Regular Array of L-Tyrosine Molecules on Si(111)-Au Superstructures

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Studies of adsorption of organic molecules on metal-induced super-reconstructed silicon surfaces are important for future Si-based organic electronic device. We investigated the adsorption dynamics of L-tyrosine on Si-Au surface by in situ reflection high-energy electron diffraction. Si(111)5×2-Au and Si(111)√3×√3-Au coexisting surface was exposed to L-tyrosine and the intensities of diffraction spots from corresponding domains were monitored. L-tyrosine was found to adsorb onto the Si(111)5×2-Au domains preferentially, while the Si(111)√3×√3-Au domains were found to be less active. Adsorption sites were revealed by using scanning tunneling microscopy. The molecular adsorption site on the √3×√3-Au was found to be on domain boundary suggesting that the adsorption probability is small on this domain. On the other hand, the adsorbates ordering in 2.3 unit cell distance along [110] rows were found to create the similar structure as the Si(111)5×2-Au surface. These results suggest that the Si(111)5×2-Au superstructure can be used for the control of the molecular adsorption geometry and ordering effectively.

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I. INTRODUCTION

Understanding of bonding configuration and its electronic character between adsorbed organic molecule and inorganic substrate is important for organic-inorganic hetero-junction devices such as organic electronic devices and biosensors. Adsorption of molecules on solid surface depends on the geometric structure and electronic state of surface top layer atoms.

Proteins are the basic biomolecules which are the sequences of various amino acids. By fixing amino acid molecules on the well-defined surfaces, chemical and physical responses under controlled environments can be individually studied in atomic scale. Glycine, the simplest amino acid, was found to self-assemble when adsorbed onto crystalline Cu [1], Au [2], and Si surfaces [3]. Mechanism of chiral recognition between a pair of chiral cy steine adsorbates on the Au(110) surface through formation of S-Au bonding and unique intermolecular interactions were revealed by scanning tunneling microscopy (STM) observation [4]. L-tyrosine has a phenol group in the side chain and act as a precursor of neurotransmitter such as dopamine and adrenaline [5]. Tyrosine adsorption on Cu(111) surface forming two-dimensional molecular array in electrochemical condition was also reported [6]. These arrays can be used for molecular recognitions.

Surface structure of silicon can be controlled in various ways by metal atom adsorption and annealing [7]. In the case of gold adsorption on Si(111) surface, many types of surface superstructures such as Si(111)5×2-Au [8-11], Si(111)√3×√3-Au, and Si(111)6×6-Au [12, 13] have been reported. Adsorptions on the various Si(111)-Au surface superstructures have been reported for the case of several molecules beside tyrosine. Nitric oxide (NO) adsorbed on Si(111)5×2-Au, Si(111)√3×√3-Au, and Si(111)6×6-Au surface superstructure [14]. The adsorption was observed by low energy electron diffraction (LEED) and STM. NO adsorbed on Si(111)7×7 and Si(111)5×2-Au, but did not adsorb on Si(111)√3×√3-Au and Si(111)6×6-Au surface. Au induced Si(111) reconstructed surface superstructure have different adsorption dynamics for molecule. Similar result was reported that was case of benzenethiol [15]. L-cysteine adsorption onto the Si(111)√3×√3-Au surface superstructure was investigated by XPS [16]. They proposed the adsorbate model with S-Au and COO-Si bonds and intact amino group.

In this study, the difference of the adsorption dynamics of L-tyrosine on different Si(111)-Au superstructure surfaces has been investigated by in situ reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). Pure Si(111)5×2-Au, pure Si(111)√3×√3-Au, and their coexisting surface were exposed to L-tyrosine. The adsorption probabilities on these superstructures were investigated by monitoring the intensities of RHEED diffraction spots from corresponding superstructure domains. Adsorption sites were investigated by using STM.

FIG. 1: Schematic image of L-tyrosine molecule. The green, red, dark blue, and light blue are carbon, oxygen, nitrogen, and hydrogen atoms of molecule respectively.

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FIG. 2: Core level photoelectron spectra of C 1s, O 1s, and N 1s. The open circles are experimental results. Blue and red lines are fitted curves of each peak and their summation. Peaks correspond to each L-tyrosine bond.

FIG. 3: Valence band photoelectron spectrum of L-tyrosine film (open circle) on Si(111)7×7 surface. The thickness of molecular film was about 70 Å. The solid line is calculated density of states (DOS) of neutral L-tyrosine. The dashed lines correspond to local density of states of each part of L-tyrosine. Experimental result have similar peak that of calculated DOS. This means that L-tyrosine evaporated without decomposition by present evaporation method.

II. EXPERIMENTAL

Sample preparation and all measurements were carried out under 10⁻¹⁸ Pa ultra high vacuum (UHV) condition. Au/Si(111) surface superstructures were prepared by reacted deposition epitaxy (RDE) method. Clean Si(111) surface with 7×7 structure was kept at 850 K during Au deposition. Dosage of Au was carefully controlled by using in situ RHEED observation. All the RHEED measurements were done at 15 keV. Pure Si(111)5×2-Au, pure √3×√3-Au, and their coexisting surface were prepared. The Au coverages were 0.4 ML for the pure 5×2 surface, and 0.8 ML for the pure √3×√3 surface, respectively, and it was 0.7 ML for the coexisting surface.

The chemical structure of L-tyrosine is shown in Fig. 1. L-tyrosine (Wako, 99.0 %) was dosed onto these surfaces by thermal evaporation. Since L-tyrosine decomposed over 640 K, the molecule evaporation was carried out at 450 K by using oil-bath-type evaporator where the heating oil was agitated for homogeneous temperature heating. The deposited molecule was checked by ex situ X-ray photoelectron spectroscopy (XPS) as shown in Fig. 2. We found chemical shifts corresponding to each chemical bond of L-tyrosine, which means that the molecules are not decomposed, as described later. Dosage of L-tyrosine was controlled by evaporation time. We took RHEED patterns during molecular evaporation onto several surface structures and analyzed molecular adsorption process.

STM images with various L-tyrosine dosages were taken systematically by preparing wedged thickness molecular films on the Si(111)5×2-Au and √3×√3-Au substrates. After the preparation of surface superstructure and deposition of L-tyrosine, we transferred the samples to STM measurement chamber through UHV transfer system [17]. STM measurements were carried out by UHV-STM system (UNISOKU, USS-3000) with homemade electrochemical polished W tips.

III. RESULTS AND DISCUSSION

The composition of evaporated L-tyrosine was checked by XPS measurement. Figure 2 shows C 1s, O 1s, and N 1s core level photoelectron spectra. In the C 1s spectrum, there are four components with the binding energies of 284.5 eV, 285.5 eV, 286.4 eV, and 288.7 eV. L-tyrosine includes C–C bonds in alkyl chain and aromatic group, C–N bond in amino group, C–O bond in phenol group, and C–OOH bond in carboxyl group. The largest peak at 284.5 eV corresponds to C–C bonds. Small chemical shift from C–C bond is C–N orbital from amino group. About 1.9 eV shift from C–C bond corresponds C–O bond from phenol group. The largest chemical shift is C–OOH bond from carboxyl group. In the O 1s spectrum, there are two components with binding energies of 530.1 eV, and 531.2 eV. The higher energy peak corresponds to C–OOH bond from carboxyl group. Another peak is O–H bond of phenol group. There is a single peak of N–H bond in N
FIG. 4: RHEED patterns of Si(111)5×2-Au and √3×√3-Au coexisting surface at several molecular coverages. (a) Before molecular evaporation, (b) 100 seconds (5×2 spots decreased), (c) 200 seconds (√3×√3 streaks decreased), and (d) 300 seconds (molecule covered all surface area).

1s spectrum [18–22]. These XPS result confirms that the L-tyrosine molecules were not decomposed during evaporation.

Figure 3 shows a measured valence band photoelectron spectrum (open circle) of L-tyrosine film on Si(111)7×7 surface that was prepared by present evaporation method and a calculated density of states of L-tyrosine molecule (solid line) using DV-Xα method. Although the density of states at the vicinity of Fermi level is suppressed in the measured spectra, the calculated density of states reproduce the valence band spectrum well. This means again that the deposited L-tyrosine was not decomposed by the present method.

Figure 4 shows a series of RHEED patterns of Si(111)5×2-Au and √3×√3-Au domains coexisting surface during L-tyrosine deposition. The electron beam was incident along [112] direction. In the RHEED pattern taken before the L-tyrosine deposition, 5×2 spots in between 0th and 1st Laue zones and √3×√3 streaks are seen (Fig. 4(a)). At 100 seconds after the deposition started, the 5×2 spot intensity almost disappeared, but those of √3×√3 streaks still remained (Fig. 4(b)). At 200 seconds, the √3×√3 streaks intensity almost disappeared (Fig. 4(c)). These behaviors of RHEED spot and streak intensities show that molecules adsorb onto both 5×2 and √3×√3 with different adsorption probabilities. At 300 seconds, neither 5×2 nor √3×√3 feature was observed (Fig. 4(d)). No diffraction spots due to molecular adsorption was observed. The reason of the decrease of the RHEED spot intensity is the destruction of surface superstructure by molecular adsorption. Note that these electron diffraction measurement damage the molecule, but both damaged and non-damaged molecules destroy the surface superstructure. Hence the results of RHEED intensity analysis will not change so much.

Then, intensity changes of both 5×2 and √3×√3 spots were analyzed quantitatively as shown in Fig. 5. Open squares and open circles correspond to the intensity of 5×2 spots such as (5/2, 0) and that of √3×√3 streaks such as (√3/2, 0), respectively. 5×2 spot intensity decreased more rapidly than that of √3×√3 streak. This indicates that molecule preferentially adsorb onto the 5×2 superstructure. Note that the 5×2 spot intensity curve follows an exponential decay function, while that of √3×√3 domains have a shoulder structure at 50 seconds.

Adsorption coefficients for 5×2 and √3×√3 domains

TABLE I: Optimized parameter of simulated RHEED intensity changing.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{5×2}(0) : S_{√3×√3}(0)</td>
<td>1:1</td>
</tr>
<tr>
<td>α_{5×2}</td>
<td>0.072</td>
</tr>
<tr>
<td>α_{√3×√3}</td>
<td>0.043</td>
</tr>
<tr>
<td>M_{5×2,√3×√3}</td>
<td>0.109</td>
</tr>
<tr>
<td>M_{√3×√3,5×2}</td>
<td>0.175</td>
</tr>
</tbody>
</table>

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
were derived by simulating these curves using adsorption process model described as follows. Decrease of RHEED spot intensity corresponds to the area of reacted surface \( \Delta S(t) \) at time \( t \) (second) because the surface superstructure is destroyed by molecular adsorption. If only one kind of domain exists and adsorption coefficient \( \alpha \) is constant, then the area of unreacted surface \( S(t) \) is proportional to \( \exp(-\alpha t) \) (Eqs. (1) and (2)). In the present case, we considered not only simple adsorption by the adsorption probability, but also the transfer from one kind of domain to another. We assumed that the rate of molecule transfer is proportional to the area of both domains, \( S_{5 \times 2} \) and \( S_{\sqrt{3} \times \sqrt{7}} \). Differential equations concerning both domain area are constructed as follows,

\[
\begin{align*}
S(t+1) &= S(t) - \Delta S(t) \\
\Delta S(t) &= \alpha S(t) \\
\Delta S_{5 \times 2}(t) &= S_{5 \times 2}(t)\alpha_{5 \times 2}(1 - M_{5 \times 2\rightarrow \sqrt{3} \times \sqrt{7}}S_{5 \times 2}(t)S_{\sqrt{3} \times \sqrt{7}}(t)) \\
\Delta S_{\sqrt{3} \times \sqrt{7}}(t) &= S_{\sqrt{3} \times \sqrt{7}}(t)\alpha_{\sqrt{3} \times \sqrt{7}}(1 - M_{\sqrt{3} \times \sqrt{7} \rightarrow 5 \times 2}S_{5 \times 2}(t)S_{\sqrt{3} \times \sqrt{7}}(t))
\end{align*}
\]

where \((t+1)\) means the time 1 second after \( t \), \( M \) is a constant parameter for one adsorbate to go across the domain boundary. Solid and dashed lines in Fig. 5 are the simulated intensity changes for \( S_{5 \times 2} \) and \( S_{\sqrt{3} \times \sqrt{7}} \), respectively, using optimized parameters listed in Table I. Adsorption coefficient for \( 5 \times 2 \) domains was 1.7 times larger than that of \( \sqrt{3} \times \sqrt{7} \) domains as shown in Table I. Simulated curves taking adsorbate transfer between two different domains into account well reproduced the features appeared in the experimental data.

Figure 6 shows a series of STM images for different L-tyrosine dosages on the Si(111) 5 × 2-Au surface. The row structure along [110] direction was obtained. Bright protrusions aligned along the 5 × 2 row structure in Fig. 6(a) were reported to be the dangling bonds of excess Si adatoms on the 5 × 2-Au surface [8, 9]. These Si adatoms are about 0.02 ML. In the case of low dosage, molecular adsorbates appeared as blurred features (~20 Å) much larger than the Si dangling bond bright protrusions. The number of these features increase with the dosage while that of Si adatoms decrease as shown in Figs. 6(b) and (c) suggesting that the L-tyrosine molecules bond to these Si adatoms at very initial stage. Since L-tyrosine is about 10 Å in size, blurring suggests that the molecule is anchored to Si adatom with a single bond and is moving around the bond.

Then after disappearance of Si dangling bond bright protrusions at the higher coverage, different kind of bright spots begins to appear as shown in Figs. 6(f)-(h). They were similar to that assigned to Si dangling bonds but more densely aligned along the direction of the 5 × 2 row structure. Blurred features become minority but still exist at coverage of 0.1 ML as shown in Fig. 6(h). The histograms in Fig. 7(a) show the distribution of nearest neighbor distance of the spots along 5 × 2 row direction. Open squares and open circles in Fig. 7(a) correspond to the bright spots observed at the dosage of 0.003 ML and 0.034 ML, respectively. The abscissa indicates the inter-adsorbate length scaled by substrate Si(111) unit cell length of 3.84 Å. In the low coverage case, distance
and tunneling current $I_s$ times were (a) 0 second and (b) 100 seconds.

pure Si(111)
STM image at 0.034 ML molecular coverage.

0.003 ML and 0.034 ML, respectively. The inset (b) is close-up
and blue open circles are those for the L-tyrosine coverages of
2 row direction. (a) Red open squares
protrusions along the $5\times2$ row.

FIG. 7: Histograms of distances between nearest two bright
protrusions along the $5\times2$ row direction. (a) Red open squares
and blue open circles are those for the L-tyrosine coverages of
0.003 ML and 0.034 ML, respectively. The inset (b) is close-up
STM image at 0.034 ML molecular coverage.

FIG. 8: 20 nm $\times$ 20 nm STM images of L-tyrosine adsorbed
pure Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface. Sample bias $V_s$ is $-1.5$ V
tunneling current $I_t$ is 0.15 nA. The molecular deposition
times were (a) 0 second and (b) 100 seconds.

between two neighboring bright spots corresponding to Si
adatoms was mainly 4 or 6 units in length. On the other
hand in the case of higher coverage, the most probable
distance was 2.3 units in length. The L-tyrosine molecule
align in a periodicity of $2.3$ along the row, but these is
no correlation between rows. This structure, which corre-
lated (periodicity 2.3) in one direction and uncorrelated (periodicity 5) in another direction, is similar to that of
Si(111)$-5\times2$-Au structure [23, 24].

Figure 7(b) is a close-up of the aligned adsorbates at the dosage of 0.034 ML. Note that the bright spots were
aligned not in straight but in zigzag indicating the exist-
tence of two Au adsorption sites in a $5\times2$ rows.

STM images of L-tyrosine adsorbed $\sqrt{3}\times\sqrt{3}$-Au sur-
face are shown in Fig. 8. We can see $\sqrt{3}\times\sqrt{3}$ spots and
direct boundary in Fig. 8(a) [12, 25, 26]. Ad-
sorbed molecules are seen as blurred spots in Fig. 8(b). In
Fig. 8(a) bright $\sqrt{3}\times\sqrt{3}$ islands are surrounded by linked
dark domain boundaries. In Fig. 8(b) bright area (which is
thought as molecules) is linked and surrounds dark is-
lands. Hence we can conclude that the molecules are ad-
sorbed on the domain boundary.

IV. CONCLUSION

Adsorption rates of L-tyrosine on Si(111)$5\times2$ and
$\sqrt{3}\times\sqrt{3}$-Au domains were measured by in situ RHEED
measurement during molecular deposition. L-tyrosine ad-
sorbs onto $5\times2$ domains preferentially than that onto $\sqrt{3}\times\sqrt{3}$ domains. Adsorption coefficient for $5\times2$ domains
was 1.7 times larger than that of $\sqrt{3}\times\sqrt{3}$ domains. Order-
ing of L-tyrosine adsorbates on $5\times2$ domains was observed
by STM. Adsorbates aligned along $5\times2$ row with a period of 2.3 unit cell. These results show that Si(111)$5\times2$-Au
superstructure can align L-tyrosine molecules in regular
one dimensional chain.

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