

# High-Resolution STM and XPS Studies of Thiophene Self-Assembled Monolayers on Au(111)

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Structure and binding condition of thiophene self-assembled monolayers (SAMs) formed on Au(111) were investigated by using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The STM study revealed the first molecularly resolved image for closely packed thiophene SAMs having two domain structures: disordered phases near domain boundaries and ordered domains consisting of pairs of molecules separated from each other by 4.35 Å, from the next row by 3.9 Å, and from the next columns by 8.8 Å. From the STM observation, it is considered that a cofacial interaction between thiophene molecules plays an important role in determining the surface structure of thiophene SAMs on Au(111). The XPS spectra in the S 2p region of thiophene SAMs on Au(111) were observed at 161 (S 2p<sub>3/2</sub>) and 162 eV (S 2p<sub>3/2</sub>), which are assigned to the gold-bound sulfur. In contrast to previous XPS and theoretical studies, our high-resolution STM and XPS measurements have clearly demonstrated that the sulfur headgroups in thiophene would chemically interact with gold in the self-assembly process.

Self-assembled monolayers (SAMs) formed by organosulfur compounds on gold have attracted considerable attention because they have a wide variety of potential applications in, for example, corrosion inhibition, molecular recognition, sensors, nanolithography, and molecular electronic devices.<sup>1–10</sup> Among the many organic SAMs that have been examined, in particular, the SAMs derived from alkanethiols on gold have been intensively studied because of their ease of preparation, high structural order and stability, and versatile modification of surface properties. As a result, many properties and capabilities of alkanethiol SAMs have been revealed and demonstrated; it has become increasingly important to understand the molecular ordering and adsorption state, in order to elucidate intrinsic physical and chemical aspects as well as technical applications.

More interestingly, solid surfaces can also be modified by  $\pi$ -conjugated materials, such as thiophene and its derivatives, which have electrical and chemical properties, by means of self-assembly techniques.<sup>11–17</sup> The resulting SAMs are very important and useful in the fabrication of new electronic devices because of their promising electronic properties, and they have been demonstrated in many application fields.<sup>16,17</sup> To date, although the surface chemistry of such materials has been widely studied on metal surfaces, very few papers concerning physical and chemical properties of thiophene molecules on gold have appeared. The reason may be previous results, derived from X-ray photoelectron spectroscopy (XPS)<sup>18</sup> and theoretical calculation,<sup>19</sup> which indicated that the sulfur atom in thiophene does not interact with gold. In contrast, it has recently been reported that thiophene does adsorb on gold through chemisorption, based on results of scanning tunneling microscopy (STM)<sup>12,15</sup> and surface plasmon resonance spectroscopy (SPS)<sup>15</sup>

measurements. This discrepancy is due to the different methods of sample preparation or/and different target molecules used in those works.

In this study, we introduce the simple thiophene molecule as the model system used to clarify such arguments. Herein, we report a molecularly resolved STM image showing an interesting monolayer structure and an XPS result for thiophene SAMs on Au(111). These results will provide the first meaningful information related to the structure of closely packed thiophene SAMs and the interactions between molecules and substrates during the self-assembly process of thiophene on gold.

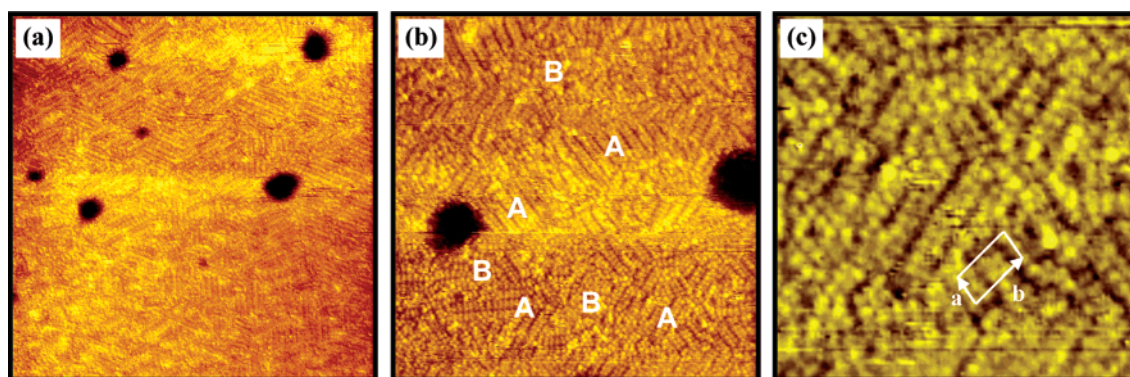
The Au(111) substrates on mica were prepared by vacuum deposition, as described in previous paper.<sup>20</sup> The SAMs were formed by the immersion of the gold substrates in a 1mM ethanolic solution of thiophene for 1 day. All STM images were taken in air at room temperature using the constant current mode. High-resolution XPS spectra were obtained using a VG ESCALAB 250 system with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV).

Figure 1 shows high-resolution topographic STM images of thiophene SAMs on Au(111) in small and large scan areas. The STM images in Figure 1 parts a and b exhibit the formation of vacancy islands with a monatomic step height of 2.5 Å and tridirectional domain orientations similar to those in the case of alkanethiol SAMs on gold, which indicate the formation of a chemisorbed monolayer on the basis of the symmetry of the Au(111) lattice.<sup>21–26</sup> Interestingly, we observed two domain structures consisting of ordered paired rows (region A) and a disordered phase (region B), as shown in Figure 1b, which have never been observed in any SAM system so far. From the paired-row domains in region A, we found that the distance between molecules in one row is 4.35 Å and the distance between rows in a paired row is 3.9 Å. In addition, the spacing between paired rows was measured to be 8.8 Å, and the angle between a molecular row in a paired row and a molecular row along paired

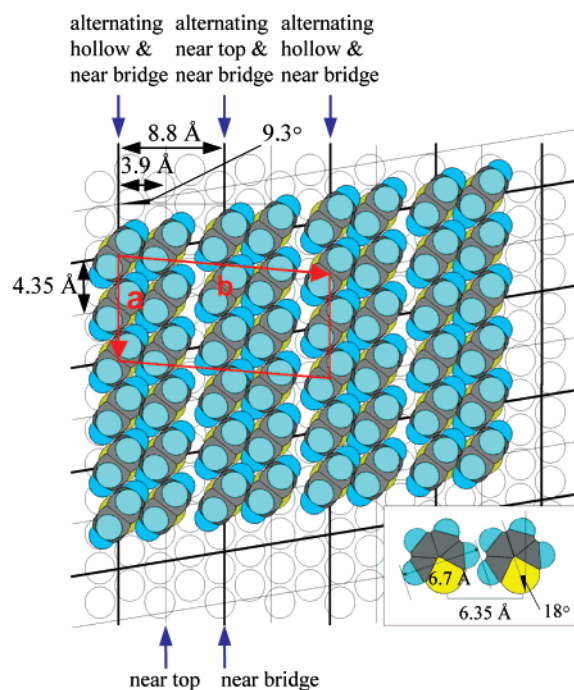
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**Figure 1.** STM images of thiophene SAMs on Au(111) showing two phase-separated domains consisting of ordered paired rows and disordered phase in small and large scan areas. Scan sizes were (a)  $60 \times 60$  nm, (b)  $28 \times 28$  nm, and (c)  $10 \times 10$  nm, and imaging conditions were (a) 0.31 nA and 0.41 V, (b) 0.28 nA and 0.41 V, and (c) 0.28 nA and 0.41 V.



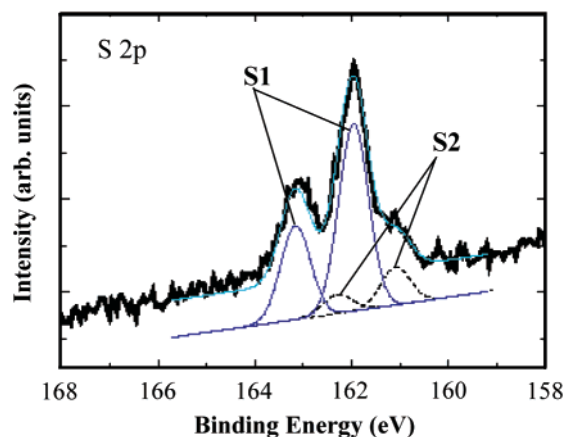
**Figure 2.** Proposed structural model for ordered paired-row structure observed in thiophene SAMs on Au(111). The lattice vectors  $a$  and  $b$ , and the angle between them is  $\alpha$  (see text). The insert (bottom right) shows the side view of adsorbed thiophenes with the tilt angle of  $18^\circ$  from the surface normal.

rows is measured to be approximately  $99.3^\circ$ . From this STM observation, we propose the sterically permitted model shown in Figure 2.<sup>27</sup> On the basis of this model, it is assumed that the sulfur headgroups in thiophene are adsorbed at various adsorption sites of the Au(111) lattice (see Figure 2), unlike alkanethiol SAMs that are adsorbed at the same adsorption site.<sup>1,8,23,28,29</sup> In addition, it is considered that thiophene molecules at saturation coverage are arranged with an upright configuration with the tilt angle of approximately  $18^\circ$  from the surface normal. The similar adsorption configuration for thiophene on gold was also confirmed by recent Fourier transform infrared reflection adsorption spectroscopy measurements.<sup>30</sup> The disordered phase in region B of Figure 1b was primarily observed around domain boundaries because mismatch of the cofacial arrangement, as shown in the model in Figure 2, can easily occur in these regions. Therefore, the disordered phase is likely to be due to such a structural inhomogeneity.

It has generally been believed that SAMs are formed by interplay between molecule–substrate interactions and molecule–

molecule interactions.<sup>2</sup> This interplay results in the specific molecular packing structure. In the case of thiophene SAMs, on the other hand, it is considered that a cofacial interaction between thiophene molecules plays an important role in the self-assembly process on Au(111). However, the observation of relatively small single-crystalline domains of less than 12 nm and disordered domains strongly implies that the molecular arrangement of thiophene SAMs is determined by interactions between the sulfur headgroups at the thiophene–gold surface as well as cofacial interactions between thiophene molecules in the self-assembly process. It is expected that the formation of thiophene SAMs is very sensitive to the balance of such interactions. In addition, although lateral interaction between thiophene molecules is one of the important factors for determining thiophene SAM structure, a degree of contribution of lateral interaction in molecular order seems to be smaller than that in the conventional well-ordered alkanethiol SAMs.

The STM image in Figure 1c shows variations in the brightness of the molecules in the ordered domains. This may be attributed to the multiple adsorption states and changes in orientation of adsorbed molecules, which reduce steric hindrance between molecules, as indicated in Figure 2. Although the evaluation of an exact structural definition is still difficult because of such irregular contrast of molecules, on the basis of high-resolution STM images and the adsorption model (Figures 1 and 2), we extract the following lattice constants:  $a = 8.7$  Å,  $b = 17.6$  Å, and  $\alpha = 85^\circ$ . The densely packed structure of thiophene SAMs observed in this study is quite different from that observed by Dishner et al., who found a low-density surface structure having an intermolecular distance of 5 Å in a row and an interrow distance of 12 Å after a relatively shorter immersion time of 2.5 h.<sup>12</sup> Actually, the 12 Å distance between rows of thiophene molecules is quite large. Therefore, they have pointed out a possibility that additional thiophene molecules occupy within a free space between the rows. Recently, we found that the formation kinetics of alkylthiophene SAMs is somewhat slower than that of alkanethiol SAMs because of the lower adsorption affinity of thiophene sulfur to the gold surface.<sup>15</sup> This result suggests that a longer time is required to form a densely packed thiophene SAMs on gold. From our STM study, after a long enough immersion time of 24 h, we found the molecularly resolved high-density structure for thiophene SAMs. Therefore, it is reasonable to consider that the longer immersion time promotes further adsorption of thiophene molecules into the vacancies on the gold surface accompanying two-dimensional reorganization of the monolayer, resulting in the formation of densely packed monolayer.



**Figure 3.** XPS spectra in the S 2p region of thiophene SAMs on Au(111) showing two bound sulfur species at 162 (S  $2p_{3/2}$ , S1) and 161 eV (S  $2p_{3/2}$ , S2). Note that there is no unbound sulfur peak for the thiophene sulfur at around 164 eV.<sup>18,34</sup>

To understand the interactions between the sulfur headgroups in thiophene and the gold surface more precisely, we observed XPS spectra in the S 2p region of thiophene SAMs on Au(111) (Figure 3). In general, the S 2p spectra are composed of  $2p_{3/2}$  and  $2p_{1/2}$  peaks with an intensity ratio of 2:1, as theoretically determined from the spin-orbit splitting effect.<sup>31–35</sup> Figure 3 shows four peaks attributed to two different sulfur species. Main strong high binding peaks (S1 species) were observed at 162 (S  $2p_{3/2}$ ) and 163.3 eV (S  $2p_{1/2}$ ). Weak low binding peaks (S2 species) were also observed at 161 (S  $2p_{3/2}$ ) and 162.3 eV (S  $2p_{1/2}$ ). Both sulfur species can be assigned to the bound sulfur because such similar binding peaks are usually observed for various thiol SAM samples on gold.<sup>32,33,35</sup> In particular, the bound S2 peaks were mainly found in annealed or low-coverage alkanethiol SAMs<sup>32,33</sup> or aromatic thiol SAMs.<sup>33,35</sup> However, the origin of S2 peak is still unclear and under discussion.<sup>33</sup> In addition, we could not find any unbound sulfur species for thiophene sulfur at around 164 eV.<sup>19,34</sup> Contrary to earlier reports,<sup>18,19</sup> our XPS results clearly demonstrate that thiophene SAMs form through chemical interaction between the sulfur headgroups in thiophene and the Au(111) surface. We consider that the simple thiophene molecule used in the present work is the best model system for better understanding the binding nature between the thiophene sulfur and the gold substrate, compared to complicated thiophene systems such as functionalized thiophenes, oligothiophenes, and polythiophenes. This is because the side chains in these molecules provide side effects such as steric hindrance and structural distortion when the sulfur headgroups in thiophene react with gold, which can induce misunderstanding of the nature of the binding of thiophene sulfur on gold.

In conclusion, from our high-resolution STM and XPS studies, we have revealed, for the first time, the closely packed structure of thiophene SAMs having two phase-separated domains composed of ordered paired rows and the disordered

phase. However, there still remain further questions on whether the observed structure is in equilibrium or how we can obtain better-ordered SAMs. Answers may be acquired by using a longer immersion time in the preparation of SAMs or by annealing SAMs. Studies along these lines are now in progress. We have also demonstrated that the sulfur headgroups in thiophene chemically interact with gold during the self-assembly process.

## References and Notes

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