

Surface Potential Change Depending on Molecular Orientation of Hexadecanethiol Self-Assembled Monolayers on Au(111)

Eisuke Ito,* Takayuki Arai,[†] Masahiko Hara,[†] and Jaegeun Noh^{*,‡}

Flucto-order Functions Asian Collaboration Team, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

*E-mail: eito@riken.jp

[†]Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midoriku, Yokohama 226-8502, Japan

[‡]Department of Chemistry, Hanyang University, Seoul 133-791, Korea. *E-mail: jgnoh@hanyang.ac.kr

Received March 24, 2009, Accepted April 13, 2009

Surface potential and growth processes of hexadecanethiol (HDT) self-assembled monolayers (SAMs) on Au(111) surfaces were examined by Kelvin probe method and scanning tunneling microscopy. It was found that surface potential strongly depends on surface structure of HDT SAMs. The surface potential shift for the striped phase of HDT SAMs chemisorbed on Au(111) surface was +0.45 eV, which was nearly the same as that of the flat-lying hexadecane layer physisorbed on Au(111) surface. This result indicates that the interfacial dipole layer induced by adsorption of alkyl chains is a main contributor to the surface potential change. In the densely-packed HDT monolayer, further change of the surface potential was observed, suggesting that the dipole moment of the alkanethiol molecules is an origin of the surface potential change. These results indicate that the work function of a metal electrode can be modified by controlling the molecular orientation of an adsorbed molecule.

Key Words: Surface potential, Work function change, Self-assembled monolayer, Kelvin probe method, Scanning tunneling microscopy

Introduction

A change in the work function of an organic layer on metal surfaces is typically observed, which is considered to be due to the formation of an interfacial dipole layer at or near the interface from a charge transfer reaction, image-force effect, and/or rearrangement of the electrons on the metal surface.^{1,2} In addition to these factors, the orientation of the polar organic molecules is expected to induce the polarization in the film, further contributing to the work function change.³

Self-assembled monolayers (SAMs) on metal surfaces have attracted much attention not only because of their potential use in molecular electronic devices but also for modifying the surface properties of metal electrodes. It is expected that dipole-aligned SAMs can be fabricated from molecules containing a polar functional group, resulting in a surface potential change or work function change. Indeed, control of the work function of a metal electrode by SAM formation is one of the key issues necessary to improve the carrier injection in organic electronic devices.⁴⁻¹⁹ Previous studies have investigated surface potential of organic SAMs,⁴⁻¹³ and the observed surface potential change was explained as the aligning the dipole moment of the molecule and/or the charge transfer in the S-Au bond.

Conversely, surface potential value should vary with the molecular orientation. Indeed, it was recently found that the surface potential depends upon the molecular orientation in the SAM. Howell *et al.* measured the surface potential of π -conjugated molecules and found that there is a slight change in surface potential of a xylyldithiol monolayer possessing a lying orientation.⁹ Further, Ichii *et al.* reported that the surface potential of the standing 1-dodecanethiol is 100-150 mV higher than that of the lying 1,10-dodecanedithiol.¹⁰ In both cases, the

surface potential decreases for molecules in lying orientation compared to those in a standing orientation, as the directions of the dipole moments in such molecules lie along the molecular axis.

To more clearly elucidate the effect of molecular dipole moments on modification of the surface potential, it is essential to measure the surface potential of other molecular systems with a different adsorption configuration on their surface. In this study, we investigated the relationship between surface potential change and the adsorption configuration of *n*-hexadecanethiol (HDT, CH₃(CH₂)₁₅SH) during SAM formation using a Kelvin probe method and scanning tunneling microscopy (STM), respectively. On the basis of nanometer-scale STM observation, we compared the surface potential of the striped phase, in which the molecular axis is oriented parallel to the surface with that of the standing-up phase where the molecular axis is oriented vertical to the surface. In addition, to examine the effect of the binding condition of molecules on surface potential, we compared the surface potential measured from the striped phase of HDT SAMs chemisorbed on a Au(111) surface with that measured from a *n*-hexadecane (HD, CH₃(CH₂)₁₄CH₃) physisorbed on a Au(111) surface. Although the alkyl chains are in a flat-lying orientation for both systems, the interactions between the molecules and the Au surface are different.

Experimental Section

HDT was purchased from TCI, and used without further purification. Au(111) surfaces were prepared by vacuum deposition of Au on cleaved mica plates, as the same procedure in the previous paper.²⁰ HDT SAMs were prepared by immersion of the Au surface into the 1 μ M or 10 μ M ethanolic

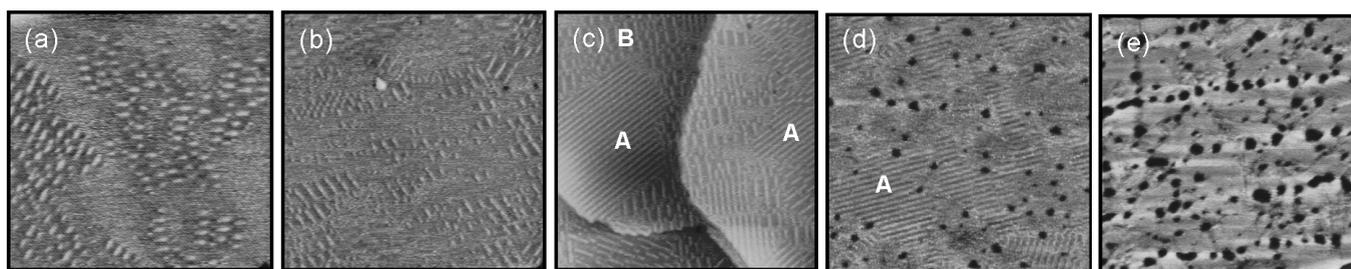


Figure 1. STM images showing the growth process of HDT SAMs on Au(111) after immersion of Au(111) surfaces in a 1 μM solution as a function of immersion time: (a) 1 min, (b) 5 min, (c) 10 min, (d) 30 min, and (e) 24 h. The scan size of all STM images is 120 nm \times 120 nm.

solution of HDT. After immersion, the samples were rinsed by pure solvent to remove the physisorbed molecules. HD sample was prepared by placing a droplet of the neat HD on the Au(111) surface. Although it was not a monolayer film, the surface potential change was considered to originate primarily from the interface between the 1st layer of HD and Au, as will be discussed later.

Nanometer-scale growth processes of the HDT SAMs were investigated using STM (Nanoscope E, Veeco) in the air. Surface potential was determined with a Kelvin probe system (KP-6500, McAllister Inc.) under the ultrahigh vacuum condition (on the order of 10^{-7} Pa). After preparation of SAMs in the air, the sample was introduced to the vacuum chamber. A stainless steel plate with a diameter of 4 mm was used as the reference electrode, the work function of which was not determined. As a result, we could only determine the contact potential difference between the two electrodes, or surface potential change relative to the reference electrode. In this paper, we took the surface potential change relative to the bare Au(111) surface, corresponding to the work function change by adsorption of the molecules. A positive shift of the surface potential means that the surface side becomes positive compared to the bare Au surface, indicating a decrease in the work function.

Results and Discussion

Control of the adsorption configuration of organic SAMs on gold is a major issue for their technological applications, because the surface properties of SAMs can be easily tuned by the molecular orientation of adsorbed molecules. To date, the growth mechanism of alkanethiol SAMs on gold has been thoroughly studied with both *ex situ* and *in situ* measurements. In particular, the STM studies have revealed the molecular-scale growth processes of various alkanethiol SAMs with different alkyl chain lengths prepared.²⁰⁻²⁴ To understand the relationship between the adsorption configuration of SAMs and surface potential, we optimized the experimental conditions to obtain the desired adsorption structure of SAMs by changing the immersion time of Au(111) surfaces in a 1 μM HDT solution. We successfully observed phase transitions of HDT SAMs from the gas phase to the standing-up phase *via* the striped phase with increasing surface coverage. The STM images in Figure 1 show phase transitions of HDT SAMs on Au(111) as a function of immersion time. After immersion for 1 min, the STM image in Figure 1a shows aggregations of

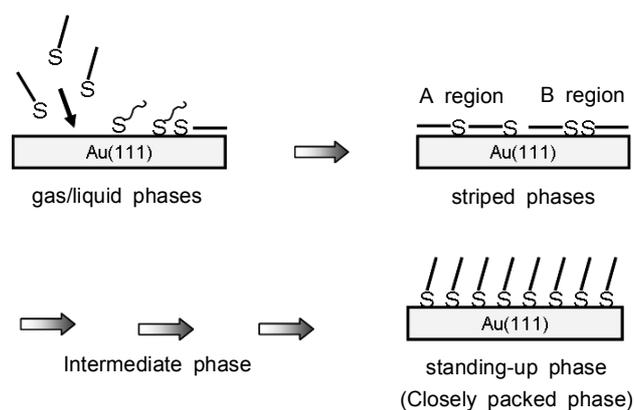


Figure 2. Schematic illustration of the growth process of HDT SAM on Au(111).

molecules, which can be often observed at the very initial growth stage of SAMs with a very low surface coverage (gas phase or liquid phase). Partially covered striped phases were then newly observed from the SAM sample obtained after immersion for 5 min, as shown in Figure 1b. With a longer immersion time of 10 min, the STM image clearly revealed fully covered striped phases as shown in Figure 1c. The periodicity of the striped phases was measured as approximately 2.4 nm, which corresponds to the length of HDT molecules, implying that the striped phases A (shown in Figure 1c) were formed as a result of their head-to-tail molecular orientation on the gold surface. In addition, the periodicity of the striped phases B was measured as approximately 4.2 nm, which is slightly smaller than the length of two HDT molecules. We therefore assumed that the striped phases B were formed as a result of head-to-head molecular orientation on a gold surface. Although striped phases are still present on the surface after immersion for 30 min, vacancy islands (VIs, dark holes) were newly observed as a result of chemisorption of thiol molecules and crystallization of SAMs (Figure 1d). After immersion for 24 h, HDT molecules formed closely packed SAMs (standing-up phase) containing the ordered structure, domain boundaries, and many VIs, as observed from various alkanethiol SAMs (Figure 1e).^{22,23,25} Quite Recently, infrared spectroscopic ellipsometry measurements revealed that the average tilt angle of alkyl chain for closely packed HDT SAMs on gold is about 22° from the surface normal.²⁶ Based on our STM results, we developed a schematic view showing the growth of HDT SAMs from the gas phase to

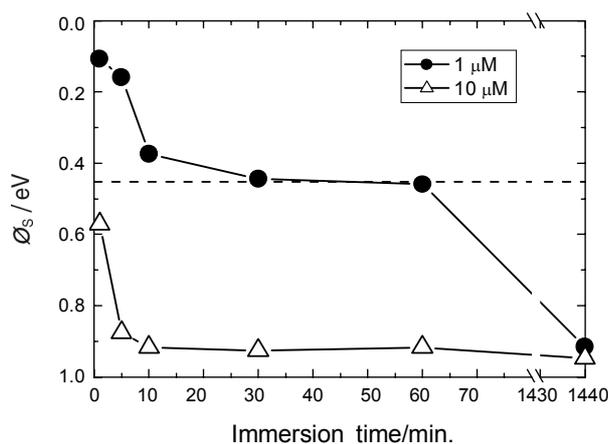


Figure 3. Surface potential change as a function of growth of HDT SAMs on Au(111) prepared in a 1 or 10 μM solution. The abscissa is the immersion time of the Au surface in the ethanol solution. The surface potential values were taken relative to the value of the bare Au(111) surface. The dashed line shows the surface potential change for the striped phase of HD SAMs physisorbed on Au(111).

the standing-up phase *via* the striped phase on Au(111), as shown in Figure 2. On the other hand, the several intermediate phases have also been often observed during the phase transitions from the striped phase to standing-up phase.²²

Figure 3 shows surface potential change following adsorption of HDT SAM prepared under various conditions (immersion times and concentrations). The abscissa is the immersion time of the Au surface in the ethanol solution. When the Au surface was immersed in the more concentrated 10 μM solution, the surface potential immediately changed, reaching a constant value of $+0.92 \pm 0.1$ eV after 10 minute immersion. Many defects sites were also observed with the STM imaging as demonstrated in Figure 1d, signifying the formation of a standing-up phase. Therefore, the obtained value corresponds to the surface potential of the standing-up phase of the HDT.

The direction of the shift was the positive, which is consistent with previous studies,^{4,9} although we were unable to directly compare our results with the reported values due to the use of a different reference. The observed positive shift originates from the alignment of the dipole moment of the alkanethiol.^{4,7,9,13} The S-Au chemical bond at the interface is considered to induce a negative shift, when an ionic bonding of the $\text{S}^- \text{-Au}^+$ is assumed.⁴ Recent theoretical calculations have suggested that there is no charge transfer between the Au and the S atoms.¹³ Thus, while the contribution of the S-Au chemical bond to the surface potential change can not be quantitatively estimated from our result, it should be small compared to that of the dipole moment of the alkyl thiolate.

In contrast, an intermediate state was found for the SAM prepared with the immersion in the 1 μM solution, although the total amount of the change after 24 hour immersion was similar to the case of the 10 μM solution. Within the range of 30 minutes to 60 minutes, the work function change remained constant at $+0.45 \pm 0.1$ eV. The STM image in Figure 1c shows that the striped phase of the HDT molecules was the dominant form at a 30 minute immersion time. Therefore, this surface potential change was caused by the adsorption of the

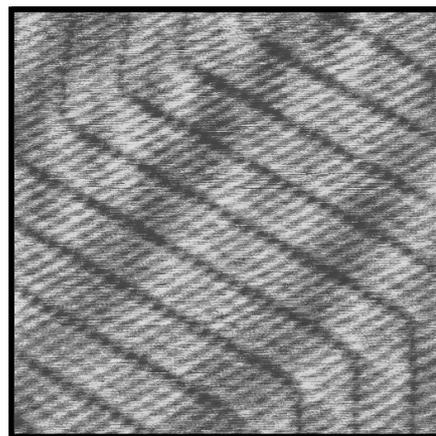


Figure 4. High-resolution STM image showing the striped phase of HD SAMs physisorbed on Au(111). The scan size of the STM image is 20 nm \times 20 nm.

HDT molecules in the lying orientation.

The dipole moments of the molecules are considered to be lying down in the striped phase, suggesting that their alignments are not the origin of the potential change. The HDT molecule has 16 carbon atoms and only one S atom, and the area occupied by the S atom on the Au surface is considerably smaller compared to that of the alkyl chain in the striped phase. Thus, the contribution of the S-Au bond formation, if it even exists, is negligibly small in the lying orientation, suggesting that the surface potential change in the striped phase results from the formation of the interfacial dipole layer of the physisorbed alkyl chain.

It is generally accepted that the work function can be changed by the physisorption of atoms or molecules on the metal surface.^{1,27-30} For instance, the work function change in the *n*-tetratetracontane (TTC: $n\text{-C}_{44}\text{H}_{90}$) monolayer on a clean Au surface is approximately 0.7 eV,²⁸ where the TTC molecules are physisorbed on the Au surface in the lying orientation, which was also the case of the striped phase in the alkanethiol SAM. The origin of this shift is the dipole layer formation at the interface between the alkane monolayer and the Au surface. Further, while the sign of the shift in our experiments is the same, our value is smaller than that reported for TTC. An explanation for this difference may be found in the handling of the Au surface, which was exposed in air before surface potential measurement, causing contamination. Such contamination may indicate the decrease in the work function compared to that of the clean Au surface prepared in the ultra-high vacuum. Thus, the small work function of the surface likely leads to the decrease in the surface potential change.

To examine the surface potential change due to the adsorption of alkyl chains, we measured the surface potential of alkane molecules physisorbed on a Au(111) surface. The molecular-scale STM image in Figure 4 clearly revealed that HD molecules form SAMs containing a striped phase in which the alkyl chain of HD molecules are oriented parallel to the Au(111) surface. The molecular orientation of HD molecules in the striped phase was largely influenced by the herring-bone structure of Au(111); further structural details

for the HD monolayers have been previously described.³¹ From the view point of adsorption configuration, the striped phase of HD molecules physisorbed on Au(111) was identical with that of HDT molecules chemisorbed on Au(111).

It was suggested that contribution of the surface potential change results from the interface between the SAMs and the Au substrate. The surface potential change by adsorbing HD molecules on the Au(111) was measured to be +0.45 eV, as shown as the dotted line in Figure 3. The observed surface potential value was the same as that of the striped phase of HDT SAMs. This results strongly implies that the presence of the S-Au chemical bond in HDT SAMs on Au(111) does not significantly affect the change in surface potential. Therefore, it is reasonable to conclude that the surface potential change of the striped phase is mainly due to the formation of an interfacial dipole layer, and not the bond formation between the molecules and the Au surface.

Conclusion

We monitored the surface potential change of Au(111) surface in the process of SAM formation by HDT. By combining our STM observations, we found a relationship between the surface potential change and the molecular orientation of the alkanethiol SAMs. The surface potential of the striped phase of the alkanethiol SAM on the Au(111) surface was determined using Kelvin probe method. The obtained value was between those of the bare Au(111) surface and the standing-up phase of the SAMs, indicating that the change of the molecular orientation in the SAMs was responsible for the work function change. Based on the comparison of the surface potential of the HD on the Au(111) substrate, we suggest that the origin of the surface potential change in the striped-phase is due to formation of a dipole layer at the interface between the lying alkyl chain and the Au(111) surface.

Acknowledgments. This work was supported by the research fund of Hanyang University (HYU-2008-T). This work was also supported by the Seoul R&BD Program (10919) and the Korea Foundation for International Cooperation of Science & Technology (KICOS) through a grant provided from the Korean Ministry of Science & Technology (MOST), No. K20501000002-07-E0100-00210.

References

- Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mat.* **1999**, *11*, 605.
- Hill, I. G.; Milliron, D.; Schwarz, J.; Kahn, A. *Appl. Surf. Sci.* **2000**, *166*, 354.
- Kera, S.; Yabuuchi, Y.; Yamane, H.; Setoyama, H.; Okudaira, K. K.; Kahn, A.; Ueno, N. *Phys. Rev. B* **2004**, *70*, 085304.
- Evans, S. D.; Ulman, A. *Chem. Phys. Lett.* **1990**, *170*, 462.
- Campbell, I. H.; Rubin, S.; Zawodzinski, T. A.; Kress, J. D.; Martin, R. L.; Smith, D. L.; Barashkov, N. N.; Ferraris, J. P. *Phys. Rev. B* **1996**, *54*, 14321.
- Miura, Y.; Kimura, S.; Kobayashi, S.; Iwamoto, M.; Imanishi, Y.; Umemura, J. *Chem. Phys. Lett.* **1999**, *315*, 1.
- Lü, J.; Delamar, E.; Eng, L.; Bennewitz, R.; Meyer, E.; Güntherodt, H.-J. *Langmuir* **1999**, *15*, 8184.
- Lü, J.; Eng, L.; Bennewitz, R.; Meyer, E.; Güntherodt, H.-J.; Delamar, E.; Scandella, L. *Surf. Inter. Anal.* **1999**, *27*, 368.
- Howell, S.; Kuila, D.; Kasibhatla, B.; Kubiak, C. P.; Janes, D.; Reifemberger, R. *Langmuir* **2002**, *18*, 5120.
- Ichii, T.; Fukuma, T.; Kobayashi, K.; Yamada, H.; Matsushige, K. *Appl. Surf. Sci.* **2003**, *210*, 99.
- De Renzi, V.; Rousseau, R.; Marchetto, D.; Biagi, R.; Scandolo, S.; Pennino, U. *Phys. Rev. Lett.* **2005**, *95*, 046804.
- Ray, S. G.; Cohen, H.; Naaman, R.; Liu, H.; Waldeck, D. H. *J. Phys. Chem.* **2005**, *109*, 14064.
- Rousseau, R.; De Renzi, V.; Mazzarello, R.; Marchetto, D.; Biagi, R.; Scandolo, S.; Pennino, U. *J. Phys. Chem. B* **2006**, *110*, 10862.
- Lee, J.; Jung, B.; Lee, J.; Chu, H.; Do, L.; Shim, H. *J. Mater. Chem.* **2002**, *12*, 3494.
- Hatton, R. A.; Willis, M. R.; Chesters, M. A.; Rutten, F. J. M.; Briggs, D. *J. Mater. Chem.* **2003**, *13*, 38.
- Senda, T.; Wakamatsu, S.; Nakasa, A.; Akiba, U.; Fujihira, M. *Ultramicroscopy* **2003**, *97*, 27.
- Pernstich, K. P.; Haas, S.; Oberhoff, D.; Goldmann, C.; Gundlach, D. J.; Batlogg, D.; Rashid, A. N.; Schitter, G. *J. Appl. Phys.* **2004**, *96*, 6431.
- Saito, N.; Lee, S. H.; Takahiro, I.; Hieda, J.; Sugimura, H.; Takai, O. *J. Phys. Chem. B* **2005**, *109*, 11602.
- Appleyard, S. F. J.; Day, S. R.; Pickford, R. D.; Willis, M. R. *J. Mater. Chem.* **2000**, *10*, 169.
- Noh, J.; Hara, M. *Langmuir* **2000**, *16*, 2045.
- Kondoh, H.; Kodama, C.; Sumida, H.; Nozoe, H. *J. Chem. Phys.* **1999**, *111*, 1175.
- Poirier, G. E.; Fitts, W. P.; White, J. M. *Langmuir* **2001**, *17*, 1176.
- Noh, J.; Hara, M. *Langmuir* **2002**, *18*, 1953.
- Li, S.; Xu, L.; Wan, L.; Wang, S.; Jiang, L. *J. Phys. Chem. B* **2006**, *110*, 1794.
- Fukuma, T.; Kobayashi, K.; Horiuchi, H.; Yamada, H.; Matsushige, K. *Appl. Phys. A* **2001**, *72*, S109.
- Rosu, D. M.; Jones, J. C.; Hsu, J. W. P.; Kavanagh, K. L.; Tsankov, D.; Schade, U.; Esser, N.; Hinrichs, K. *Langmuir* **2009**, *25*, 919.
- Zangwill, A. *Physics at Surfaces*; Cambridge University Press: Cambridge, 1988; p 185.
- Ito, E.; Oji, H.; Ishii, H.; Oichi, K.; Ouchi, Y.; Seki, K. *Chem. Phys. Lett.* **1998**, *287*, 137.
- Morikawa, Y.; Ishii, H.; Seki, K. *Phys. Rev. B* **2004**, *69*, 041403.
- Hückstädt, C.; Schmidt, S.; Hüfner, S.; Forster, F.; Reinert, F.; Springborg, M. *Phys. Rev. B* **2006**, *73*, 075409.
- Uosaki, K.; Yamada, R. *J. Am. Chem. Soc.* **1999**, *121*, 4090.