Molecular simulation study of nanoscale friction for alkyl monolayers on Si(111)

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Molecular dynamics (MD) simulations were performed to study nanoscale friction for alkyl monolayers terminated with -CH$_3$ (hydrophobic) and -OH (hydrophilic) on Si(111) in the presence of water molecules. Variation of the -OH/-CH$_3$ ratio results in different surface hydrophobicities. To calculate friction in MD simulations, two Si(111) surfaces coated with the alkyl monolayers were slid against each other. It was shown that the friction coefficient decreased quickly for hydrophilic monolayers, whereas it remained almost the same for hydrophobic monolayers, as the number of water molecules (relative humidity) increased. Simulation results are in good agreement with those from scanning force microscopy measurements for both hydrophilic and hydrophobic monolayers. The behavior of water molecules confined between hydrophobic or hydrophilic monolayers was also discussed. A fundamental understanding of nanoscale friction is critical to the design of coatings for microelectromechanical systems. © 2002 American Institute of Physics.

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I. INTRODUCTION

There is a growing interest in developing technologies that use silicon and other electronic materials as mechanical materials. Using standard processes of the integrated circuit (IC) industry, researchers have successfully fabricated miniaturized mechanical components, such as membranes, gears, motors, pumps and valves. The integration of miniaturized mechanical components with microelectronic components has spawned a new technology, micro- or nanoelectromechanical systems (MEMS/NEMS). It promises to extend the benefits of microelectronic fabrication to sensing and actuating functions. However, surface forces, such as adhesion and friction, are often detrimental to the fabrication and operation of MEMS/NEMS devices. Thus, a fundamental understanding of nanoscale friction and adhesion is critical to MEMS/NEMS technology.

A self-assembled monolayer (SAM) is one of several strategies used for minimizing adhesion and reducing friction in MEMS/NEMS. The most often used SAMs are alkanethiols on gold. However, the technologically important monolayers are alkylsilanes on silicon. Monolayers on silicon traditionally rely on siloxane chemistry on oxidized surfaces. However, it is difficult to prepare compact silane monolayers on silicon. The alternative approach is the direct thermal reaction between alkene and hydrogen-terminated silicon surface to form stable and compact organic films via Si–C linkage. Such organic thin films are also prepared by other methods, such as electrospray.

The new monolayer coating via Si–C linkage has several key advantages over the previously reported silane-based SAMs: (i) The coating does not produce HCl; (ii) the coating does not require the formation of an intervening oxide layer; (iii) the film formation procedure is simpler; (iv) the coating process is much more robust; (v) the coated surface has much fewer particulates; and (vi) the film is stable up to 615 K. The direct reaction between alcohols and H-terminated or Cl-terminated silicon surfaces has also been proposed to form stable organic films via Si–O linkage. Further modification of these stable monolayers can be performed for other applications, such as biosensors and lab-on-chips.

To study the friction and adhesion of SAM surface, molecular simulation and experimental techniques have been used. On the experimental front, scanning probe microscopy (SPM) was used to determine nanoscale friction for SAMs on solid substrates. Scherge et al. measured the friction and adhesion of hydrophobic hydrogen-terminal silicon surfaces and hydrophilic silicon surfaces under different humidities. Molecular simulation is a powerful tool to investigate the friction and adhesion of monolayers on solid substrates. Molecular dynamics (MD) simulations have been performed previously to study the friction properties of various systems. Tupper and Berner studied the friction of alkanethiol SAMs on Au(111). Cagin et al. investigated the atomic scale origin of friction between two hydrogenated diamond-(100) surfaces. Harrison and co-workers focused on the model system of alkane monolayers on diamond (111) and investigated the effect of chain length, packing density and compression on friction. Recently, friction between alkylsilane monolayers was simulated by Chandross, Grest and Stevens. In this work, we performed MD simulations to study the nanoscale friction of alkyl monolayers on Si(111). To the best of our knowledge, no molecular simulation study of friction has been performed for such a system. To perform MD simulations of alkyl on silicon, it is necessary to have the packing structure of the monolayers. Previ-
Simulation study of nanoscale friction

A. Simulation systems

The optimal packing structure of alkyl monolayers was found by molecular mechanics simulation. The unit cell for this packing structure has a dimension of 13.301 Å × 7.679 Å. In the packing structure, there is a 50% substitution of alkyl chains on Si(111), zigzag-like pattern, and such orientations that two of four chains orient the next-nearest neighbors (NNN) and other two chains orient the next–next-nearest neighbors (NNNN). The unit cell is marked by solid lines in Fig. 1. The monolayers were constructed from a (3×8) array of the unit cell, leading to surface dimensions of 3.99 Å × 6.14 Å. The constructed C₉ alkyl monolayers on Si(111) are shown in Fig. 2. Each wall consisted of four layers of silicon atoms, which were cleaved from the bulk. The total number of silicon atoms in each wall is 768. The walls were coated with C₉ alkyl monolayers, with terminal groups of -CH₃ (hydrophobic) and -OH (hydrophilic). Variation of the composition of the mixed terminal groups results in different surface hydrophobicities. The whole system for a simulation contains ~3500 interaction particles. In this work, monolayers terminated with 100% -CH₃ represent hydrophobic surfaces, whereas monolayers terminated with a mixture of 50% -OH and 50% -CH₃ represent hydrophilic surfaces.

The simulation box used in this work is shown in Fig. 3. The origin is located at the center of the box. Water molecules are confined between the monolayers. The origin is located at the center of the box.

FIG. 3. A schematic representation of the simulation box. Two Si(111) surfaces coated with C₉ alkyl monolayers with mixed terminal groups of -OH (hydrophilic) and -CH₃ (hydrophobic) are sheared against each other. Water molecules are confined between the monolayers. The origin is located at the center of the box.

II. SIMULATION DETAILS

A. Simulation systems

The optimal packing structure of alkyl monolayers was found by molecular mechanics simulation. The unit cell for this packing structure has a dimension of 13.301 Å × 7.679 Å. In the packing structure, there is a 50% substitution of alkyl chains on Si(111), zigzag-like pattern, and such orientations that two of four chains orient the next-nearest neighbors (NNN) and other two chains orient the next–next-nearest neighbors (NNNN). The unit cell is marked by solid lines in Fig. 1. The monolayers were constructed from a (3×8) array of the unit cell, leading to surface dimensions of 3.99 Å × 6.14 Å. The constructed C₉ alkyl monolayers on Si(111) are shown in Fig. 2. Each wall consisted of four layers of silicon atoms, which were cleaved from the bulk. The total number of silicon atoms in each wall is 768. The walls were coated with C₉ alkyl monolayers, with terminal groups of -CH₃ (hydrophobic) and -OH (hydrophilic). Variation of the composition of the mixed terminal groups results in different surface hydrophobicities. The whole system for a simulation contains ~3500 interaction particles. In this work, monolayers terminated with 100% -CH₃ represent hydrophobic surfaces, whereas monolayers terminated with a mixture of 50% -OH and 50% -CH₃ represent hydrophilic surfaces.

The simulation box used in this work is shown in Fig. 3. The origin is located at the center of the box. Water molecules are confined between the two solid walls covered by alkyl monolayers. Top and bottom walls have opposite sliding directions and the sliding directions are along the X-axis. The solid walls are infinite in both X and Y directions. Two-dimensional periodic boundary conditions (PBC) were applied to the simulation cell. The pore size H is defined by the distance between the topmost atoms on each wall, as shown in Fig. 3. The pore size was kept constant in simulations. Water molecules were randomly inserted into the pore by grand canonical Monte Carlo (GCMC) simulations. MD simulations were then performed to calculate friction properties of the monolayers with different numbers of water molecules, corresponding to different relative humidities.
TABLE I. Intra-molecular interaction parameters.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
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<th></th>
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<tbody>
<tr>
<td>CH₂–CH₃</td>
<td>1.545</td>
<td>CH₂–CH₃</td>
<td>1.545</td>
</tr>
<tr>
<td>Si–CH₃</td>
<td>1.910</td>
<td>CH₂–O</td>
<td>1.600</td>
</tr>
<tr>
<td>H–O</td>
<td>1.000</td>
<td></td>
<td></td>
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<table>
<thead>
<tr>
<th>Angle</th>
<th>Kₜ(K/radian²)</th>
<th>θ₀(degree)</th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>CH₂–CH₂–CH₃</td>
<td>62545.1</td>
<td>114.6</td>
<td>CH₂–CH₂–CH₂</td>
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<td>110.0</td>
<td>H–O–H</td>
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<tr>
<td>H–O–H</td>
<td>109.7</td>
<td></td>
<td>H–O–CH₂</td>
<td>72167.4</td>
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<table>
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<tr>
<th>Torsion (K)</th>
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<tr>
<td>V₀</td>
<td>1037.76</td>
<td>V₁</td>
<td>2426.07</td>
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<td>V₂</td>
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<td>V₃</td>
<td>−3129.46</td>
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<tr>
<td>V₄</td>
<td>163.28</td>
<td>V₅</td>
<td>−252.73</td>
</tr>
</tbody>
</table>

B. Potential models

The simulation systems consist of C₉ alkyl chains terminated with -OH or -CH₃, Si atoms, and water molecules. Generally, the total potential energy of a given molecular chain can be written as a superposition of short-range valence (U correlated) and long nonbond interactions (Unbond).

\[ U_{total} = U_{valence} + U_{nonbond} \]  

where the valence (or internal) terms consist of bond stretch (Ubond), bond-angle bending (Uangle), and dihedral angle torsion (Utorsion) terms,

\[ U_{valence} = U_{bond} + U_{angle} + U_{torsion} \]  

while the nonbond (external) interactions consist of van der Waals (Uvdw) and electrostatic (UQC) terms,

\[ U_{nonbond} = U_{vdw} + U_{QC} \]

where the Uvdw term takes into account both intermolecular and intramolecular interactions.

The united atom (UA) model with bond constraints is adopted to describe alkyl molecules. The bond angle potential is described by a cosine harmonic potential:

\[ E_{angle} = \frac{1}{2} k_\phi (\cos \theta_i - \cos \theta_0)^2 \]  

The torsional potential is represented by

\[ E_{torsion} = \sum_{m=0}^{5} V_m (\cos \phi)^m \]

The valence parameters of the force field used in this work are listed in Table I. The torsion parameters for X–CH₂–CH₂–Y are the same regardless X and Y groups. The parameters used in this work were from the universal force field (UFF). The inter- and intra-molecular nonbond interactions are described by the shifted-force potential truncated at \( r_e = 2.5 \sigma_f \). The shifted-force potential is used to remove the discontinuities in the potential and force. The intermolecular interactions are from the interaction sites in different molecular chains, whereas intramolecular interactions are from the interaction sites separated by three or more atoms in the same molecular chain. Lennard-Jones (LJ) interaction parameters for various terminal groups in alkyl chains are given in Table II. The LJ cross parameters for site–site interactions were calculated using the Lorentz–Berthelot (LB) rules.

The walls were modeled using the explicit silicon atoms forming two (111) planes. To reduce the computational time, wall atoms were treated as static in all MD simulations. It has been shown that dynamics of the wall atom has no significant influence on simulation results. The parameters of the LJ potential for the Si(111) wall atoms are also listed in Table II. The interactions between Si atoms and fluids are described by the LJ potential with the cross parameters calculated using the LB rules. The LJ parameters for Si–CH₃ (or CH₂) were tested in our previous molecular simulations of alkyl monolayers on Si(111).

For -CH₃-terminated monolayers, atoms in the chains were assumed to be no charge. For those terminated with -OH, the optimized potential for liquid simulations (OPLS) potential model was used. Only the last three interaction sites in the terminal groups were assumed to have charges. In the OPLS model, charges are placed on three sites (C, O, and H) while short-range interaction sites are on the carbon (C) and oxygen (O) nuclei only. LJ parameters and charges for -OH-terminated groups are listed in Table II.

For a water molecule, there are several potential models available, such as the four point transferable intermolecular potential function (TIP4P), TIP3P, and the simple point charge model (SPC). In this work, water molecules were modeled using a site–site SPC potential model that contains three sites. The SPC potential model was derived from the TIP3P model by Berendsen et al. The SPC potential results in nine pairs of electrostatic interactions and one pair of LJ interaction between two oxygen sites for water–water interactions. LJ parameters and charges for water molecules are given in Table II. The angle between two O–H bonds is 109.47°, whereas the O–H bond length is 1.00 Å. Water molecules were held rigid by fixing two O–H bonds and the
distance between the two H atoms (1.633 Å) with the RATTLE algorithm.\textsuperscript{32}

The Coulombic interactions were truncated at distance equal to half of the simulation box length. It is difficult to take into account long-range forces in simulations of confined media due to the anisotropy of the system. Previously, the simulation of adsorption of a water–methanol mixture on graphite by Shevade et al.\textsuperscript{38} showed that the difference in potential energy is only 0.5–0.7% between the use of two-dimensional (2D) Ewald sum and half box length cutoff techniques with comparable density profiles obtained using both these methods. However, the 2D Ewald sum technique is two orders of magnitude slower than the half box length cutoff technique. In MD simulations of 3D systems, the reciprocal space sum in the Ewald method can be simplified to run over single atoms rather than pairs, so the computational time is significantly reduced. Since the Ewald method is still expensive, new methodology, such as the cell-multipole method (CMM) was developed.\textsuperscript{39} Computational time in CMM is approximately proportional to the number of particles, for large systems. Recently, CMM has been extended to quasi-2D systems (2D-CMM).\textsuperscript{40} The application of the 2D-CMM to simulations of friction is in progress.

C. Simulation methodology

MD simulation is a technique to compute the equilibrium and transport properties of a system by solving Newton’s equations of particles in the system.\textsuperscript{41} In this study, both monolayers and water molecules were dynamic, while solid wall atoms were fixed. The algorithm used in this work is similar to that used previously.\textsuperscript{35} Temperature was kept constant using the Nose–Hoover thermostat.\textsuperscript{42} The equations of motion of the methylene segments and water molecules were solved by the velocity Verlet algorithm with bond constraints (RATTLE)\textsuperscript{32} using a time step of 1.0 femtosecond (fs).

The initial configuration of the system was set up by the commercial software CERIUS\textsuperscript{2} 43 For the monolayers with mixed terminal groups of -CH\textsubscript{3} and -OH, a random distribution of the terminal groups on the surface was applied. The temperature of all simulations was set to 300 K. In MD simulations, systems (both hydrophobic and hydrophilic monolayers) were equilibrated for 15,000 steps and properties were accumulated over another 15,000 steps. The parameters used in this work were reduced as follows: length with $\sigma_f$ ($\sigma_{\text{CH}_3}$), energy with $\varepsilon_f$ ($\varepsilon_{\text{CH}_3}$), and mass with $m(m_{\text{CH}_3})$. The reduced length, temperature, pressure, density, force and time are $L^* = L/\sigma_f$, $T^* = kT/\varepsilon_f$, $P^* = \rho \sigma_f^2/\varepsilon_f$, $\rho^* = \rho \sigma_f$, $F^* = F \sigma_f/\varepsilon_f$, and $t^* = t (\varepsilon_f/m \sigma_f^2)^{1/2}$, respectively.

III. RESULTS AND DISCUSSION

In this work, MD simulations were performed to study the nanoscale friction of Si(111) surfaces covered by alkyl monolayers with -OH and/or -CH\textsubscript{3} terminal groups in the presence of different numbers of water molecules. Two systems were investigated in this study—surfaces covered by pure CH\textsubscript{3}-terminated monolayers (hydrophobic) and by mixed 50% -OH- and 50% -CH\textsubscript{3}-terminated monolayers (hy-

The number of water molecules was fixed for each MD simulation and was varied to account for different relative humidities. In fact, the number of water molecules under a certain relative humidity can be determined by GCMC simulations. In our MD simulations, normal loads and frictional forces were calculated by averaging the forces exerted on the monolayers in Z and X directions, respectively. A friction coefficient was then obtained from the friction force divided by the normal load.

Figure 4(a) presents the friction coefficients for both hydrophobic (terminated with -CH\textsubscript{3}) and hydrophilic (terminated with a mixture of 50% -OH and 50% -CH\textsubscript{3}) monolayers when different numbers of water molecules were confined between the monolayers for a pore size of 6.0 Å. For the hydrophobic monolayers, the friction coefficient remains almost the same (~0.17) as the number of water molecules increases. However, for the hydrophilic monolayers,
the friction coefficient decreases quickly from 0.90 to 0.30 with the increase of the number of water molecules. As the number of water molecules continues to increase, the friction coefficient approaches a constant. A similar trend for the effect of water on the friction coefficient was observed in our previous SFM measurements for both systems of alkanethiol/Au and alkyl/Si. For example, Fig. 4 shows that the frictional force for alkyl/Si from SFM measurements is strongly dependent on relative humidity for hydrophilic surfaces terminated with -COOH, while there is only a very weak dependence on humidity for hydrophobic surfaces (terminated with -CH₃). For hydrophobic monolayers, friction coefficients (0.16–0.19) from MD simulations agree quite well with those from SFM measurements (0.15–0.19), while a similar trend is observed from MD simulations and SFM measurements for hydrophilic monolayers used, even though the monolayers have different terminal groups (-COOH for SFM measurements and -OH for MD simulations in this work). Therefore, the dependence of friction on the number of confined water molecules for both hydrophilic and hydrophobic surfaces from our simulations is consistent with that in SFM measurements.

The behavior of confined water molecules in hydrophobic and hydrophilic pores is different from each other. Figures 5(a) and 5(b) show the final configurations from MD simulations for both hydrophobic and hydrophilic pores (H = 6.0 Å), in which a specific number of water molecules (density is about 1.0 g/cm³ in the figures) was confined. As can be seen, for hydrophobic pores, there is a gap between water molecules and monolayer terminal groups -CH₃. For hydrophilic monolayers, however, water molecules are filled in the entire pore. The difference in configuration can be also seen in water density profiles along the Z direction, shown in Fig. 6. Water molecules adsorb closer to surfaces along the Z direction for the hydrophilic than the hydrophobic pore due to the formation of hydrogen bonds between water molecules and -OH terminal groups on the hydrophilic monolayers. For the configuration shown in Fig. 5(b), each -OH-terminated group formed a ~0.75 hydrogen bond with water molecules. The formation of hydrogen bonds was defined by the interaction energy of ~2.25 kcal/mol or less.

Figure 7 shows the density profiles of water molecules in the hydrophilic pore (H = 6.0 Å) when different numbers of water molecules (W = 240, 340, 370 and 420) were confined in the pore. It was found that in all cases water molecules adsorbed close to monolayers since hydrogen bonds formed...
between water molecules and -OH terminal groups of the monolayers. The formed hydrogen bonds were 0.54, 0.67, 0.69 and 0.75 per -OH-terminated alkyl chains for those cases with water molecules of 240, 340, 370 and 420, respectively. With the increase of water molecules in the hydrophilic pore, water molecules started to show a layering behavior. A similar layering behavior of various solvents between two solid walls was also found in other previous MD simulations. It can be seen from Fig. 7 that two water layers were formed when 420 water molecules were confined. It was speculated from experiments that the layering behavior of water molecules contributes to the decrease of the friction coefficient. As shown in Fig. 8, the increase of lateral force was much slower than that of normal force as the number of confined water molecules increased, leading to the decrease of the friction coefficient, as shown in Fig. 4a.

We also performed MD simulations with different pore sizes \( H = 4, 5, 6, \) and 9 Å. Figure 9 plots the friction coefficient versus the number of confined water molecules. For each pore size, water molecules continue to fill the pore until water density reaches 1.0. It can be seen from this figure that the trend of the friction coefficient versus the number of water molecules is the same for all pore sizes. When pores were filled with liquid water, friction coefficients were about 0.30 for all hydrophilic pores. Friction coefficients for all hydrophobic pores are all around 0.17 regardless of the number of water molecules in the pores. When each pore was fully filled with water molecules, our results showed that the normal load on the monolayers exhibited oscillation with pore size.

It was observed from MD simulations that the tilt direction of molecular chains in monolayers changed when two Si(111) surfaces were sheared against each other if the initial configurations of alkyl chains for both top and bottom Si(111) surfaces have opposite tilt directions. Figure 10
shows a sequence of snapshots of hydrophilic monolayers and confined water molecules from MD simulations. At the initial stage, the monolayers have two opposite tilt directions, as shown in Fig. 10(a). At $t = 3.0$ ps, the tilt direction of molecular chains for the monolayers on the top started to change toward the direction opposite to shear. Since the monolayers became disordered in this intermediate stage, a few water molecules penetrated into the monolayers. However, the penetrated water molecules were squeezed out the monolayers at $t = 10.0$ ps, where the monolayers completely changed their tilt directions. After $t = 10.0$ ps, the system reached steady state. The configuration at steady state can be seen from Fig. 10(d), in which no water molecules are inside the monolayers and molecular chains of the monolayers tilt opposite to the sliding direction.

IV. CONCLUSIONS

Molecular dynamics simulations were performed to study the nanoscale friction of alkyl monolayers terminated with different groups of -OH and -CH$_3$ on Si(111) in the presence of water molecules, corresponding to different relative humidities. To the best of our knowledge, this is the first molecular simulation study on the nanoscale friction of alkyl monolayers on Si(111). For surfaces covered by hydrophilic monolayers (terminated with 50% -OH and 50% -CH$_3$), the friction coefficient decreases quickly, whereas it remains almost the same for surfaces covered by hydrophobic monolayers (terminated with -CH$_3$), as the number of water molecules increases. The dependence of the friction coefficient on adsorbed water molecules for both hydrophilic and hydrophobic pores is consistent with that from SFM measurements. With the increase of the number of water molecules, the lateral force increases much slower than the normal force, leading to the decrease of the friction coefficient.

Water molecules confined between two surfaces covered by hydrophobic or by hydrophilic monolayers behave differently. Water molecules adsorb closer to the surfaces along the Z direction for hydrophilic than hydrophobic pores since hydrogen bonds form between water molecules and -OH terminal groups on hydrophilic monolayers. As the increase of the number of water molecules confined between hydrophilic monolayers, water molecules show a layering behavior, which may be responsible for the decrease of the friction coefficient. A fundamental understanding of nano-scale friction is critical to the design of coatings for MEMS/NEMS.

ACKNOWLEDGMENTS

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