Transactions of the Materials Research Society of Japan 31[3] 589-591 (2006)

Adsorption States of Thienylalkanethiol on Au(111)

Tohru Nakamura[1,*], Katsuyuki Ueki[2], Hideki Sakai[2,3], Mutsuyoshi Matsumoto[3,4,5], Masahiko Abe[2,3], Ikuyo Nakai[6], Hiroshi Kondoh[6], and Toshiaki Ohta[6]

[1]Nanotechnology Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5-2, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
Fax: 81-29-861-4669, e-mail: tohru.nakamura@aist.go.jp
[2]Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510, Japan
[3]Institute of Colloid and Interface Science, Tokyo University of Science, 1-3 Kagurazaka, Tokyo 162-8601
[4]Faculty of Industrial Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda 278-8510
[5]CREST, Japan Science and Technology Corporation (JST), 4-1-8 Honcho, Kawaguch 332-0012, Japan
[6]Department of Chemistry, The University of Tokyo, Hongo, Tokyo 113-0033, Japan

Adsorption states of thienylalkanethiols having two different types of sulfur group were studied on Au(111) by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) measurements. XPS spectra show that the molecules form a dense monolayer with the Au-thiolate bond and that the thiophene moieties are situated at the top of the monolayer. The odd-even effect of methylene number of alkyl chain linking thiolate and thiophene induces an alternate change in molecular density of the saturated phases as confirmed by XPS. NEXAFS results clearly indicated the odd-even effect of methylene number upon the average tilt angle of thiophene rings.

Key words: thienylalkanethiol, Au(111), XPS, NEXAFS

1. INTRODUCTION

The understanding of the interplay between substrate/anchoring group interaction and intermolecular interaction in organic monolayers plays a key role to explore the fundamental research of surface science and to develop industrial products like new display devices. Organic molecules with anchoring groups have been used to develop organic monolayers that are physically and chemically stable. Various anchoring groups using heteroatoms such as silicon (Si) and chalcogen (O, S, Se, Te) have been widely studied to obtain appropriate binder to solid surfaces.

On the other hand, one of the fundamental issues of the inner moiety in organic monolayers is the odd-even effect of alkyl chain. The odd-even effects have been amply observed in many areas [1] and applied to optical [2] and medical [3] materials. Among them, the odd-even effects of alkyl chain in biphenylalkanethiol self-assembled monolayers (SAMs) were thoroughly investigated on gold and silver surfaces [4-6]. Although C1s core level XPS technique was used for characterization of the effect in the SAMs, significant overlap of spectral components from different carbon-species such as aromatic and aliphatic species made it somewhat difficult to analyze their adsorption states. High-resolution XPS was found to be effective to overcome this problem [7]. We report XPS and NEXAFS analyses of modified alkane derivatives having the different types of sulfur group at both ends, *i.e.* thiol group and thiophene ring. The combination of S2p XPS and C-K NEXAFS techniques enables us to analyze more easily the odd-even effects of the thienylalkanethiols adsorbed on gold surfaces.

2. EXPERIMENTAL

Thienylalkanethiols (TC_nSH, n = 3–5, T: ω-(2-thienyl), C: methylene, SH: thiol) were prepared by the deprotection of the corresponding thioacetate. Thienylethanethiol (TC_2SH) was synthesized by the reduction of *O*-ethyl 2-thienylthioacetate (chart 1).

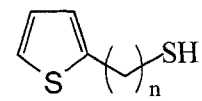

Chart 1. Chemical structure of thienylalkanethiol.

Au(111) surfaces were prepared by thermally evaporating gold on mica at 673 K under vacuum conditions. Self-assembled monolayers were prepared by atmospheric-vapor-adsorption (AVA) method [8], exposing Au surfaces in a vessel to the vapor of the organic thiols (TC_nSH) under ambient conditions for 24h followed by rinsing in ethanol. XPS spectra were recorded to check the reproducibility with hemispherical electron analyzers (Thermo VG Scientific) under high vacuum conditions. All binding energies were calibrated using the Au $4f_{7/2}$ peak (84.0 eV). The NEXAFS measurements were carried out at the soft X-ray beam line 7A of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF). Carbon K-edge NEXAFS spectra were obtained by the partial electron yield method using a micro-channel plate with a retarding voltage of 200 eV in an ultra-high vacuum chamber.

3. RESULTS AND DISCUSSION

3.1. XPS measurements

We focused on S 2p XPS spectra to analyze the adsorption state of TC_nSH on Au(111). Figure 1 shows typical S 2p XPS spectra for saturated TC_4SH and TC_5SH monolayers. It is obvious that the spectra consist of two components of sulfur species. The peaks observed at ca. 162.0 and 163.2 eV are assigned to a spin-orbit split pair ($2p_{3/2}$ and $2p_{1/2}$, respectively) of a thiolate sulfur species. The normalized intensity of the S2p peaks to that of Au 4f peaks is in agreements with that of the saturated octanethiolate SAM, indicating that TC_nSH molecules form a dense monolayer by the AVA method. Higher binding-energy peaks at 163.9 and 165.1 eV are associated with the thiophene moiety. Since the binding energies agree with those of thiophene multilayers, the thiophene moiety in the monolayer does not interact with the Au surface. The other TC_nSH molecules (n = 2, 3) also gave similar S2p XPS spectra. These results indicate that the thiol groups of TC_nSH molecules react with gold surface to afford Au-thiolate covalent bonds and that the thiophene moieties are apart from the surface, resulting in an upright configuration of the TC_nSH molecules on the Au(111) surfaces.

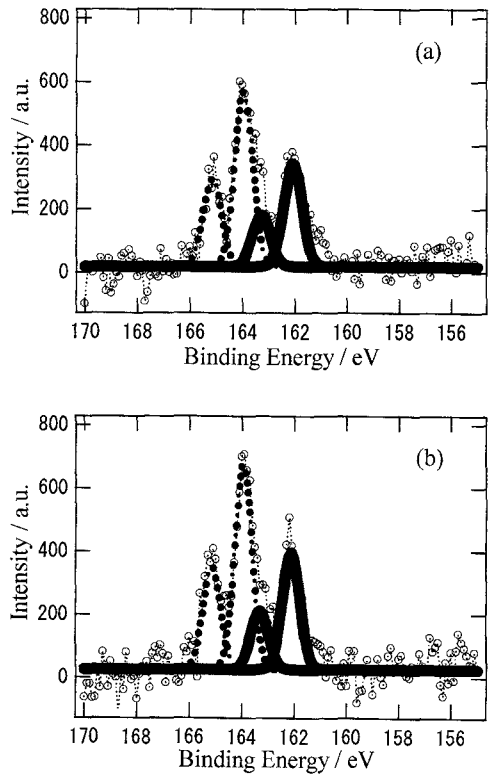

Figure 1. S 2p XPS spectra of (a) TC_4SH, (b) TC_5SH. The observed emission structures (open circles) are fitted by two doublets of S 2p related to thiolate (solid lines) and thiophene (dotted lines).

Figure 2 summarizes the intensity changes of S 2p for thiolate and thiophene as a function of methylene number of TC_nSH. The intensity changes in the thiolate peaks cannot be correlated to the molecular densities because the photoelectrons from the thiolate species are attenuated by the upper-lying organic layer. On the other hand, the peak intensity of thiophene moiety directly corresponds to the TC_nSH density since it is positioned at the top of monolayers. Obviously an odd-even effect is seen for the intensity change of the thiophene moiety. Monolayers prepared by AVA method under the different conditions (shorter exposure time, *e.g.* 3h, different temperature, *e.g.* 40 degree) reproducibly showed similar odd-even phenomena. These results strongly suggest that TC_nSH molecules having odd methylene units adopt a high surface density compared with TC_nSH molecules having even methylene units.

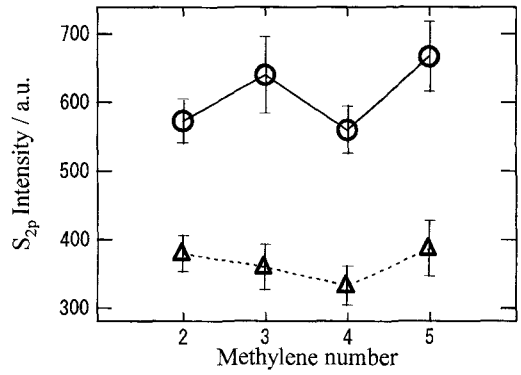

Figure 2. The intensity change of S 2p XPS signal as a function of methylene number of thienylalkanethiol. Circle: thiophene, triangle: thiolate.

3.2. NEXAFS measurements

XPS measurements suggest the alternate density change by the odd-even effect of alkyl group of TC_nSH. This density change might be caused by a change of average tilt angle of thiophene ring, *i.e.* TC_nSH molecules having odd methylene units adopt smaller tilt angles of the ring on gold surfaces than TC_nSH having even methylene units. We next study NEXAFS spectra for saturated TC_nSH SAMs on Au(111) to clarify this point.

Figure 3(a) and (b) show typical NEXAFS spectra of TC_4SH and TC_5SH, respectively. Three prominent peaks observed at 285, 287, and 293 eV are attributed to the excitations to π^*_1 of thiophene ring, π^*_2+ σ^*(C-H) and σ^*(C-C), respectively [9]. It is evident that the degree of polarization dependence is different between TC_4SH and TC_5SH, particularly for the π^*_1 peak which is correlated with the orientation of thiophene rings. The average tilt angle of the thiophene ring of even-TC_nSH (n = 2, 4) and odd-TC_nSH (n = 3, 5) from surface normal is estimated to be 35° ± 5 and 22-27° ± 5 from the NEXAFS spectra using curve-fitting analyses with a step function and Gauss functions.

Figure 4 summarizes the average tilt angle depending on alkyl chain of TC_nSH. It is clear that TC_nSH molecules having odd methylene units adopt smaller tilt angles than TC_nSH molecules having even methylene units. The average difference of tilt angles between odd- and even-TC_nSH is ca. 11°, which is in good agreement with ca. 13° on the basis of NEXAFS measurements for biphenylalkanethiols on gold [4].

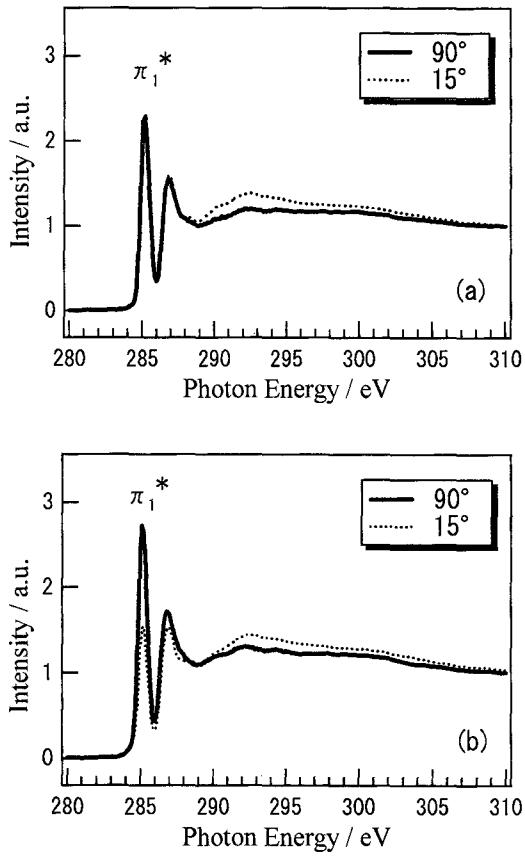

Figure 3. C-K NEXAFS spectra of (a) TC_4SH and (b) TC_5SH using different photon incident angles of 90° (solid line) and 15° (dotted line) with respect to the surface.

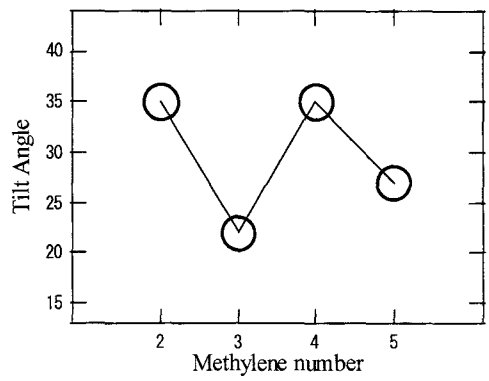

Figure 4. Average tilt angle changes of thiophene ring for thienylalkanethiol (TC_nSH).

Although the scenario on odd-even effect of TC_nSH monolayers on Au(111) is still unclear, we propose the following mechanism for the effect in the series of thienylalkanethiolate monolayers: (1) an even-effect of methylene group attached on thiolate-gold enhances steric hindrance to adjacent molecules by thiophene ring. This situation is consistent with the results of NEXAFS. (2) This effect leads to a decrease of molecular density. This is in good agreement with the results of XPS. XPS spectra in Figure 1 indicate that the density of even-TC_nSH is smaller than that of odd-TC_nSH by ca. 10 %. This 10% decrease of density is presumably caused by the 11° increase of tilt angle of thiophene ring in TC_nSH SAMs on Au(111).

4. CONCLUSION

We studied the photoemission spectroscopies of aromatic thiols having two different types of sulfur group to clarify the odd-even effect of alkyl groups connecting aromatic thiophene ring and thiol. XPS measurements show the density of TC_nSH molecules having odd methylene group (n = 3, 5) is larger than that of even-TC_nSH (n = 2, 4) by ca. 10 %. NEXAFS measurements indicate the alternate change of average tilt angle of thiophene ring with a difference of ca. 11° depending on the methylene number of alkyl group of TC_nSH. These results clearly indicate the odd-even effect of methylene number of thienylalkanethiol on the gold surface.

Acknowledgment

TN is indebted to Dr. T. Ishida for the XPS measurements. NEXAFS study was supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area "Molecular Nano Dynamics" from MEXT and performed under the approval of PF-PAC (No. 2004G318).

References

[1] For example, D. Wintgens, D. G. Yablon, G. W. Flynn, *J. Phys. Chem. B*, **107**, 173-179 (2003).

[2] For example, (a) V. Bekiari, E. Stathatos, P. Lianos, F. Konstandakopoulou, J. Kallitsis and S. Couris, *J. Lumin.*, **93**, 223-27 (2001). (b) V. A. Mallia and N. Tamaoki, *J. Mater. Chem.*, **13**, 219-224 (2003).

[3] For example, Y. Qi and J. L. Zakin, *Ind. Eng. Chem. Res.*, **41**, 6326-6336 (2002).

[4] M. Zharnikov, S. Frey, H. Rong, Y.-J. Yang, K. Heister, M. Buck and M. Grunze, *Phys. Chem. Chem. Phys.*, **2**, 3359-3362 (2000).

[5] S. Frey, H.-T. Rong, K. Heister, Y.-J. Yang, M. Buck and M. Zharnikov, *Langmuir*, **18**, 3142-3150 (2002).

[6] W. Azzam, P. Cyganik, G. Witte, M. Buck and Ch. Woll, *Langmuir*, **19**, 8262-8270 (2003).

[7] K. Heister, H.-T. Rong, M. Buck, M. Zharnikov and M. Grunze, *J. Phys. Chem. B*, **105**, 6888-6894 (2001).

[8] T. Nakamura, R. Kimura, H. Sakai, M. Abe, H. Kondoh, T. Ohta, M. Matsumoto, *Appl. Surf. Sci.*, **202**, 241-251 (2002).

[9] (a) P. S. Bagus, K. Weiss, A. Schertel, Ch. Wöll, W. Braun, C. Hellwig, C. Jung, *Chem. Phys. Lett.*, **248**, 129-135 (1996). (b) P. Väterlein, R. Fink, E. Umbach, *J. Chem. Phys.*, **108**, 3313-3320 (1998).

(Received December 10, 2005;Accepted February 3, 2006)