Preferential adsorption of C\textsubscript{60} molecules to step edges of the Si(110)-16 × 2 single domain surface

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Abstract. The Si(110) surface has a quite unique one-dimensional (1-D) stable structure with 16 × 2 reconstruction. Since the perfectly straight rows extend over micrometers, the 16 × 2 structure can be a superior template for 1-D nanostructures. However, controlled nanostructures using the Si(110)-16 × 2 template has not been fabricated yet. In this study, we have investigated the adsorption of C\textsubscript{60} molecules on the Si(110)-16 × 2 surface at various surface temperatures, and found that the C\textsubscript{60} preferable adsorption sites are substantially changed, depending on the surface temperature. The obtained results indicate that the organic 1-D nanostructure can be fabricated on the Si(110)-16 × 2 surface by controlling the surface temperature.

1. Introduction
The Si(110) surface has been recently attracting the interests as a candidate for the next-generation metal-oxide-semiconductor field effect transistor (MOSFET) devices because of its high hole mobility compared with other low-index Si surfaces [1-3]. At the same time, it is also known that Si(110) has a quite unique one-dimensional (1-D) 16 × 2 reconstructed structure [4,5]. The 16 × 2 reconstructed structure consists of straight rows of Si adatom units (pair of pentagons; PP}s), which run along two equivalent directions, [-112] and [1-12] [6-8]. Therefore, the clean Si(110)-16 × 2 surface usually exhibits a double-domain structure. Furthermore, various reconstructed structures other than 16 × 2 are generated due to small amounts of impurities [9].

Well-defined single domain Si(110)-16 × 2 surface is fabricated by means of controlled dc resistivity heating [10,11]. The dc heating can bring about the electromigration of surface Si atoms to line up the reconstruction rows when the electric current direction matches the...
orientation of the rows. The annealing temperature, time and current direction are dominant parameters for the $16 \times 2$ single domain preparation. In this study, we have prepared the surface under the optimized condition; the dc heating along [-112] orientation at 1473 K for 30 sec and prolonged annealing at 873 K for 20 min followed by quenching to room temperature (RT). Figure 1(a) displays a set of the low energy electron diffraction (LEED) and the scanning tunneling microscope (STM) images of the Si(110) surface after dc heat treatment. Figure 1(a) clearly shows that the $16 \times 2$ single domain is formed throughout the specimen. Figures 1(b) and (c) show the magnified STM images of the $16 \times 2$ surface at different sample biases ($V_s$). At the positive $V_s$, Si atoms that constitute PPs are resolved (lower right of fig. 2(b)). On the other hand, at the negative $V_s$, the electronic states originating from step edges are visualized.

Figure 1: (a) STM and LEED images of the clean Si(110)-$16 \times 2$ single domain surface (1 $\mu$m × 1 $\mu$m, $V_s = 2.0$ V). Magnified images (15 nm × 15 nm) obtained at different sample biases of (b) $V_s = 0.5$ V and (c) $V_s = -2.0$ V.

Since the perfectly straight rows can extend over micrometers, the $16 \times 2$ structure can be used as a template of low-dimensional nanostructures. However, the controlled synthesis of nanostructures using the Si(110)-$16 \times 2$ template has not been achieved yet. Especially, the initial process of organic nanostructure formation on the Si(110)-$16 \times 2$ surface has not been studied. Investigating the initial process of adsorption is of great importance, which is needed for controlled nanostructure fabrication. In this study, we have deposited a small amount of C$_{60}$ molecules on the Si(110)-$16 \times 2$ single domain surface at various temperatures to investigate the initial process of nanostructure formation. C$_{60}$ is a typical n-type organic semiconductor material, and is a very important molecule for organic semiconductor devices. Moreover, since the size of C$_{60}$ is suited to the width of stripe structure, we expect to align well it on the $16 \times 2$ substrate.

2. Experimental
The experiments have been carried out by using an ultrahigh vacuum (UHV) STM (JEOL Ltd. JSPM 4500A) system equipped with molecular deposition sources and LEED. The base pressure in the measurement chamber is $\sim 2 \times 10^{-9}$ Pa. A medium-doped p-type Si(110) of 0.01 ~ 0.02 $\Omega$ cm (size of $1 \times 7 \times 0.38$ mm$^3$) has been used for the specimen. A single domain $16 \times 2$ reconstruction surface has been prepared by the dc heating procedure. The deposition of C$_{60}$ molecules are carried out by using a Ta crucible. The deposition rate is calibrated by using a quartz microbalance located at the sample position. All the STM measurements have been carried out at RT.
3. Results and Discussion
First of all, we deposited a small amount of \( \text{C}_{60} \) molecules on the clean Si(110)-16 \( \times \) 2 single domain surface at RT. The obtained STM image is shown in fig. 2 (a). The \( \text{C}_{60} \) molecules about 2 nm in diameter are found on the surface. Note that the apparent size of isolated molecule is measured bigger than the real size of the molecules in STM image. We classify the \( \text{C}_{60} \) adsorption sites on the clean Si(110)-16 \( \times \) 2 surface into three sites as shown in fig. 2(e). The labeled A site is the upper terrace, B site is the lower terrace and C site is the step edge. In fig. 2 (a), it is found that the \( \text{C}_{60} \) are preferentially adsorbed onto the upper terrace (A site) at RT.

Next, to investigate the \( \text{C}_{60} \) adsorption features at different surface temperatures, we deposited the \( \text{C}_{60} \) molecules at 423 K, 573 K and 873 K. Figures 2 (b) ~ (d) show the STM images after depositing at different temperatures. In the case of \( \text{C}_{60} \) deposited on the Si(110) surface at 423 K, it seems that the number of \( \text{C}_{60} \) molecules adsorbed at the step edge largely increases. Preferential adsorptions of \( \text{C}_{60} \) molecules at step edge are found more obviously in the cases of 573 K and 873 K. Moreover, it is observed that several \( \text{C}_{60} \) molecules are aligned on the step edges at 573 K. It is known that the \( \text{C}_{60} \) is polymerized by ultraviolet or electron irradiation [12]. However, the STM image suggests that the polymerization has not occurred in this system since the shapes of \( \text{C}_{60} \) are maintained the same in fig. 2 (c). According to the recent studies of Feng et al., the electronic state of \( \text{C}_{60} \) nanowires formed on the Cu surface are connected each other and new electronic states called SAMOs (superatom molecular orbitals) are formed [13]. Therefore, detailed electronic states should be investigated on this surface.

The ratios of classified adsorption sites as a function of adsorption temperature are shown in fig. 3 (a). This result confirms that the ratio of molecules adsorbed onto the upper terrace is
substantially larger than that of the other sites at RT. That is, the upper terrace is a preferential adsorption site at RT. However, this is strange in terms of the site reactivity because the upper and lower terraces have the same structure. Now, we have considered the Ehrlich-Schwoebel barrier (ES barrier) [14] to explain the results. It is known that, in order for a surface adsorbate to diffuse from the upper terrace to the lower terrace, the adsorbate must overcome a large barrier located at step edge (ES barrier). The ES barrier on the Si(110)-16 × 2 surface are illustrated in figs. 3 (b) and (c). Since the C$_{60}$ molecules that adsorbed on the upper (lower) terrace cannot diffuse to the lower (upper) terrace at lower temperatures, C$_{60}$ molecules remain within the 1-D terrace where C$_{60}$ molecule impinges (fig. 3 (b)). The C$_{60}$ molecules impinging on the upper terrace shift to the center of the upper terrace, which is probably preferable adsorption sites within the terrace, since the C$_{60}$ cannot reach the step edge of the upper terrace due to the ES barrier. On the other hand, C$_{60}$ molecules impinging on the lower terrace are divided into the center and the edge of the lower terrace. Although the step edge of the lower terrace may be potentially reactive, an activation barrier partly blocks the adsorption at the edge. Because of this reason, the A site adsorption ratio is almost equal to the sum of the B + C site adsorption ratios at RT.

At higher surface temperatures, the features of C$_{60}$ adsorption are drastically changed. Contrary to about 16 % of C$_{60}$ molecules adsorbed at the step edge at RT, about 69 % of C$_{60}$ molecules adsorbed at the step edge at 873 K. At higher substrate temperatures, it is considered that the C$_{60}$ molecules can overcome the ES barrier and surface diffusion from the upper terrace to the step edge is allowed (fig. 3 (c)). Moreover, C$_{60}$ can also overcome the activation barrier at the step edge adsorption from the lower terrace. As a result, while the A site adsorption ratio decreased, the C site adsorption ratio increased remarkably. The similar adsorption ratios of A and B sites at higher temperatures correspond to the similar reactivities of the centers of the upper and lower terraces.

![Figure 3](image_url)

Figure 3: (a) Ratio of adsorption sites deposited at various temperatures which are normalized for the same length of the stripe. Schematic images of ES barrier on the Si(110)-16 × 2 surface at (b) lower temperatures and (c) higher temperatures.
Moreover, it is noticed that the apparent sizes of C\textsubscript{60} molecules become different for adsorption sites at high surface temperatures. Figures 4 (a) and (b) show the magnified STM image at 873 K and line profiles along the C\textsubscript{60} molecules adsorbed on the upper terrace (red line) and the step edge (green line), respectively. It is shown that the diameter and the height of C\textsubscript{60} molecules on the step edge are smaller than that of the upper or lower terrace. It is speculated that the smaller apparent size of adsorbed C\textsubscript{60} is due to the strong interaction between Si substrate and C\textsubscript{60} molecule. In the previous study, Yao et al. has reported that the apparent size of the chemisorbed C\textsubscript{60} on Si(100) surface becomes smaller [15]. In the Si(110)-16 × 2 surface, it is known that the step edge has a high reactivity because the electronic states originating from the step edge exist near the Fermi level [16]. Figure 4 (c) shows the magnified STM image of step edge taken at the negative \(V_s\). It is found that the C\textsubscript{60} molecules adsorbed in-between of the protrusions (white circles in fig. 4 (c)) reflecting the electronic states of the step edge.

Figure 4: (a) Magnified STM image of C\textsubscript{60} deposited at 873 K. (b) Line profiles along the C\textsubscript{60} molecules adsorbed on the upper terrace (red line) and at the step edge (green line) as shown in (a). (c) Magnified STM image taken at the negative bias (\(V_s = -2.3\) V).

4. Conclusion

The C\textsubscript{60} molecules are deposited on the Si(110)-16 × 2 single domain surface at various temperatures. We found that the C\textsubscript{60} preferable adsorption sites are substantially changed depending on the surface temperature. At RT, it has been found that the C\textsubscript{60} molecules preferentially adsorbed onto the upper terrace. It is consider that the adsorbed C\textsubscript{60} are not able to be diffused from the upper terrace sites to lower terrace sites and vice versa due to the high potential barrier originating from ES barrier at the step edge. In contrast, at higher surface temperatures, it has been found that the C\textsubscript{60} molecules are preferentially adsorbed on the step edge, which is the most reactive on the surface because the C\textsubscript{60} molecules can overcome the potential barrier. Moreover, the apparent size of C\textsubscript{60} which adsorbed at the step edges becomes small at higher surface temperatures. It is speculated that the charge transfer from Si atom to C\textsubscript{60} molecule occurs at the step edge. The obtained results indicate that the organic 1-D nanostructure can be fabricated on the Si(110)-16 × 2 surface by controlling the surface temperature.

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