



Adsorption and ordering of PTCDA on various reconstruction surfaces of In/Si(1 1 1)



Dongchul Shin, Zheng Wei¹, Hyungjoon Shim, Geunseop Lee*

Department of Physics, Inha University, 253 Yonghyun-Dong, Nam-Gu, Incheon 402-751, Republic of Korea

ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form 26 February 2016

Accepted 3 March 2016

Available online 6 March 2016

Keywords:

Scanning tunneling microscopy (STM)

3,4,9,10-perylene-tetracarboxylic-

dianhydride

(PTCDA)

Molecular self-assembly

ABSTRACT

The adsorption and ordering of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecules on various reconstruction surfaces of the In/Si(111) at room temperature were examined by using scanning tunneling microscope. On the semiconducting $\sqrt{31}\times\sqrt{31}$ surface, the PTCDA molecules adsorbed randomly and were isolated without ordering, whereas the molecules adsorbed on the metallic 4×1 and 'striped' surfaces were mobile and self-assembled to form regular structures. The assembled structures were governed by the dimensionality of the substrate structures. On the quasi-one-dimensional 4×1 surface, the PTCDA molecules with the same orientations were confined between the In chains to form molecular wires. On the other hand, the molecules formed a herringbone arrangement on the two-dimensional 'striped' surface via hydrogen bonding between the molecules. The different molecular arrangements on the two metallic surfaces reflect the relative predominance of the molecule-substrate interactions on the 4×1 surface and of the molecule-molecule interactions on the 'striped' surface.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Organic semiconductors have attracted considerable attention for their electronic and optoelectronic applications. Thin films of organic molecules are required for a range of applications in the organic semiconductors including organic light-emitting diodes [1,2], organic thin films transistors [3,4], organic solar cells [5,6] and photodetectors [7]. The structural properties such as molecular aggregation, packing, and orientation in thin films govern the electric and optical properties of the organic semiconductor devices. These structural properties of the organic thin films depend strongly on the interface properties of the organic materials and substrate, which are determined by the initial stages of the film growth. Therefore, a study of the adsorption, assembly, and ordering of organic molecules on substrates at the monolayer level is needed both for fundamental understanding and for applications that involve artificial tuning the epitaxial growth of organic molecules.

The perylene-derivative 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) has been used as an archetype organic molecule for studies of the epitaxial growth and electronic properties of

organic semiconductor thin films [8]. The PTCDA molecule is suited for epitaxial growth, because of its layered stacking structure in bulk crystals and high chemical and thermal stability. The initial-stage growth behaviors of PTCDA molecules on different substrates at the submonolayer and monolayer level have been extensively studied [9–28]. Most studies were carried out on metal and insulator substrates where the molecule-substrate interaction is relatively weak [9–20]. On those substrates, the PTCDA molecules assemble via the molecule-molecule interactions and formed a range of ordered structures, including herringbone [10,11,13,14,16–18], square [9,15], and brick-wall [12,19] structures. On the other hand, PTCDA molecules on reactive semiconductor surfaces adsorbed mostly as isolated molecules without ordering because of strong interaction of molecules with the dangling bonds of the semiconductor surfaces [21–23]. Passivation of the substrates using H, Se, or S [23–25] was reported to enhance the mobility of adsorbed molecules, resulting in submonolayer ordering and the formation of crystallites with bulk structures.

Another tactic for improving the epitaxial growth of PTCDA molecules on semiconductor substrates is to use metal-adsorbed Si(1 1 1) surfaces. Previously, the adsorption and ordering of PTCDA molecules on Ag/Si(1 1 1)- $\sqrt{3}\times\sqrt{3}$ and Sn/Si(111)- $2\sqrt{3}\times 2\sqrt{3}$ surfaces have been examined [26–28]. Molecular ordering in the submonolayer range has been achieved on both semiconducting surfaces, whereas the ordered structures were quite different. On Ag/Si(1 1 1), the ordered structures (herringbone and square)

* Corresponding author.

E-mail addresses: zheng_wei@cqu.edu.cn (Z. Wei), glee@inha.ac.kr (G. Lee).

¹ Present address: College of Material Science and Engineering, Chongqing University, 400044 Chongqing, P. R. China.

were two-dimensional (2D) and similar to those on metal surfaces [26,27]. On the other hand, the molecules on Sn/Si(111) were anchored to the substrate and formed quasi-one-dimensional (quasi-1D) ordering [28]. These studies suggest that growth can be controlled by the relative strength of the competing the molecule–molecule and molecule–substrate interactions on the metal/Si(111) surfaces.

In/Si(111) can be an ideal substrate for comparative studies of initial-stage growth because it shows a range of ordered phases with different surface reconstructions depending on the In coverage [29]. Surfaces with different structures also show different electric properties, ranging from semiconducting to metallic. Therefore, the growth behavior and molecular orderings on these semiconducting and metallic surfaces can be compared. In this work, we studied the adsorption and ordering of the PTCDA molecules on different surfaces of In/Si(111), $\sqrt{31} \times \sqrt{31}$, 4×1 , and a so-called ‘striped’ phase [29], at room temperature by using scanning tunneling microscope (STM). On the semiconducting $\sqrt{31} \times \sqrt{31}$ surface, PTCDA molecules adsorbed as isolated molecules at random sites and in random molecular orientations. In contrast, on the metallic 4×1 and ‘striped’ surfaces, the adsorbed molecules were mobile and formed ordered structures at room temperature. On the 4×1 surface, the PTCDA molecules were arranged to form an array of quasi-1D wires along the In chain direction, whereas a 2D herringbone structure formed on the ‘striped’-phase surface. The distinct adsorption behaviors on the semiconducting and metallic substrates originate from the different strength of the molecule–substrate interaction.

2. Experiments

The experiments were performed in an ultra-high vacuum chamber (a base pressure below 1.0×10^{-10} Torr) equipped with a commercial STM (SPECS GmbH). After outgassing the Si(111) sample (*p*-type doped with a resistivity of 1–10 Ω cm) overnight at 600 °C using a direct heating method, a clean Si(111)-(7 \times 7) surface was prepared by repeated flashings at 1200 °C, followed by slow cooling to room temperature. Indium was deposited onto the Si(111) surface from an In source enclosed with tantalum foil and heated by the attached tungsten filament. Different reconstruction surfaces of In/Si(111) were produced by depositing different amounts of In atoms onto the Si(111)-(7 \times 7) substrate held at a fixed temperature (\sim 400 °C) by varying the deposition time [29]. The PTCDA molecules (Sigma-Aldrich) contained in the tantalum boat were degassed carefully before sublimation to the substrate at room temperature. The STM images were obtained at a constant height mode at room temperature using a mechanically cut Pt-Ir tip.

3. Results and discussion

Fig. 1(a) shows a representative STM image of PTCDA adsorption on an In/Si(111) surface with coexisting $\sqrt{31} \times \sqrt{31}$ and 4×1 phases. STM images of the bare surfaces of the $\sqrt{31} \times \sqrt{31}$ and 4×1 surfaces with high resolution are also shown in Fig. 1(b) and (c). In the image, bright protrusions can be seen on both phases. These bright features were attributed to PTCDA molecules. The adsorbed PTCDA molecules were distributed in a disorder manner in the $\sqrt{31} \times \sqrt{31}$ region, while they tended to assemble along the indium chains in the 4×1 region. On the surface of the $\sqrt{31} \times \sqrt{31}$ phase, most of the PTCDA molecules were adsorbed as isolated single molecules or small clusters with a few molecules. This suggests that the PTCDA molecules interact strongly with the $\sqrt{31} \times \sqrt{31}$ substrate. The strong interaction prevents the molecules from diffusing on the surface and forming ordered structures at room

temperature. In contrast, the interaction of the molecules with the surface of the 4×1 phase is relatively weak, allowing the molecules to diffuse and assemble with each other.

Fig. 2(a) and (b) are enlarged images showing details of the PTCDA molecules adsorbed on the $\sqrt{31} \times \sqrt{31}$ phase and on the 4×1 phase. The atomic structure of the $\sqrt{31} \times \sqrt{31}$ surface has not been established, although some models have been proposed [30–32]. Therefore, the locations of the adsorbed molecules are designated schematically in Fig. 2(a) (bottom panel) without attempting to propose detailed adsorption sites. On the other hand, the internal structure of the adsorbed molecule is clearly resolved, revealing the molecular orientations. The resolved intramolecular structures of the adsorbed molecules in the different sites in the image clearly show that both the adsorption sites and the molecular orientations are diverse, i.e., random. The adsorption of PTCDA molecules as isolated entities with different orientations on the $\sqrt{31} \times \sqrt{31}$ semiconducting surface is similar to the cases on the Si(001)–2 \times 1 [21] and Si(111)–7 \times 7 surfaces [22]. On these surfaces, the interactions of the adsorbed PTCDA molecules with dangling bonds at the surfaces are strong. Therefore, strong binding of the adsorbed PTCDA molecule to the $\sqrt{31} \times \sqrt{31}$ surface can also be achieved through the interaction of the molecule with the dangling bond of the underlying Si atoms by breaking the Si–In bonds of the substrate [31,33].

On the 4×1 surface, however, some molecules are mobile at room temperature, appearing as noisy or continuously bright features while other molecules are fixed, as shown in the STM image [Fig. 2(b)]. These adsorption features are located on the dark trenches (the Si zigzag chains) confined between the two neighboring In chains on the 4×1 surface (see the schematics) and extends along the chain direction. The molecules can move freely in the empty regions of the In chains, leaving long, continuous molecular traces at room temperature. Traces of adsorbed molecules, whether moving or fixed, commonly show a depression in the middle of the feature along the chain direction. This suggests that the adsorbed molecules are oriented in the same direction, which is in contrast to adsorption on the $\sqrt{31} \times \sqrt{31}$ surface in random directions. This can be also confirmed in the high-resolution image

Fig. 3(a) shows the adsorption of increased amounts of PTCDA molecules on another In/Si(111) surface containing about 1 ML of In. The In-induced reconstructed surface with ca. 1 ML of In consists mostly of the 4×1 phase, coexisting with the so-called ‘striped’ phase [29,34]. The row structure in the ‘striped’ phase runs in the $[1\bar{2}1]$ direction, whereas the chains in the 4×1 phase are along the $[1\bar{1}0]$ direction in Fig. 3, making an angle of 30° [35]. The 4×1 surface area is covered almost completely with the molecules that are ordered along the chain direction. The molecules on the 4×1 surface are no longer mobile at this coverage. They form molecular chains with a regular arrangement of fixed rectangular shapes [36]. In comparison, most areas of the ‘striped’-phase region remain uncovered [a resolved image is shown in an inset of Fig. 3(a)]. This suggests that the sticking coefficient of the molecule on the ‘striped’-phase surface is much lower than that on the 4×1 surface. On the other hand, some molecular islands were formed on the ‘striped’-phase area, as shown in Fig. 3(a). Outside the island of the molecules, there is no clear indication of molecules on the bare surface except for some isolated bright features, which are associated to PTCDA molecules adsorbed at defect sites. However, the image of the area outside the molecular island in the ‘striped’ phase is reproducibly noisy, whereas the molecule-covered area could be imaged clearly without noise. The highly-mobile single molecules may also exist outside the molecular island on the ‘striped’ surface. These molecules, moving so fast at room temperature, cannot be imaged clearly but leave noisy traces in the STM images (the scanning rate was approximately 7 lines per second). On the periphery

Download English Version:

<https://daneshyari.com/en/article/5356508>

Download Persian Version:

<https://daneshyari.com/article/5356508>

[Daneshyari.com](https://daneshyari.com)