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Structure of 2-Mercaptomethylthiophene Monolayers on Au(111)

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The orientation of 2-mercaptomethylthiophene adsorbed on Au(111) was studied by near-edge X-ray absorption fine structure (NEXAFS). It was found that the orientation changed depending on the coverage of the molecules on Au(111); at low coverages the molecules formed striped islands in which the thiophene ring were inclined with a tilt angle of $45 \pm 10°$ from the surface normal, while at the saturated coverage they were aligned almost vertically with a tilt angle of $17 \pm 10°$.

Keywords: mercaptomethylthiophene; thienylmethanethiol; gold single crystal surface; near-edge X-ray absorption fine structure

INTRODUCTION

Molecular electronics has been receiving considerable attention because of scientific interest and industrial application. Rectification based on a single organic molecule is one of the most important subjects in the molecular electronics field. In order to confirm the performance of the molecular rectification it is essential to compare I-V characteristics of molecules having the opposite sequence of the donor and the acceptor with respect to the anchoring group. Further, we need other criteria for the set of molecules: the same molecular density and the same molecular orientation on the substrate. In this sense, 2-mercaptomethylthiophene derivatives will provide an ideal set because these molecules have the same nanostructures with the same periods on Au(111) unless the molecules have bulky substituents [1]. In this study, we have investigated the orientation of 2-mercaptomethylthiophene (C_4H_3S-CH_2SH; C_4H_3S = thiophene), the simplest molecule in this class of molecules, on Au(111) using C K-edge NEXAFS.

EXPERIMENTAL

2-Mercaptomethylthiophene was synthesized by the mercaptomethylation of thiophene [2] and purified by Kugelrohr distillation (110 - 120 °C / 12 - 13 mmHg). Single crystal Au(111) surfaces were prepared by vacuum deposition of gold onto mica with a thickness of *ca.* 100 nm followed by annealing in H_2 flame. The 2-mercaptomethylthiophene SAMs were prepared on Au(111) by the atmospheric vapor adsorption method [1]. The nanostructures of the SAMs were checked with STM (PicoSPM, Molecular Imaging). C K-edge NEXAFS spectra were taken at BL-7A (KEK-PF, Tsukuba) using the partial electron yield method with a retarding voltage of 200 eV.

RESULTS AND DISCUSSION

STM observations revealed that nanostructures of the SAMs depended on the coverage of molecules. Low exposures to gaseous 2-mercaptomethylthiophene failed to induce any ordered structures while medium exposures gave rise to the formation of two different structures; one-dimensional rows with an inter-row spacing of 1.40 nm as shown in Figure 1(a) and a honeycomb-like structure with an inter-hole periodicity of 1.16 nm [1]. Further exposure caused transformation from the ordered structure to a disordered one shown in Figure 1(b), which is the saturated phase.

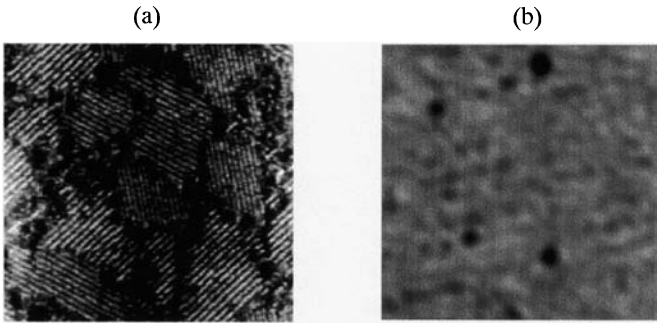

FIGURE 1. STM topographs of a Au(111) surface covered by 2-mercaptomethylthiophene; (a) medium coverage (80 nm × 80 nm), (b) saturated coverage (80 nm × 80 nm).

Figure 2(a) shows C K-edge NEXAFS spectra of the 2-mercaptomethylthiophene SAM with a medium coverage, which has the ordered structures as shown in Figure 1(a). The lowest-energy peak at 285.9 eV and a shoulder structure at 287.4 eV are assigned to excitations to π^*_1 and π^*_2+(C-S)* of thiophene, respectively. Higher-energy features observed at 288.9 and 292.8 eV are attributed to σ^*(C-H) and σ^*(C-C) resonances, respectively. Compared to the NEXAFS spectrum of multilayers of thiophene (data not shown), the π^*(C-H) and σ^*(C-C) resonances are relatively intense.

This is because the surfaces are partially covered with hydrocarbons adsorbed from atmosphere in this case. At the saturated coverage (Fig. 2(b)), the lower-energy features due to the thiophene moiety become more intense. From polarization dependence of the π^*_1 peak, the orientation angles of the thiophene rings in the ordered phase (a) and the saturated random phase (b) are estimated to be 45±10° and 17±10° from the surface normal, respectively. The tilted orientation of the thiophene rings in the ordered islands at the medium coverage in contrast to the almost vertical orientation at the saturated coverage is probably due to the lower molecular density in the former case than in the latter case, considering the intermolecular van der Waals interaction. The 2D random distribution of the molecules in the latter is interpreted in terms of a discrepancy between structural demands from the S/Au interface interactions and those from the intermolecular interaction, which is not settled to a large extent because of a lack of sufficient intramolecular degrees of freedom due to the shortest linking alkyl chain.

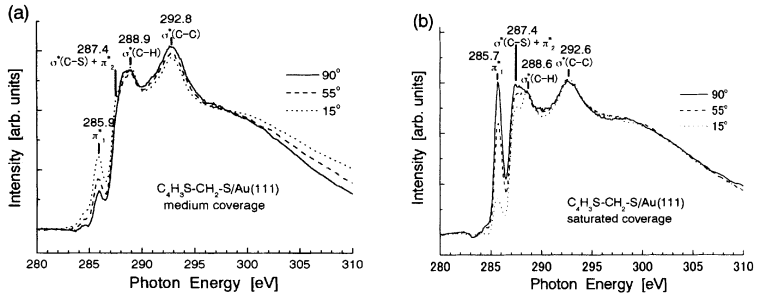

FIGURE 2. C K-edge NEXAFS spectra for 2-mercapto-methylthiophene SAMs on Au(111) with different coverages.
(a): medium coverage, (b): saturated coverage.

References

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