Molecular Dynamics Analysis on the Behavior of Water and Alcohol Liquids on a OH-Terminated SiO₂ Surface

Y. Yamaguchi^{a,b}, S. Nakaoka^a, T. Hayashi^a, M. Kawakami^c, D. Yano^c

^a Department of Mechanical Engineering, Osaka University, Suita, 562-0043, JAPAN

^b Water Frontier Science & Technology Research Center (W-FST), Research Institute for Science & Technology, Tokyo University of Science, Tokyo, 162-8601, JAPAN

^c R&D Center, Organo Corporation, Sagamihara, 252-0332, JAPAN

In this study, we carried molecular dynamics (MD) simulations of water and various alcohol liquids on a flat SiO₂ surface terminated by hydroxyl groups in order to examine the microscopic structures of these liquids near the solid surface and diffusion property for the fundamental understanding of the wet process during the semiconductor fabrication. As an equilibrium state, water as well as methanol, ethanol and isopropyl alcohol (IPA) molecules formed a multiple layered structure on the solid surface; however, the microscopic structures were remarkably different between water and IPA liquids because the IPA molecules in the first adsorption layer strongly adsorbed on the solid surface through the hydrogen bond with the surface hydroxyl groups with directing hydrophobic CH₃ groups toward the second layer. Non-equilibrium MD simulations of the dilution of water/IPA adsorption layer by IPA/water solvent revealed that the strongly adsorbed IPA layer can easily be replaced by water molecules.

Introduction

Upon continuous advance of semiconductors, the line width of the processors has reached down to several nanometers (1). Even at this scale, cleaning processes by using water as a typical liquid medium are needed during the fabrication process to remove contaminations in the line trench. More concretely, the sequential process of water infiltration into the nanoscale trench, replacement of water with isopropyl alcohol (IPA), and drying of IPA, are iterated. Then, a very simple and fundamental question arises: can water really remove the impurities, or can water really infiltrate into such nanoscale trench? Up to the micrometer scale, the macroscopic governing equation of fluid mechanics can give a feasible answer to these questions; however, the continuum approximation as the base of fluid mechanics is in principle no longer applicable at the nanometer scale. Nevertheless, to avoid possible defects due to contaminations, profound understanding of the liquid behavior at such scale is essential.

Molecular dynamics (MD) analysis is a possible choice for such purpose as a microscopic approach. We have carried out MD simulations on the liquid behavior including wetting (2-6), velocity slip at the liquid-solid interface (7-12), and the water-behavior in a nanometer scale slit (13). In Ref. (13), as the first step, we modeled the solid slit composed of a simple fcc crystal and assumed a simple 12-6 Lennard-Jones (LJ) interaction as the inter-molecular potential between water and constituent particle of the

solid. Specifically, we examined the effects of wettability on the possibility of infiltration by changing the strength of the LJ interaction as a parameter, and we showed that the infiltration feature significantly differed below and above a threshold contact angle of 90 degrees because of the extremely high Laplace pressure induced at this scale. In addition, we explored the effects of residual gas on the infiltration behavior by initially locating gas molecules in the slit, and revealed that the effects of gas was almost negligible because the gas molecules easily dissolved into water in the case where water could infiltrate into the slit, *i.e.*, when the contact angle was below 90 degrees. This high solvability of gas seemed to be explained through macroscopic Henry's law considering that the gas was subject to the high Laplace pressure mentioned above. Interestingly, even at the nanometer scale, these results obtained in the model systems were not significantly contradictory to the behavior expected from macroscopic concepts of Laplace pressure and Henry's law, and this indicated that such macroscopic concepts should be considered at least for a rough estimation and prediction of the phenomena at the primary stage of the analysis. On the other hand, the physical properties of water in the adsorption layers formed near the solid was apparently different from those of bulk water, and this effect should be properly evaluated to examine the cleaning process that should largely be governed by the diffusion property of the liquid.

In this study, we changed the solid surface from a simple fcc crystal to a more realistic SiO₂ surface terminated by flexible hydroxyl groups in order to explore the microscopic equilibrium behavior of water and various alcohol liquids with respect to their microscopic structures near the solid surface as well as diffusion property. In addition, we carried out non-equilibrium simulations of the dilution of water/IPA adsorption layer by IPA/water solvent considering the replacement process during the semiconductor fabrication. For fundamental understanding, a flat SiO₂ crystal surface without edge was adopted instead of dealing with a solid surface with a slit as in our previous study (13).

Simulation Method

Figures 1 and 2 show the side snapshots of the equilibrium MD simulation systems of single component water or alcohol on the SiO₂ crystal surface, and detail of the surface, respectively. We adopted water, methanol, ethanol and isopropyl-alcohol (IPA) as the liquid molecules with applying SPC/E (14) and OPLS/UA (15) models for water and alcohols molecules, respectively. As shown in the top panel of Fig. 1, CH, CH₂ and CH₃ were dealt with as single united points with corresponding mass, and the interaction among these sites were expressed by the following Lennard-Jones (LJ) potential Coulomb potential:

$$\Phi_{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad [1]$$

$$\Phi_{\text{C}}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad [2]$$

where r_{ij} is the distance between site i and j , and ε_{ij} , σ_{ij} , q_i , and ε_0 denote the energy and length parameters, electric charge and dielectric constant of vacuum, respectively. The water and methanol molecules were dealt with as a rigid body whereas the ethanol and IPA molecules were expressed as a combination of two rigid bodies having a relative rotational

Figure 1. Side snapshots of equilibrium simulation systems of single water, methanol, ethanol and isopropyl alcohol (IPA) liquids on OH-terminated SiO₂ surface. The numbers of liquid molecules are 3000, 1250, 750 and 750, respectively.

Figure 2. Details of the SiO₂ crystal surface of a diamond structure with exposed (111) surface. All the dangling bonds on the surface were terminated with hydroxyl (OH) groups.

degree of freedom around O-CH₂ or O-CH axis shown in Fig. 1, respectively. For intra-SiO₂, the BMH potential (16) given by

$$\Phi_{\text{BMH}}(r_{ij}) = f_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} \quad [3]$$

was applied as well for the interaction between constituent silicon and oxygen atoms shown in Fig. 2, where a_i , b_i and c_i are the effective radius, softness parameter, and van der Waals

TABLE I. Potential and mass parameters of water and alcohol molecules.

	m [amu]	σ [Å]	ε [$\times 10^{-21}$ J]	q [e]
O (water)	16.00	3.166	1.079	-0.8476
H (water)	1.008	-	-	0.4238
CH ₃ (methanol)	15.02	3.775	1.439	0.265
O (methanol)	16.00	3.070	1.182	-0.700
H (methanol)	1.008	-	-	0.435
CH ₃ (ethanol)	15.02	3.905	1.216	-
CH ₂ (ethanol)	14.02	3.905	0.8202	0.265
O (ethanol)	16.00	3.070	1.182	-0.700
H (ethanol)	1.008	-	-	0.435
CH ₃ (IPA)	15.02	3.910	1.112	-
CH (IPA)	13.00	3.850	0.5561	0.265
O (IPA)	16.00	3.070	1.182	-0.700
H (IPA)	1.008	-	-	0.435

TABLE II. Potential and mass parameters of wall atoms

	m [amu]	σ [nm]	ε [$\times 10^{-21}$ J]	q [e]	a_i [nm]	b_i [nm]	c_i [$J^{1/2} \text{ nm}^3$]	f_0 [$J \text{ nm}^{-1}$]
Si	28.1	0.3920	4.171	2.40	0.08688	0.00329	5.8667×10^{-12}	6.951×10^{-20}
O	16.0	0.3279	5.906	-1.20*	0.20474	0.01757	1.9325×10^{-12}	
H	1.01	-	-	0.60	-	-	-	

* charge value for the oxygen atoms on the bottom was halved to keep the total charge of the system at zero

parameter. The LJ parameters for the inter-site interaction were set by the following Lorentz-Berthelot mixing rules:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad [4]$$

$$\varepsilon_{ii} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad [5]$$

The parameters used in this study are summarized in TABLES 1 and 2. Note that the methyl groups (CH₃) for each molecule has no electric charge and is hydrophobic.

As shown in Fig. 2, three layers of SiO₂ with a diamond structure with exposed (111) surface were located on the bottom of the simulation system. Periodic boundary conditions were applied in the lateral x - and y -directions whereas mirror boundary condition was imposed on the top of the system. All the dangling bonds on the surface were terminated with hydroxyl (OH) groups, which had a constant Si-O-H angle while having a rotational degree of freedom around the Si-O axis as shown in Fig. 2 (18,19). The bottom layer was frozen and the temperature of the middle layer was controlled at 300 K by the Langevin thermostat (17). Note that the equilibrium contact angle for water and the three alcohol liquids with the present condition was zero, meaning that the surface was very hydrophilic due to the strong hydrogen bonds formed between the liquid molecule and surface OH group.

The Particle Mesh Ewald method (20) was used for the calculation of the Coulomb interactions, and the velocity Verlet method with the modified quaternion constraint technique (21) as well as RATTLE method (22) were applied to numerically integrate the equation of motion with a time step of 1 fs.

Figure 3. (Left) density distributions around the SiO₂ surface, and (middle, right) corresponding snapshots for water and IPA systems.

Results and Discussion

Density Distribution and Diffusion of Single Liquid Component on OH-terminated SiO₂

Figure 3 shows the density distributions of water and three alcohol near the SiO₂ surface and corresponding snapshots for water and IPA systems. The density distributions were obtained as the time-averaged mass in equally divided bins normal to the z -direction, where the mass of each interaction site was summed up upon averaging. As usually observed for various liquids on various solid surfaces (2-13), each liquid formed multiple layered structures around the SiO₂ surface, and the density converged to a constant bulk value about 2.5 nm away from the surface. Interestingly, the separation between the 1st and 2nd peaks of the density in the left panel became more pronounced as the alcohol molecule became larger from methanol to IPA, and a remarkable void layer with zero-density was formed for IPA around $z = 0.5$ nm. This void layer between the 1st and 2nd adsorption layers can be clearly observed in the snapshot of the IPA system in right panel. This can be explained as follows: the OH group of each IPA molecule formed hydrogen bonds with the OH on the SiO₂ surface, and thus the IPA molecules aligned on the SiO₂ surface as the 1st adsorption layer with locating the two hydrophobic methyl groups toward the top; hence the IPA molecules in the 2nd adsorption layer preferred to form hydrogen bond with the bulk side above with their OH group with locating the hydrophobic methyl groups in the bottoms side. This tendency became less pronounced for smaller alcohol molecules with less hydrophobic groups, and it was no longer the case for water molecules because the water molecules in the 1st layer may form multiple hydrogen bonds with the OH groups on the SiO₂ surface as well as with those in the 2nd layer.

Figure 4 shows the distributions of diffusion coefficient for each system, and corresponding trajectories of water and IPA molecules within 50 ps from the initial position, where only the molecules in the 1st or 2nd adsorption layer are displayed for better visualization for the trajectories. The local diffusion coefficient D as a function of the

Figure 4. (Left) distributions of diffusion coefficient as a function of position z normal to the solid surface, and (middle, right) corresponding trajectories of water and IPA molecules within 50 ps from the initial position, where only the molecules in the 1st or 2nd adsorption layer are displayed for better visualization.

position z normal to the surface was evaluated from the mean square displacement within time t from the initial position at time t_0 as

$$\langle |\vec{r}(t + t_0|z, t_0) - \vec{r}(z, t_0)|^2 \rangle = 6D(z)t \quad [6]$$

where $\langle \cdot \rangle$ and $\vec{r}$ denote the average for sample molecules and initial time t_0 and position vector, where the average was taken for molecules existed at height z at time t_0 . Note that the surface normal position at time $t + t_0$ is basically different from the initial value z , and Eq. [6] can give only a rough estimate of the local diffusion coefficient (23). As shown in the left panel, the diffusion coefficient was overall reduced near the solid surface, and the diffusion coefficient of larger alcohol molecules in the 1st adsorption layer was especially decreased down to nearly zero. This is highly related to the orientation of the alcohol molecules there. As seen in the right panel for IPA molecules in the 1st layer (or enlarged snapshot in Fig. 3), the IPA molecules there formed strong hydrogen bond while they had weak interaction with those in the 2nd layer, and this resulted in the immobile feature of IPA in the 1st layer. The IPA molecules in the 2nd layer was relatively mobile as also seen in the right panel. On the other hand, the reduction of diffusion coefficient of water in the 1st layer shown in the left panel was small compared that for alcohols. This is also remarkable in the trajectory in the middle panel, indicating that water molecules were still mobile even in the 1st layer which were subject to a strong interaction with the OH groups on the SiO₂ surface through the hydrogen bonds.

Dilution of IPA/Water Layer by Water/IPA Solvent

Another question arises from the analysis of diffusion coefficient above: can we remove the immobile IPA molecules strongly attached to the hydrophilic SiO₂ surface by diluting with water as the solvent? In order to answer this question and to consider the

Figure 5. Snapshots of the nonequilibrium simulation systems of diluting process. (Top) IPA layer diluted by water solvent, and (bottom) water layer diluted by IPA solvent. Except the initial conditions, the solvent molecules are show semitransparent for better visualization.

reversed case as well, *i.e.*, water removal by diluting with IPA, we carried out two kinds of non-equilibrium simulations as shown in the left panel of Fig. 5, where for instance for the system in top left panel, the SiO_2 surface fully covered with a single IPA layer was preliminary equilibrated, and a bulky water slowly approached the layer from the top as the initial condition. Note that the volume of water solvent in the top case was less than that of IPA solvent in the bottom case due to our rather arbitrary choice. Most of the IPA layer dissolved in the water solvent in 4 ns after the initial contact as shown in the top panel although the IPA molecules rather strongly adsorbed on the solid surface and immobile as seen in Fig. 4. On the other hand, only a certain fraction of the water molecules initially in the adsorption layer detached and most of the water molecules stayed on the solid surface. From the present result with a system keeping the number of molecules constant, it is not clear whether the water layer can dissolve in IPA in case the water concentration in the IPA solvent can be kept low, *e.g.*, by removing the water molecules in the solvent IPA from the top. Whereas, we can expect from the present result that IPA molecules can dissolve in the water solvent if more water molecules are provided.

These results indicates that water has a very strong cleaning effect at least on a hydrophilic surface, and this seems to be due to the specific property of water molecules that they have smaller volume without hydrophobic group. With this property, water molecules easily cut in the existing hydrogen bond between hydrophilic groups, *e.g.*, between IPA and OH on the SiO_2 surface.

Concluding Remarks

In this study, we carried molecular dynamics (MD) simulations of water and various alcohol liquids on a flat SiO₂ surface terminated by hydroxyl groups in order to investigate the microscopic structures of these liquids near the solid surface and diffusion property for the fundamental understanding of the wet process during the semiconductor fabrication. As an equilibrium state, water as well as methanol, ethanol and isopropyl alcohol (IPA) molecules formed a multiple layered structure on the solid surface; however, the microscopic structures were remarkably different between water and IPA liquids because the IPA molecules in the first adsorption layer strongly adsorbed on the solid surface through the hydrogen bond with the surface hydroxyl groups with directing hydrophobic CH₃ groups toward the second layer. Non-equilibrium MD simulations of the dilution of water/IPA adsorption layer by IPA/water solvent revealed that the strongly adsorbed IPA layer can easily be replaced by water molecules.

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