidation were prepared for analyzing CMP mechanisms, shown in Fig. 3. Since CMP is the process of removing an uneven part from the surface, a surface Si atom modeling an artificial surface bump was placed on each silicon nitride surface, the same as the previous presentation[5]. Overall views of simulation models and enlarged views of the surface bumps are shown in Fig. 3. Fig. 3(a) is the β- Si_3N_4(0001) fully covered with amino groups modeling a new surface. A $Si(NH_2)_2$ cluster which forms two Si-N-Si bonds with the Si_3N_4(0001) surface was arranged as the surface Si atom. (b) is the β-Si_3N_4(0001) surface terminated with hydroxyl groups. The surface Si atom is a $Si(OH)_2$ cluster which forms a Si-N-Si bond and a Si-O-Si bond with the β-Si_3N_4(0001) surface, indicating that (b) is more oxidized condition than (a). (c) is the almost same structure as (b), but the Si-N-Si bond of the surface bump in (b) is replaced to a Si-O-Si bond for modeling more oxidized state than (b). A ceria cluster ($H_4Ce_6O_{12}$) and 72 water molecules were placed on these three surfaces. Force and shear were applied to each ceria cluster in the direction of the arrow shown in Fig. 3(a). The external load and the shear force were 50 and 741 pN/atom, respectively. Lengths of Si-N and Si-O bonds at the surface Si atoms were monitored in order to verify polishing progress. The measurement targets were the bonds for (a1), (a2), (b2) of Si-N bonds, and (b1), (c1), (c2) of Si-O bonds shown in the images for the surface Si atoms of Fig 3. When two bond lengths for the surface Si atom get longer, it means that the surface Si atom is removed. According to the reference[12], a Si-O bond was defined as it broke when it stretched to 2.7 Å. A Si-N bond was defined as it broke when it stretched to 2.9 Å [13].

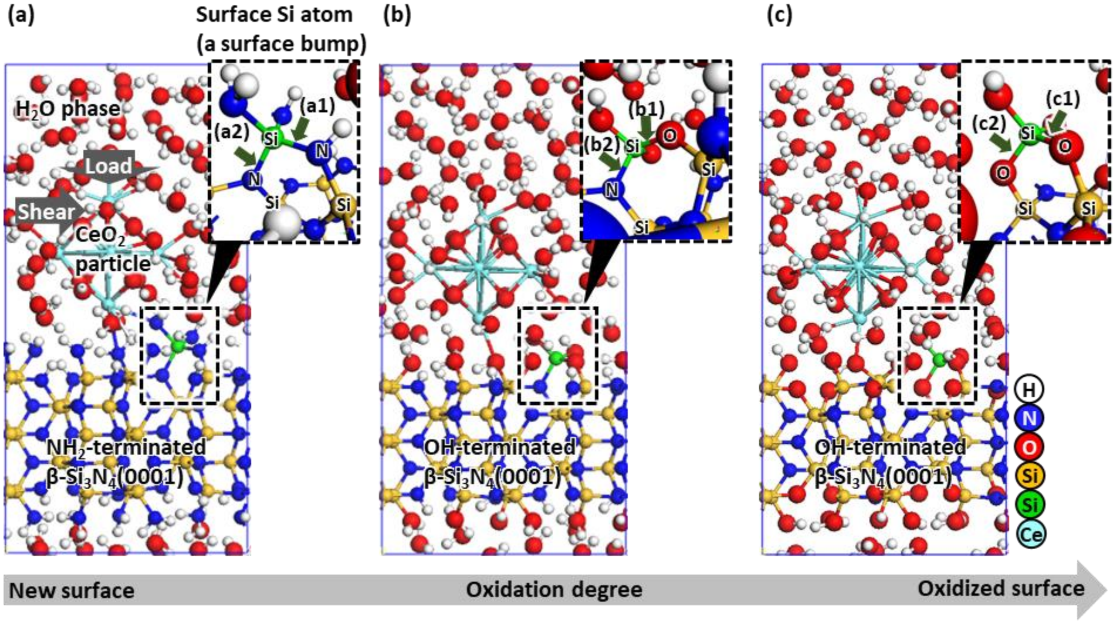

Fig. 3 Simulation models for analyzing the effect of surface oxidation of Si_3N_4 on the polishing behavior. (a) NH_2- terminated surface modeling the new surface of siicon nitride, (b) and (c) OH-terminated surface as oxidiazed surfaces. The number of Si-O-Si bonds in (c) is greater than (b), which means (c) is more oxidized than (b).

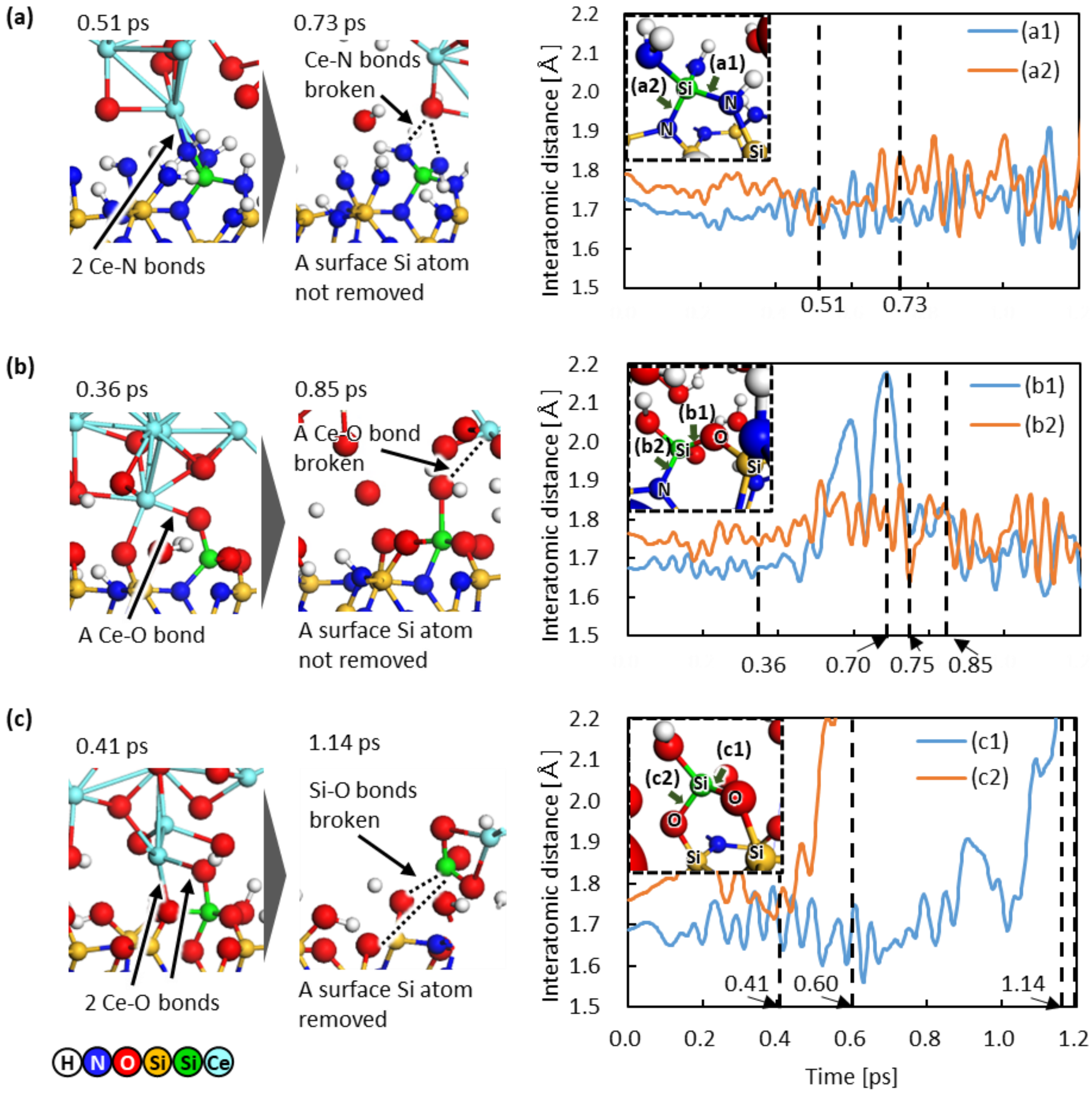

Fig. 4 The snapshots during the FPMD simulations and interatomic distances for Si-O and Si-N bonds of the surface Si atoms at Si_3N_4 surfaces. (a) NH_2-terminated surface with two Si-N bonds at the surface Si atom modeling a new surface, (b) OH-terminated surface with a Si-N bond and a Si-O bond at the surface Si atom modeling a partially oxidized surface, (c) OH-terminated surface with two Si-O bonds at the surface Si atom modeling a oxidized surface.

Fig. 4 shows the snapshots during the FPMD simulations on the left side and the change of interatomic distance over time on the right side. A new surface modeled in (a) was firstly analyzed. From the snapshots of the simulation, two Ce-N bonds were formed between the ceria cluster and the surface Si atom when the ceria cluster approached to the Si atom at 0.51 ps. However, the snapshot at 0.73 ps showed that the Si atom was not removed while both Ce-N bonds were broken. The bond lengths of two Si-N bonds (a1) and (a2) were not stretched over time based on the bond lengths analysis. In the model (b), a Si-O bond (b1) and a Si-N bond (b2) were analyzed. Two snapshots showed that once a Ce-O bond formed between the ceria cluster and the surface Si atom at 0.36 ps, but this Ce-O bond was broken and the Si atom was not removed. From the bond lengths analysis, the Si-O bond (b1) stretched to almost 2.2 Å at 0.70 ps. This bond length change seemed to occur after a Ce-O bond was formed based on the snapshot of 0.36 ps. The bond (b1) returned to its original state at 0.75 ps. On the other hand, the Si-N bond (b2) did not change over time. From this result of bond lengths, it suggests that a Si-O bond is easier to break than a Si-N bond when the ceria cluster adsorbs onto the Si atom. In the model (c), targets for calculating bond length were two Si-O bonds (c1) and (c2). From the snapshots, two Ce-O bonds were observed between the ceria cluster and the surface Si atom at 0.41 ps. After that, two Si-O bonds of the Si atom were observed to be broken while newly formed Ce-O bonds were remained. From the bond lengths analysis, the Si-O bond (c2) was broken at 0.60 ps, then the Si-O bond (c1) was broken at 1.20 ps. Thus the surface Si atom at the oxidized surface was removed by adsorbing a ceria abrasive grain.

From three FPMD simulations, the differences of the polishing behavior by surface conditions were observed as follows. At the new surface, Ce-N bonds were formed temporarily when the ceria cluster approached to the surface Si atom. However, these Ce-N bonds were broken as the ceria cluster moved by shearing force, and the surface Si atom was not removed. At the oxidized surface, Ce-O bonds were formed when the ceria cluster approached. As the ceria cluster moved by shearing force, the surface Si atom was removed by breaking Si-O bonds while Ce-O bonds between the ceria cluster and the surface Si atom were remained. These differences suggest that adsorption of the ceria cluster affected Si-O bonds, while it had little influence on Si-N bonds. To further investigate the effect of the surface conditions on polishing, we compared the change of bond lengths for a Si-N bond and a Si-O bond by adsorbing a ceria model on silicon nitride or silica. Fig. 5 shows the bond lengths which are marked with black arrows in the molecule models. A $H_{13}Si_2N_7$ cluster is the model of a new surface, while a $H_6Si_2O_7$ small cluster is the model of a oxidized surface. Adsorption of a ceria abrasive onto each surface was modeled by forming a Ce-N or a Ce-O bond between a ceria cluster and the $H_{13}Si_2N_7$ or the $H_6Si_2O_7$ cluster. From the results shown in Fig. 5, the Si-N bond did not change much with or without adsorption of the ceria cluster. On the other hand, the Si-O bond significantly lengthened by interacting with the ceria cluster. Therefore, it is estimated that ceria abrasives helped to weaken Si-O bonds, resulting in promoting Si-O bonds breaking. The adsorption of ceria abrasives seems to have little influence on Si-N bonds, that is why polishing of the new surface of silicon nitride was not observed by FPMD simulations.

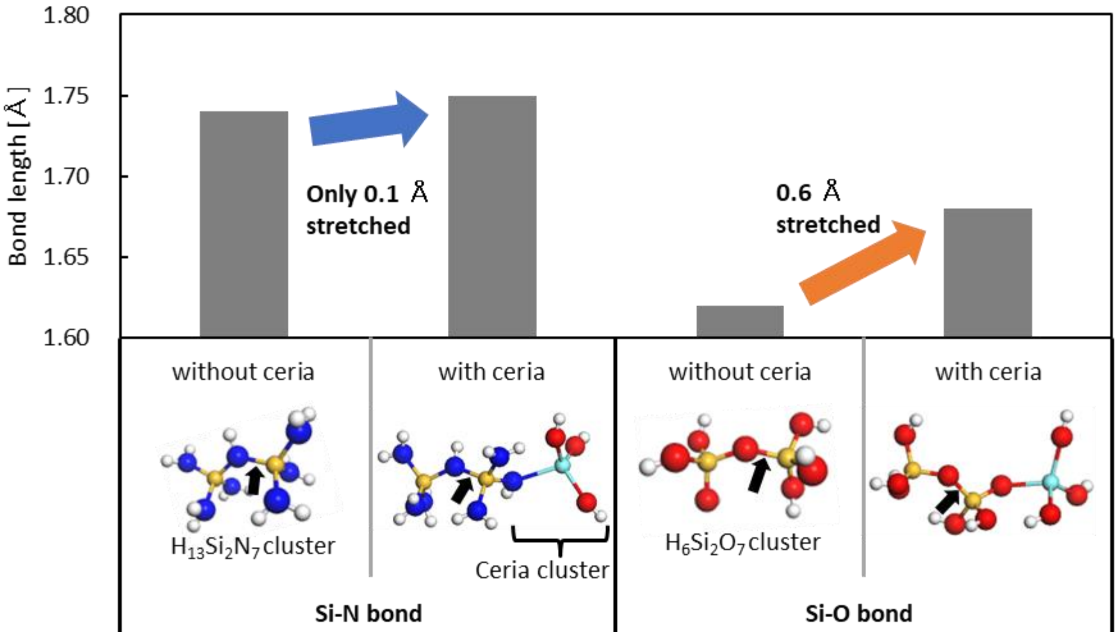

Fig. 5 The change of bond lengths for Si-N and Si-O bonds by adsorbing a ceria model and the structures of molecule models. Si-N/Si-O bond lengths marked with black arrows on the models were measured.

Based on these results, we found that CMP of silicon nitride was easier to take place on the oxidized Si_3N_4 surface. It means that the surface oxidation is the key reaction to control polishing rate for silicon nitride surface.

CONCLUSIONS

In this study, the CMP mechanism for silicon nitride surfaces polished with ceria abrasive grains was theoretically investigated. Two considerations were verified using FPMD simulations. First, surface conditions of silicon nitride during CMP process were clarified. Simulation results showed that surface oxidation of Si_3N_4 and generation of NH_4^+ ions were occurred under friction in a water phase. It means that there are several kinds of silicon nitride surface during CMP process. Thus we performed the second simulations for studying the effect of surface oxidation of silicon nitride on the polishing behavior. Results clearly indicated that CMP was promoted on the oxidized Si_3N_4 surface. Controlling the reaction rate of surface oxidation is important for CMP performance on silicon nitride.

References:

[1] T. Yokosuka, H. Kurokawa, S. Takami, M. Kubo, A. Miyamoto & A. Imamura (2002). Development of New Tight-Binding Molecular Dynamics Program to Simulate Chemical-Mechanical Polishing Processes. *Jpn. J. Appl. Phys.*, 41, 2410.

[2] A. Rajendran, Y. Takahashi, M. Koyama, M. Kubo & A. Miyamoto (2005). Tight-Binding Quantum Chemical Molecular Dynamics Simulation of Mechano-Chemical Reactions during Chemical-Mechanical Polishing Process of SiO_2 Surface by CeO_2 Particle. *Appl. Surf. Sci*., 244, 34.

[3] X. Guo, S. Yuan, Y. Gou, X. Wang, J. Guo, Z. Jin & R. Kang (2020). Study on chemical effects of H_2O_2 and glycine in the Copper CMP process using ReaxFF MD. *Appl. Surf. Sci*., 508, 125262.

[4] K. Kawaguchi, H. Ito, T. Kuwahara, Y. Higuchi, N. Ozawa, M. Kubo (2016). Atomistic mechanisms of chemical mechanical polishing of a Cu surface in aqueous H_2O_2 : tight-binding quantum chemical molecular dynamics simulations, *ACS Appl. Mater. Interfaces* 8 11830–11841.

[5] T. Onodera, H. Takahashi & S. Nomura (2019). A Molecular Mechanism on CeO_2/SiO_2 Sliding Interface toward Accelerating Polishing Rate, *ICPT 2019, Taiwan.*

[6] T. Onodera, H. Takahashi & S. Nomura (2020). First-Principles Molecular Dynamics Investigation of Ceria/Silica Sliding Interface toward Functional Materials Design for Chemical Mechanical Polishing Process. *Appl. Surf. Sci*., 530, 147259.

[7] Y. Z. Hu, R. J. Gutmann & T. P. Chow, (1998). Silicon Nitride Chemical Mechanical Polishing Mechanisms. *J. Electrochem. Soc.*, 145, 11.

[8] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G.Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari & R.M. Wentzcovitch (2009). Quantum Espresso: a modular and opensource software project for quantum simulations of materials, *J. Phys.:Condens. Matter* 21, 395502

[9] J. P. Perdew, K. Burke & M. Ernzerhof, (1996). Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 77, 3865.

[10] A.M. Rappe, K.M. Rabe, E. Kaxiras & J.D. Joannopoulos, (1990) Optimized pseudopotentials, *Phys. Rev. B.,* 41, 1227.

[11] L. Verlet, (1967) Computer “Experiments” on classical fluids. I. Thermodynamical properties of lennard-jones molecules, *Phys. Rev.* 159, 98.

[12] S. Iarlori, D. Ceresoli, M. Bernasconi, D. Donadio, & M. Parrinello, (2001). Dehydroxylation and Silanization of the Surfaces of β-Cristobalite Silica: An ab Initio Simulation, *J. Phys. Chem. B.*, 105, 8007-8013

[13] V. P. Feshin & E. V. Feshina, (2014) Nature of Coordination Bond in Silatranes and Its Formation Dynamics According to the Ab Initio Calculations, *Russian Journal of General Chemistry*, 84, 1, 70–74.

Corresponding Author:
Hitomi Takahashi
Tel: +81-70-4209-2289
E-mail: hitomi.takahashi.ne@hitachi.com
Research & Development Group, Hitachi, Ltd.
7-1-1 Omika, Hitachi, Ibaraki, 319-1292, Japan