Molecular Simulation Study of Alkyl Monolayers on Si(111)

Luzheng Zhang†
Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506
Karen Wesley
Division of Engineering, Brown University, Providence, Rhode Island 02912
Shaoyi J. Jiang*
Department of Chemical Engineering, University of Washington, Seattle, Washington 98195

Received April 30, 2001

Molecular mechanics and molecular dynamics simulations were performed to search for the optimal packing structure of C18 alkyl monolayers on a Si(111) surface. The optimal molecular packing was found based on the consideration of three major factors: molecular substitution, substitution pattern, and molecular orientation on the Si(111) surface. Ab initio quantum chemical calculations were also performed to validate the force field used for the alkyl/Si(111) system. It was shown that the optimal packing structure was size-independent when it was extended to large systems. Molecular dynamics simulation results based on the optimal packing structure in a temperature range from 50 to 500 K agree with those from experimental measurements for various properties, including system and molecular tilt angles, film thickness, and gauche defects. The optimal packing structure found in this work is a basis for further molecular simulation study of alkyl monolayers on silicon for various engineering applications, such as adhesion and friction reduction in micro- or nanoelectromechanical systems.

1. Introduction

Self-assembled monolayers (SAMs) are one of strategies used for minimizing stiction and reducing adhesion and friction in micro- or nanoelectromechanical systems (MEMS/NEMS). Alkyl monolayers on silicon traditionally rely on siloxane chemistry on oxidized surfaces. The alternative approach is the direct thermal reaction between alkenes and H-terminated silicon surfaces to form stable organic films via Si–C linkage. Other methods such as electrochemistry were used by various groups. This 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. (vi) The film is stable up to 615 K. The direct reaction between alcohols and H-terminated or Cl-terminated silicon has also been proposed to form stable organic films via Si–O linkage.

Alkyl molecular chains are covalently bound to the Si(111) surface, resulting in stable monolayers. Surface functionalization and modification can be further performed on the monolayers for various applications, such as biosensors and MEMS/NEMS. A fundamental understanding of the structures of the monolayers is needed for further simulation studies of the monolayers for their applications. Various techniques including scanning probe microscopy (SPM), IR spectroscopy, contact angle goniometry, ellipsometry, X-ray reflectivity, and X-ray photoelectron spectroscopy (XPS) measurements have been used to characterize these thin films. However, measurements by different techniques have produced quite different results in various properties. For example, film thickness measured by X-ray reflectivity and by ellipsometry differs as much as 4 Å. Recently, Sieval et al. performed molecular mechanics (MM) simulations to study the molecular packing structures of C18 alkyl monolayers on Si(111). However, they found that the molecular packing structures were size-dependent. That is, packing energies decreased when the packing structures were extended to large systems. It is therefore

† Current address: Department of Chemical Engineering, University of Washington, Seattle, Washington 98195.
* To whom correspondence should be addressed. E-mail: sjiang@u.washington.edu.

© 2001 American Chemical Society
Published on Web 09/05/2001

10.1021/la0106337 CCC: $20.00

Langmuir 2001, 17, 6275–6281
necessary to re-examine the structures found in those simulations and to search for an optimal packing structure of alkyl monolayers on Si(111).

In this work, we first performed MM simulations to obtain the detailed packing structures of C₁₈ alkyl mono-

layers on Si(111). The flat Si(111) (1 × 1) surface is capped with only one hydride to satisfy the tetravalency of the silicon atoms, whereas Si(100) (1 × 1) is capped with more than one hydride. H-terminated Si(111) surfaces prepared by standard wet chemical treatments in fluoride solutions are among the best substrates to start with because they can be prepared flat at the atomic level and are chemically homogeneous. Thus, Si(111) surface was used in this work. Previously, Klein and co-workers found that temperature has an effect on the properties of alkanethiol monolayers on Au(111). Tilt angles at room temperature could be very different from those at 0 K. Thus, molecular dynamics (MD) simulations were then performed on the optimal molecular packing structure at different temperatures to study various properties of alkyl monolayers on Si(111). To validate the force field for alkyl/Si(111), ab initio quantum chemical (QC) calculations were carried out. The detailed information on the optimal molecular packing from this work will provide a basis for further molecular simulation study of alkyl monolayers on silicon for various engineering applications, such as adhesion and friction reduction in MEMS/NEMS.

2. Computational Approach

All MM and MD studies were performed using CERIUS² (version 4.2) from Molecular Simulations Inc. The modules Minimizer and Dynamics Simulation were used for MM and MD simulations, respectively. The universal force field (UFF) was employed in these simulations. Ab initio QC calculations were carried out using AGUAR (version 4.0) from Schrödinger Inc.

The unit cell for MM studies consists of four Si atoms in four layers and one terminated hydrogen atom on the surface. It has a dimension of 3.840 Å × 3.840 Å. This (1 × 1) unit cell was then extended in two dimensions to generate simulation cells (e.g., (2 × 1), (2 × 2), (2 × 3), and (2 × 4)) using the Surface Builder module in CERIUS². C₁₈ alkyl molecular chains were preoptimized, and then replaced H atoms were used to terminate the Si(111) surface.

Molecular substitution, substitution pattern, and molecular orientation on Si(111) are three important factors to be considered for the characterization of the monolayers. Molecular substitution will determine the percentage of the terminated hydrogen atoms on Si(111) being replaced by alkyl molecules for an optimal packing structure when a reaction occurs. The optimal molecular substitution was determined by comparing molecular packing energies when different percentages of hydrogen atoms on Si(111) were replaced. For a specific molecular substitution, different substitution patterns could be formed when terminated hydrogen atoms at different locations on the surface were substituted. The substitution pattern will determine which terminated hydrogen atoms will be replaced by alkyl chains. The optimal substitution pattern was found by comparing molecular packing energies per chain from these patterns. Since molecular chains on the Si(111) surface may have different orientations, the optimal packing structure was found by considering molecular orientations of alkyl on Si(111). Taking into account these three factors, the optimal structure of alkyl monolayers on Si(111) will be obtained by MM simulations.

Molecular packing energies were determined by excluding substrate Si atoms and terminated H atoms on the surface. The low-energy structures were characterized by analyzing a variety

![Figure 1](image.png)

**Figure 1.** A cluster used in ab initio quantum chemical calculations. Si atoms are terminated by hydrogen atoms (the smallest balls).

of properties, such as system and molecular tilt angles and film thickness. The system tilt angle is defined as the one between surface normal and the vector from the first to the last carbon atom in a molecular chain. The molecular tilt angle is an average value of the angles between surface normal and the vectors from two bisection points of adjacent C–C bonds. The low-energy structures were extended to larger systems in two dimensions. The larger systems were also minimized to check the dependence of molecular packing structure on system size. The agreement in packing energy per chain among the systems of different sizes allows one to find the optimal packing structure. In MM simulations, Si substrate atoms were fixed, but it was found that relaxing the substrate Si atoms has a negligible effect on simulation results.

MD simulations were performed on the optimal molecular packing structure at different temperatures. The simulation temperature was varied from 50 to 500 K. The Crystalline module in CERIUS² was used to build the simulation cells for these simulations. Three-dimensional periodic boundary conditions (PBC) were applied to the simulation cells. A vacuum of 20 Å in height was placed on the top of the monolayers. The detailed molecular structures from MD simulations were analyzed in the same way as we did in MM simulations. Simulation results (molecular and system tilt angles and film thickness) were compared to those from experimental measurements. The structures at various temperatures from MD simulations were also characterized by a gauche factor, representing overall gauche defects in molecular chains. The gauche defects in molecular chains were determined by analyzing torsion angles. If a torsional angle in molecular chains is different from that in the all-trans conformation (±180°) by more than ±10°, it is defined as a gauche defect. The gauche factor is defined as the fraction of the number of gauche defects over the total number of torsion angles in molecular chains.

All QC calculations were carried out at the Hartree–Fock (HF) level using the LAV3P** basis set. The LAV3P** uses the Hay and Wadt effective core potential (ECP) for the atoms Na–La and Hf–Bi and an all-electron 6-31G basis description for atoms H–Ne. The clusters consist of –CH₂–CH₃ adsorbed on one surface site atom (Si) and one (or two) layers of Si atoms which are closest to the surface site. Si atoms in the clusters were terminated by hydrogen atoms. The UFF for the alkyl/Si(111) system was validated by these ab initio results.

3. Results and Discussion

3.1. Ab Initio and Molecular Mechanics Calculations

The UFF of CERIUS² was used in all MM and MD simulations. Ab initio QC calculations of clusters were performed to validate the UFF. One cluster is shown in Figure 1, in which one layer of neighbor Si atoms is included. It consists of 2 C atoms, 4 Si atoms, and 14 H atoms. The Si–C bond length and Si–C–C bending angle from ab initio calculations were 1.91 Å and 109.5°, respectively. MM calculations based on the UFF were performed on C₁₈ alkyl/Si(111). The Si–C bond length from MM was 1.90 Å, which is in good agreement with the one

(19) CERIUS², version 4.2, MatSci; Molecular Simulations Inc.: San Diego, CA, 2000.
(20) J AGUAR, version 4.0; Schrödinger, Inc.: Portland, OR, 2000.
from ab initio calculations. In fact, the experimental value of the Si–C bond is about 1.87 Å. The bending angle Si–C–C (112°) from MM was also close to the ab initio result. Since the UFF reproduces ab initio results well, the default parameters in the UFF were kept for further MM and MD simulations in this work. When one more layer of neighbor Si atoms was included, the cluster contained 10 Si atoms. It was found that the Si–C bond length increased by 0.01 Å and the Si–C–C angle remained the same, indicating that inclusion of the first layer of Si atoms in the cluster was sufficient to mimic Si(111) structure.

The optimal molecular packing structure of alkyl on Si(111) was obtained in MM simulations by taking into account the three factors discussed in the previous section. To consider the first factor, molecular substitution, a series of MM simulations were performed on various simulation cells in which different numbers of hydrogen atoms on the Si(111) surface were replaced by alkyl molecular chains, leading to different percentages of molecular substitution. The simulation cells were obtained by extending the unit cell in two dimensions \((nx \times ny)\), where \(nx\) and \(ny\) are the numbers of the unit cell repeated in the \(x\) and \(y\) directions, respectively. Figure 2a presents various simulation cells of different percentages of molecular substitution by extending the unit cell in two dimensions \((2 \times 1), (2 \times 2), (3 \times 1), (3 \times 1), (2 \times 2), (1 \times 1)\), and \((2 \times 1)\). The packing energies per molecular chain were calculated based on minimized structures when substrate Si atoms and hydrogen atoms were excluded. Figure 2b shows the molecular packing energies per chain as a function of the percentages of molecular substitution. A substitution of about 50% has the lowest energy among all substitutions. This result is in agreement with those from the simulation work by Sieval et al. and from experimental observation by Linford et al., in which ~53% substitution was found to be favorable.

When the H-terminated surface does not occur with 100% substitution, there are a few substitution patterns on the surface for a specific substitution percentage. To consider the second factor, substitution pattern, a number of different molecular patterns were placed on the Si(111) surface to generate initial structures at the specified 50% molecular substitution. Figure 3 depicts the simulation cells, which form various substitution patterns when molecular substitution was fixed at 50%. Patterns a, b, and c were obtained by extending the unit cell in two dimensions \((2 \times 1), (2 \times 2), (2 \times 3)\), and \((2 \times 4)\). MM simulations were then performed on these structures of different substitution patterns. Molecular packing energies per chain for these patterns are listed in Table 1. As shown in Table 1, the packing energy per chain from pattern i is the lowest. Packing energies for patterns b–f are relatively low. However, patterns d–j formed disordered packing structures from MM simulations, even if their molecular packing energies were low. For those patterns, molecular chains were packed very closely and molecular interactions made chains twist, resulting in disordered packing structures. For patterns b and c, no disordered packing was found from MM results. Therefore, patterns b, c, and i were used for further study on how molecular orientations affect packing structures. It was found in previous studies by Sieval et al. that pattern i was favorable. Recent simulation results by the same group

Figure 2. (a) Simulation cells for various percentages of molecular substitution and (b) packing energy per chain vs percent substitution for C\(_{18}\) alkyl on Si(111) from MM simulations.

Figure 3. Simulation cells of different substitution patterns at 50% molecular substitution. The solid circles represent substituted sites. The open circles represent unsubstituted sites. These simulation cells were obtained by extending the unit cell in two dimensions: a, \((2 \times 1)\); b, \((2 \times 2)\); c, \((2 \times 3)\); d–j, \((2 \times 4)\).
As shown in Figure 5b, two molecular chains orient toward the bottom in molecular chains are all-trans conformation. Carbon atoms except for the first two carbon atoms from the topmost carbon atoms in the molecular chains. A thickness of 17.0 Å was obtained from the simulations.

Table 1. Packing Energies per Chain of C_{18} Alkyl/Si(111) for Different Patterns at 50% Substitution from MM Simulations

<table>
<thead>
<tr>
<th>pattern</th>
<th>simulation cell</th>
<th>packing energy per chain (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>(2 x 1)</td>
<td>-18.9298</td>
</tr>
<tr>
<td>b</td>
<td>(2 x 2)</td>
<td>-21.2022</td>
</tr>
<tr>
<td>c</td>
<td>(2 x 3)</td>
<td>-24.4742</td>
</tr>
<tr>
<td>d</td>
<td>(2 x 4)</td>
<td>-23.4592</td>
</tr>
<tr>
<td>e</td>
<td>(2 x 4)</td>
<td>-23.6487</td>
</tr>
<tr>
<td>f</td>
<td>(2 x 4)</td>
<td>-22.7926</td>
</tr>
<tr>
<td>g</td>
<td>(2 x 4)</td>
<td>-11.1291</td>
</tr>
<tr>
<td>h</td>
<td>(2 x 4)</td>
<td>-5.2649</td>
</tr>
<tr>
<td>i</td>
<td>(2 x 4)</td>
<td>-26.1275</td>
</tr>
<tr>
<td>j</td>
<td>(2 x 4)</td>
<td>-8.8844</td>
</tr>
</tbody>
</table>

*a* The simulation cell in each pattern was obtained by extending the unit cell in two dimensions (nx x ny).

Molecular orientation is the third factor to be considered. Since alkyl molecules could orient in different directions when they covalently bind to the Si(111) surface, there are several orientations for each molecular chain. Figure 4 shows the orientations of one alkyl molecule on pattern I: the nearest neighbors (NN or the first neighbors), the next-nearest neighbors (NNN or the second neighbors), the next-next-nearest neighbors (NNNN or the third neighbors), and so on. On the basis of patterns b, c, and i, a series of starting structures of different orientations were generated. MM simulations were then performed to minimize these structures. By trying various orientations, the lowest-energy structures were found for patterns b, c, and i and termed as packings I, II, and III, respectively. For packing I, the second neighbor orientation was found. For packings II and III, both the second and the third directions were observed for different chains. Table 2 gives molecular packing energies per chain for these structures. As seen from this table, packing III has the lowest energy. The detailed molecular structure of packing III from MM simulations is shown in Figure 5. The side view of this packing in Figure 5a shows that the backbone carbon atoms except for the first two carbon atoms from the bottom in molecular chains are all-trans conformation. As shown in Figure 5b, two molecular chains orient toward the second neighbors (NNN), whereas the other two molecules orient toward the third neighbors (NNNN). Furthermore, the two molecular backbone planes are almost perpendicular to those of the other two molecular chains. Previously, Sieval et al. found that the first torsional angle (Si–C–C–C) varied over a wide range: most values ranged from 0 to 15°, but several molecular chains had torsional angles up to 36°. The first torsional angle was found to be 15° for packing III in this work. For the second torsional angle (C–C–C–C), trans was found in the work by Sieval et al., whereas 162° was observed for packing III in this work. However, the packing structure found by Sieval et al. was size-dependent. The other properties, such as film thickness and molecular system tilt angles, are also presented in Table 2. Film thickness was determined by averaging the z positions of the topmost carbon atoms in the molecular chains. A thickness of 17.0–17.4 Å was obtained from the simulations. In the MM simulations shown above, the substrate was fixed. To see the effect of the relaxed substrate on molecular packing structures of the monolayers, MM simulations were extensively carried out on the structures in which different layers of Si atoms were relaxed. The packing energies per molecular chain are presented in Table 3. As expected, a negligible effect of the relaxed substrate was observed. To reduce computational time for these systems, particularly for extended large systems, the substrate Si atoms in the systems were fixed.

To check the dependence of molecular packing structures on system size, the simulation cells for packings I–III were extended to larger systems in two dimensions.
co-workers found the temperature dependence of various molecular chains. Thermore, two molecular backbone planes are perpendicular to those of the other two molecular chains. Two of the molecular chains orient toward the third neighbors. Furthermore, two molecular backbone planes are perpendicular to those of the other two molecular chains.

Table 3. Packing Energies per Chain for C_{18} Alkyl/Si(111) from MM Simulations When Si Substrate Layers Are Relaxed (kcal/mol)

<table>
<thead>
<tr>
<th>layer relaxed</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 layer</td>
<td>-21.5721</td>
<td>-25.6912</td>
<td>-26.9794</td>
</tr>
<tr>
<td>2 layers</td>
<td>-21.6230</td>
<td>-25.8651</td>
<td>-26.9402</td>
</tr>
<tr>
<td>3 layers</td>
<td>-21.6231</td>
<td>-25.8985</td>
<td>-26.9235</td>
</tr>
<tr>
<td>4 layers</td>
<td>-21.6256</td>
<td>-25.9137</td>
<td>-27.0854</td>
</tr>
</tbody>
</table>

Table 4. Packing Energies per Chain for C_{18} Alkyl/Si(111) in the Extended Systems of Different Sizes from MM Simulations (kcal/mol)

<table>
<thead>
<tr>
<th>size (a)</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>((1 \times 1))</td>
<td>-21.2022</td>
<td>-25.3884</td>
<td>-26.4652</td>
</tr>
<tr>
<td>((2 \times 2))</td>
<td>-21.2019</td>
<td>-25.3884</td>
<td>-26.7525</td>
</tr>
<tr>
<td>((3 \times 3))</td>
<td>-21.2022</td>
<td>-25.3884</td>
<td>-26.7660</td>
</tr>
<tr>
<td>((4 \times 4))</td>
<td>-21.2022</td>
<td>-25.3884</td>
<td>-26.7659</td>
</tr>
<tr>
<td>((5 \times 5))</td>
<td>-21.2022</td>
<td>-25.3884</td>
<td>-26.7659</td>
</tr>
</tbody>
</table>

\(a\) Large systems were obtained by extending the simulation cells (i.e., patterns b, c, and i) in two dimensions.

Figure 6. (a) Side and (b) top views of the molecular packing structure of the extended system with 64 chains from pattern i. The hydrogen atoms are removed from (a) for clarity.

from \((2 \times 2)\) to \((5 \times 5)\), in which 4–64 chains were included. Table 4 presents packing energies per chain in the extended systems of different sizes. Because computational time increases dramatically as the number of particles in the extended system increases, the simulation cell for packing I was extended up to \((5 \times 5)\), in which a total of 50 chains were included, whereas other simulation cells were extended up to \((4 \times 4)\), where 48 chains were included for packing II and 64 chains were included for packing III. Unlike the packing structures found in ref 16, results in Table 4 show that the packing energy per chain is size-independent. One of the extended larger systems (64 chains) from packing III is shown in Figure 6. The properties such as tilt angle, film thickness, and torsional angles remained the same for the extended systems. Simulation results show that packing III is indeed the optimal structure of alkyl on Si(111). Packing III contains four alkyl chains per simulation cell with 50% substitution and a zigzag-like pattern. Two of the molecular chains orient toward the second neighbors, whereas the other two molecules orient toward the third neighbors. Furthermore, two molecular backbone planes are perpendicular to those of the other two molecular chains.

3.2. Molecular Dynamics Simulations. Klein and co-workers found the temperature dependence of various properties of alkanethiols/Au(111) monolayers, such as tilt angle, film thickness, and conformation. Thus, MD simulations were carried out in the work on the optimal packing structure (packing III) in a temperature range from 50 to 500 K. Generally, molecular and system tilt angles become small as temperature increases. Smaller tilt angles result in thicker monolayers. In MD simulations, tilt angles are expected to decrease, whereas film thickness increases as temperature increases. The tilt angle and film thickness of the monolayers are plotted as a function of temperature in parts a and b of Figure 7, respectively. Both system and molecular tilt angles have the similar trend as temperature increases. Linford et al. found that the film thickness of C_{18} alkyl monolayers on Si(111) was 16.0 Å by X-ray reflectivity and 20.0 Å by optical ellipsometry. Wasserman and co-workers found that the measured film thickness by different techniques could have an uncertainty of 2 Å. Recently, a thickness of 19.1 Å was obtained by Sieval et al. It seems that 16 Å is low. The film thickness is 18.1 Å at 300 K from MD simulations in this work. This simulated thickness agrees with those from experimental measurements. On the basis of the thickness from X-ray reflectivity (16.0 Å), a tilt angle of 45° was hypothecated by Linford et al. However, the tilt angle was measured to be about 36°, which is close to 39° obtained from MD results at 300 K in this work. Therefore, the hypothetical model may not be the optimal packing structure. Similarly, the hypothetical torsional angle \((\text{Si}-\text{C}-\text{C}-\text{C})\) of 37° (based on 16 Å film thickness) may not be right. In fact, a torsional angle of \(~28°\) was obtained from MD simulation at 300 K. As an example, Figure 8 shows the detailed molecular packing structure of C_{18} alkyl on Si(111) obtained from MD results at 300 K. The backbone carbon atoms except for the first two carbon atoms from the bottom remain all-trans conformation. It is found that the structure from MD simulations at 300 K is similar to that from MM simulations (Figure 5).

Temperature has an effect not only on tilt angles and film thickness but also on gauche defects. Figure 9 shows the effect of temperature on the gauche factor in molecular chains. The gauche factor is defined as the number of gauche defects over the total number of torsional angles except for the first two torsion angles in all molecular chains of the monolayers. In the case of C_{18} alkyl monolayers, 14 torsional angles in each chain were counted for the calculation of the gauche factor. As shown in Figure 9, the gauche defect changes dramatically with temperature, particularly at high temperatures. When temperature was increased to 500 K, the defect was as large as 35%. Experimental results showed that C_{18} alkyl monolayers were decomposed from the Si(111) surface at 615 K. For the gauche defect, a further analysis revealed that the distribution of the defect within molecular chains is not uniform. We found the topmost carbon atom has the highest defect in molecular chains for all MD simulations. A similar gauche defect distribution was also observed by Klein et al. for the system of alkanethiol SAMs on Au(111).

The optimal molecular packing of C_{18} alkyl monolayers on Si(111) found in this work is a basis for our further molecular simulation study of friction in MEMS/NEMS, in which two Si(111) surfaces coated with alkyl monolayers were constructed based on this optimal molecular packing structure. The two surfaces were then slid against each other in the presence of water molecules to study friction.

in MD simulations, as shown in Figure 10. The monolayers in these simulations consist of 192 alkyl molecular chains terminated by mixed $-\text{OH}$ and $-\text{CH}_3$ groups. Variation of the $-\text{OH}/-\text{CH}_3$ ratio results in different surface hydrophobicities. These further MD simulations will not only provide a fundamental understanding of friction but also guide the design of coatings for MEMS/NEMS devices.

4. Conclusions

Molecular simulations (MM and MD) and ab initio QC calculations were performed to study molecular packing structures of $\text{C}_{18}$ alkyl monolayers on the Si(111) surface. The optimal molecular packing structure was found from MM simulations by considering three factors: molecular substitution, substitution pattern, and molecular orientation on the surface. The optimal molecular packing structure has 50% molecular substitution, a zigzag-like pattern, and orientations such that two of the four molecular chains orient toward the second neighbors (NNN) and the others orient toward the third neighbors (NNNN). The effect of the relaxed substrate on molecular packing is negligible. When simulation cells for substitution patterns b, c, and i were extended to large systems in two dimensions, molecular packing energy per chain...
remained the same, indicating that the lowest-energy structure (packing III) is indeed the optimal molecular packing. Ab initio results were used to validate the UFF used in this work. It was found that the UFF can reproduce ab initio results. MD simulations were performed on the optimal packing structure obtained from MM simulations in a temperature range from 50 to 500 K. A variety of properties such as system and molecular tilt angles, film thickness, and gauche defects were calculated and compared to those from experimental measurements. The film thickness and tilt angles agree with experimental values. As temperature increases, film thickness increases, and system and molecular tilt angles decrease. The gauche defects of the monolayers increase with temperature. The optimal molecular packing structure found in this work is a basis for further molecular simulation study of alkyl monolayers on silicon for various engineering applications, such as adhesion and friction reduction in MEMS/NEMS.

Acknowledgment. The authors thank the National Science Foundation (CAREER Award, CTS-0092699) and the Department of Energy for financial support.

LA0106337