Effects of Temperature and Chain Length on the Nanoscale Islands of Alkanethiol Monolayers

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The thermal effect on the stability of nanoscale islands of alkanethiols on a gold (111) surface was examined using molecular dynamics simulation. To examine the chain length and temperature dependence, islands made of alkanethiols containing 16, 20, and 24 carbon atoms were simulated at 313–343 K. By analyzing the tilt angle, conformation, orientational order, and backbone plane orientation of alkyl chains, the minimum diameters for stable islands made of 1-hexadecanethiol, 1-ecosanethiol, and 1-tetracosanethiol were determined for different temperatures (313–343 K). These results provide a useful guideline for patterning nanopatterns of thiol by soft nanolithography.

Keywords: Self-assembled monolayer, Molecular dynamics simulation, Alkanethiol, Thermal effect

Introduction

Self-assembled monolayers (SAMs) derived from the spontaneous adsorption of organic molecules on metal surfaces have attracted considerable attention for applications in nanoelectronics,[1] bio-devices,[2] alternate wetting behavior,[3] and tribology.[4] SAMs of 10–100 nm in width can be fabricated on various surfaces.[5] Although SAMs of different functional groups on various surfaces have been reported, the SAMs of alkanethiols on gold surfaces have been studied most widely because of the flexibility in changing the aliphatic chain length, the inertness of the gold surface, and the ease of preparation. It has been identified that in bulk SAMs, the adsorbed sulfur atoms of alkanethiols construct a $\sqrt{3} \times \sqrt{3}$ R30° overlayer on a Au(111) surface and are tilted approximately 30° from the surface normal.[6]

Previously, the chain length dependence of the stability of nanoscaled SAM was studied. Molecular dynamics (MD) simulations revealed the critical nuclei sizes of stable SAMs on Au(111) to be 2.29, 1.90, 4.70, and 4.76 nm in diameter for 1-tetracosanethiol, 1-ecosanethiol, 1-hexadecanethiol, and 1-dodecanethioland, respectively.[7] However, another important consideration in the application of SAMs is the thermal effect on their stability. Usually, it is essential for the films to withstand the temperatures used in the subsequent processing and packaging steps. Maboudian and coworkers reported the formation of stable SAMs of aklyltricholorosilane on an oxidized Si (100) surface up to 740 K; the alkyl chains decomposed above this temperature.[8] Uosaki and coworkers examined the effect of the temperature on the domain sizes of SAMs. Large well-ordered SAM domains formed from a solution at higher temperature.[9] Vashishta and coworkers studied the structural properties of SAMs by varying the temperature and chain length alkanethiol. They reported that at 350 K, SAMs of 13-carbon alkanethiol deformed.[10] Martin and coworkers compared the variance in the structures of alkanthiol SAMs on the Au (111) and Ag (111) surface with varying temperatures and chain lengths. They found that the average tilt angle of the alkane chain increases slightly with increasing chain length but its variation was small when the temperature was lowered from room temperature.[11]

Because SAMs can be fabricated and have versatile applications at higher temperatures, it is important to examine the impacts of temperature and chain length on the stability of nanoscaled SAM islands of alkenthiols. In SAMs, the surface-head groups and chain–chain interactions play important roles in their stability.[12] A decrease in the size of a SAM island will lessen the interchain packing and crystalline assembly of sulfur headgroups. Below a threshold size, the SAM island will be destabilized, losing its ordered structure. The present study estimated the thresholds for the sizes of stable SAM islands with varying chain lengths of alkanethiols on a Au(111) surface at different temperatures. The structural properties, such as tilt angle, orientational order, and conformations of alkyl chains as well as the compaction of adsorbed sulfur atoms were examined.

Simulation Details

SAM islands made of *n*-alkanthiols with different chain lengths were simulated on a gold (111) surface. The surface consisted of two layers of 12,800 gold atoms. The positions of the gold atoms were fixed. The periodic boundary conditions were applied with a minimum image convention.[13] Three *n*-alkanethiols were considered as SAM molecules:

1-tetracosanethiol, $SH(CH_2)_{23}CH_3$, (C24 thiol), 1-ecosanethiol, $SH(CH_2)_{19}CH_3$, (C20 thiol), and 1-hexadecanethiol, $SH(CH_2)_{15}CH_3$, (C16 thiol). The CH_3, CH_2, and SH groups of *n*-alkanethiol molecules were treated as united atoms (UAs) to reduce the simulation time.[14,15] The tilt angle, conformation, orientational order, backbone orientation of alkyl chain, and packing of adsorbed sulfur atoms were calculated by following the previous methods.[7,16,17] The bond stretching and bending angle interactions between the UAs were modeled by the harmonic potentials.[18] The four-atom torsion potential (C—C—C—C or C—C—C—S) was modeled using a triple cosine function of the dihedral angle φ, which has minima corresponding to the *trans* ($\varphi = \pm 180^\circ$) and gauche ($\varphi = \pm 60^\circ$) conformations.[18] All nonbonded interactions were the Lennard–Jones (LJ) potentials,

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (1)$$

where r is the intermolecular distance, and ε and σ are the LJ energy and length parameters, respectively.[15] The Lorentz–Berthelot combination rules[13] were used for the LJ parameters of the hetero atomic pairs. The S–Au pair interaction (chemisorptions) was modeled using the Morse potential,[19]

$$V_{Au\text{-}S}(r) = D_e \exp[-\alpha(r-r_e)]\{\exp[-\alpha(r-r_e)]-2\} \quad (2)$$

where D_e and r_e are the well depth and distance at the minimum of the potential energy, respectively. Table 1 lists the LJ and Morse parameters.

First, a circular SAM of 90 C24 thiols was prepared, where all thiol molecules were in the upright position on a gold surface. The MD simulations were performed at 1.0 K to relax the system and equilibrate the initial configuration at room temperature for 2 ns. The adsorbed S atoms of the C24 thiol molecules formed a $\sqrt{3}\times\sqrt{3}R30^\circ$ overlayer on the gold (111) surface.[6] From this equilibrated SAM island, circular SAM islands consisting of 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, and 10 molecules were generated. A similar procedure was followed for C20 and C16 thiol molecules. A 10-ns-long MD simulation was then run for each SAM island (N_{thiol} = 10–70) at four temperatures (313, 323, 333, and 343 K) using the Berendsen thermostat.[20] The equation of motion was integrated using the velocity Verlet algorithm with a time step of 1.0 fs. All MD simulations were carried out using the DL_POLY package.[21]

The diameter of a SAM island was estimated by selecting the adsorbed S atoms at the periphery (an S atom with less than six neighboring S atoms within a distance of 5.5 Å was taken to be at the periphery). The average SAM diameter was calculated by taking the average over 800 MD snapshots.

Table 1. LJ and Morse potential parameters of united atom models.

LJ			
Atoms	σ (Å)		ε (kcal/mol)
SH	4.250		0.397
CH_3	3.905		0.175
CH_2	3.905		0.118
Au	2.935		0.039
Morse			
Atoms	D_e (kcal/mol)	r_e (Å)	α
Au-SH	8.763	2.65	1.47

Results and Discussion

The MD snapshots of the SAM islands were examined at different temperatures. Figure 1 presents a side view of the SAM islands containing 65 C16 (left column), C20 (middle column), and C24 (right column) thiol molecules at different temperatures. From the top, the snapshots of SAM islands at 10 ns were shown for 313, 323, 333, and 343 K. At 313 K, all the SAM islands were stable because all molecules were packed together and upright with slight tilting. The sulfur atoms of the thiol molecules developed a $\sqrt{3}\times\sqrt{3}R30^\circ$ overlayer on the Au(111) surface. With

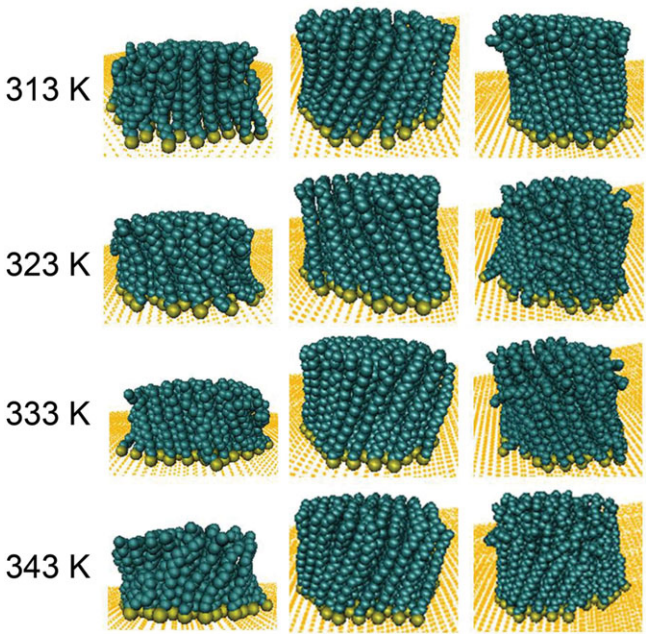

Figure 1. Stable SAM islands of alkanethiols with various chain lengths at different temperatures. Shown are the side views of the SAM islands made of C16 (left column), C20 (middle column), and C24 (right column) thiols at different temperatures. Each island was comprised of 65 molecules. The gold atoms are shown as dots.

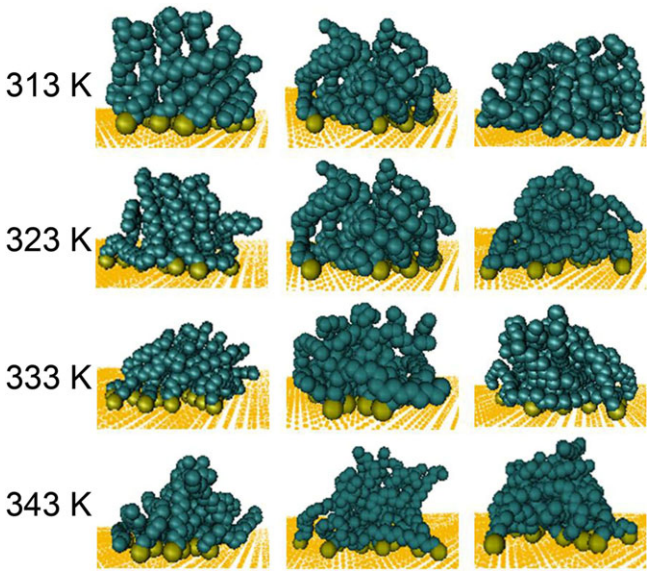

Figure 2. Unstable small SAM islands. Shown are the side views of SAM islands made of C16 (left column), C20 (middle column), and C24 (right column) thiols at different temperatures. Each SAM island was made of 15 molecules.

increasing temperature, the thiol molecules are more mobile. A few thiol molecules at the periphery of the SAM island separated momentarily from the island but returned to their original position immediately. The alkyl chains folded and unfolded frequently.

In Figure 2, the left, middle, and right columns show the side views of the SAM islands containing 15 molecules of C16, C20, and C24 thiol, respectively. Here, the snapshots at 10 ns were taken at temperatures between T = 313 K and T = 343 K in steps of 10 K. At 313 K, few thiol molecules lie down on the surface and the remainder are in the upright position. Their alkyl chains folded and unfolded frequently. Similar behavior was observed in every SAM island. When the temperature was increased, thiol molecules are dispersed due to enhanced thermal motion. Although the chain–chain interaction prevented them being apart from each other, the sulfur–sulfur distance increased with temperature. Consequently, the sulfur atoms could not develop a $\sqrt{3} \times \sqrt{3}$ R30° overlayer on Au(111). As a result, the SAM islands could not form a compact and stable structure.

Figure 3 plots the sulfur–sulfur distance (d_{SS}) as a function of the number of molecules N_{thiol} at different temperatures. The solid circles, solid triangles, and solid squares denote the results for C16 thiol, C20 thiol, and C24 thiol, respectively. The d_{SS} decreases with increasing N_{thiol} and levels off. As temperature was increased, the d_{SS} values leveled off at higher values of N_{thiol}. This means, with increasing temperature, more molecules (a bigger island) are needed to have a stable SAM island.

Figure 4 plots the tilt angle of the alkyl chains as a function of N_{thiol} with varying temperature. In the SAM island with N_{thiol} = 10, the thiol molecules cannot be upright.

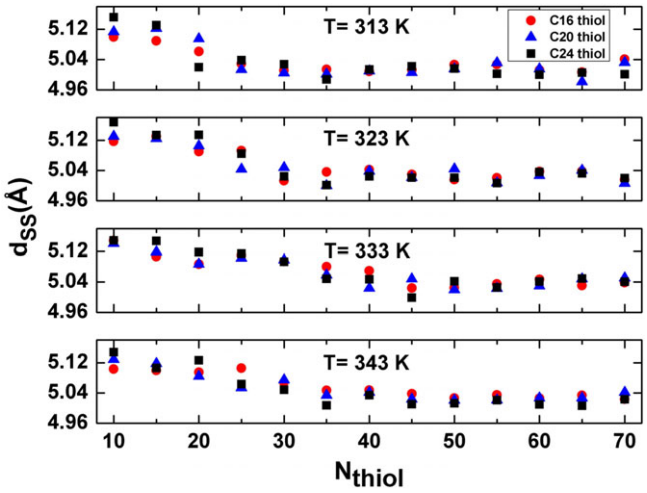

Figure 3. The mean distance between neighboring sulfur atoms (d_{SS}) vs. the number of alkanethiols (N_{thiol}) comprising the SAM islands.

They change their tilting direction frequently and sometimes bend down to the surface. As the sulfur head groups are chemisorbed on the gold surface and the alkyl chains cannot be straight, they twist. Here, the chain–chain interaction is not sufficient to keep them in the upright position. Because of this, the tilt angle of this small-sized SAM island is large. With increasing N_{thiol}, the tilt angle decreases and levels off at N_{C24} = 20, N_{C20} = 25, and N_{C16} = 30 at 313 K. When the temperature is increased, the number of thiol molecules in the SAM islands needs to increase to reach a plateau in the angle.

At 323 K, the tilt angle levels off at N_{C24} = 25, N_{C20} = 30, and N_{C16} = 30. At 333 K, the tilt angle levels off at N_{C24} = 30, N_{C20} = 35, and N_{C16} = 40. At 343 K, the lowest size of SAM islands are N_{C24} = 35, N_{C20} = 40, and N_{C16} = 45.

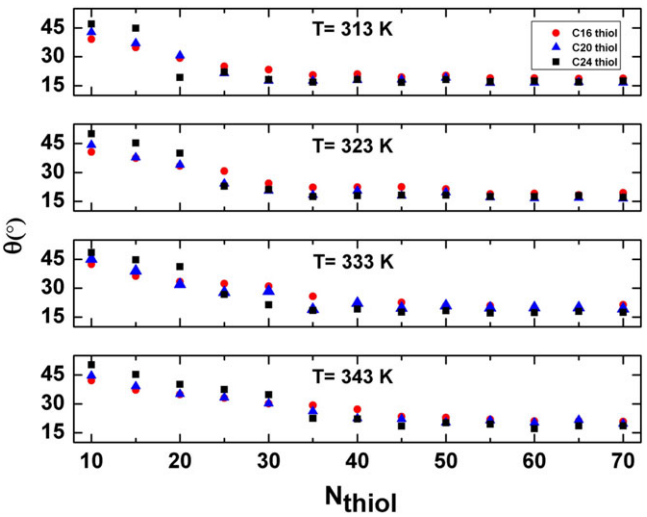

Figure 4. Average tilt angle (θ) of alkyl chains vs. N_{thiol} comprising the SAM islands at different temperatures.

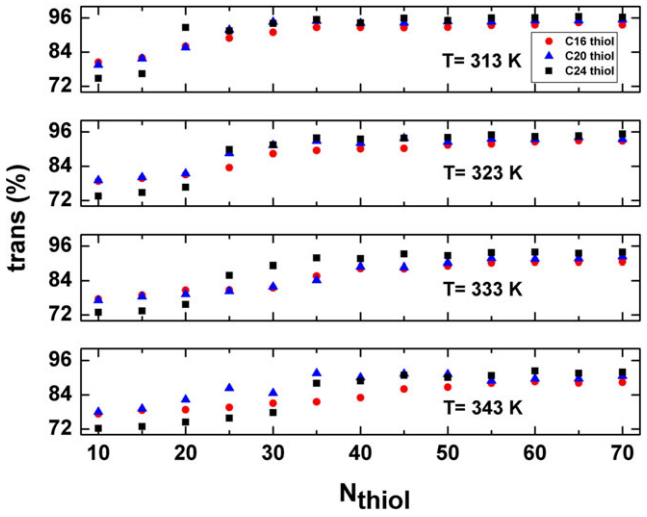

Figure 5. Percentage of the *trans* conformation of alkyl chains vs. N_{thiol} in SAM islands made of three different alkanethiols at various temperatures.

The percentage of the *trans* conformation of the alklyl chains are plotted vs. N_{thiol} (Figure 5). In small SAM islands, the molecules change their tilt direction frequently and the percentage of the *trans* conformation of alkyl chains is low. When the island size is increased, the thiol molecules do not change their tilt direction frequently and they are in the upright position due to the chain–chain interaction. The *trans* conformation increases in proportion and the island becomes stable. The threshold values where the percentage of *trans* conformation levels off are N_{C24} = 20, N_{C20} = 25, and N_{C16} = 30 at 313 K; N_{C24} = 25, N_{C20} = 30, and N_{C16} = 35 at 323 K; N_{C24} = 30, N_{C20} = 35, and N_{C16} = 40 at 333 K, and N_{C24} = 35, N_{C20} = 40, and N_{C16} = 45 at 343 K.

The effect of temperature on the orientational order of the alkyl chains was examined as a function of N_{thiol}. Figure 6 shows the order parameter of the tilt direction,[17]

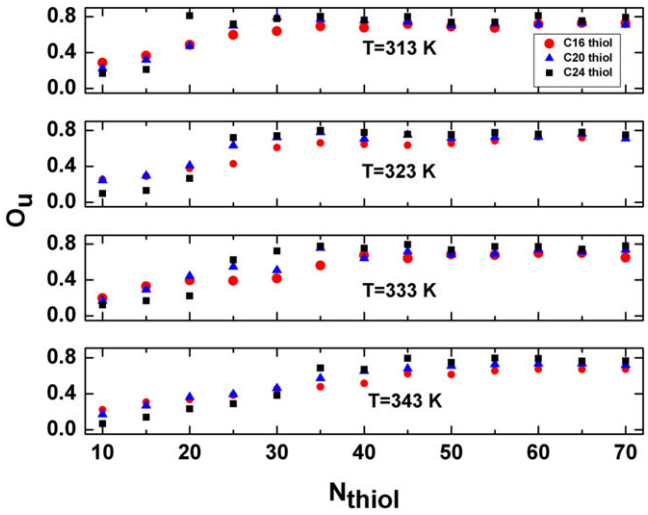

Figure 6. Order parameter of the tilt direction of alkyl chains vs. N_{thiol} for different temperatures.

O_u, vs. N_{thiol}, at different temperatures. As for the other structural properties above (tilt angle and *trans* conformation), O_u increased and plateaued with increasing N_{thiol}. With increasing temperature, the plateau shifted to a higher N_{thiol} value. At 313 K, the plateau of O_u was reached at N_{C24} = 20, N_{C20} = 25, and N_{C16} = 30; N_{C24} = 25, N_{C20} = 30, and N_{C16} = 35 at 323 K; N_{C24} = 30, N_{C20} = 35, and N_{C16} = 40 at 333 K; and N_{C24} = 35, N_{C20} = 40, and N_{C16} = 45 at 343 K.

Regardless of temperature, the converged O_u with increasing N_{thiol} for the C24 and C20 islands was higher than C16. This means that the long alkane thiols are more ordered in orientation than the short alkanethiols. All the O_us were less than 1.0, meaning that the ordering of alkyl chains is not complete.

Conclusion

The present simulation examined the effects of temperature on the size limit of SAM islands of alkanethiol chains with various lengths. The structural properties of the SAM islands were studied by examining the tilt angle, conformation, and orientational ordering of the alkyl chains as well as the packing of S atoms. Regardless of temperature, the number of molecules comprising the SAM islands must exceed a threshold to give an ordered and stable SAM island. At 313 K, the threshold values were 20, 25, and 30 for C24, C20, and C16 thiol, respectively. If the temperature is increased by 10 K, five or more molecules were needed to give stable SAM.

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References

1. F.-R. F. Fan, J. Yang, L. Cai, D. W. Price, S. M. Dirk, D. V. Kosynkin, Y. Yao, A. M. Rawlett, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2002**, *124*, 5550.
2. T. Wink, S. J. van Zuilen, A. Bult, W. P. van Bennekom, *Analyst* **1997**, *122*, 43R.
3. S.-J. Chun, S.-Y. Lee, G.-Y. Jeong, J. H. Kim, *J. Ind. Eng. Chem.* **2012**, *18*, 1122.
4. I.-H. Sung, J.-C. Yang, D.-E. Kim, B.-S. Shin, *Wear* **2003**, *255*, 808.
5. P. Manandhar, J. Jang, G. C. Schatz, M. A. Ratner, S. Hong, *Phys. Rev. Lett.* **2003**, *90*, 115505.
6. A. Ulman, *Chem. Rev.* **1996**, *96*, 1533.
7. J. K. Saha, *Bull. Korean Chem. Soc.* **2013**, *34*, 3790.
8. G. J. Kluth, M. M. Sung, R. Maboudian, *Langmuir* **1997**, *13*, 3775.
9. R. Yamada, H. Wano, K. Uosaki, *Langmuir* **2000**, *16*, 5523.
10. S. Vemparala, B. B. Karki, R. K. Kalia, A. Nakano, P. Vashishta, *J. Chem. Phys.* **2004**, *121*, 4323.
11. Y. Wang, J. G. Solano Canchaya, W. Dong, M. Alcamí, H. F. Busnengo, F. Martín, *J. Phys. Chem. A* **2014**, *118*, 4138.

12. F. Schreiber, *Prog. Surf. Sci.* **2000**, *65*, 151.
13. M. P. Allen, D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, New York, 1987.
14. P. K. Ghorai, S. C. Glotzer, *J. Phys. Chem. C* **2007**, *111*, 15857.
15. J. Hautman, M. L. Klein, *J. Chem. Phys.* **1989**, *91*, 4994.
16. Y. Ahn, J. K. Saha, G. C. Schatz, J. Jang, *J. Phys. Chem. C* **2011**, *115*, 10668.
17. J. K. Saha, Y. Ahn, H. Kim, G. C. Schatz, J. Jang, *J. Phys. Chem. C* **2011**, *115*, 13193.
18. W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **1996**, *118*, 11225.
19. X. Zhao, Y. Leng, P. T. Cummings, *Langmuir* **2006**, *22*, 4116.
20. H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* **1984**, *81*, 3684.
21. W. Smith, C. W. Yong, P. M. Rodger, *Mol. Simul.* **2002**, *28*, 385.

