Scanning-induced structure transformation between self-assembled phases of pentacene on Ag/Si(111)

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Abstract

Using variable temperature scanning tunneling microscopy, we investigated the structure transformation of pentacene molecules on the Ag/Si(111)-(√3 × √3)R30° substrate. It is demonstrated that the self-assembled brick-wall phase can be converted to another ordered chain-like phase with higher packing density in a large area (µm) by tip scanning at room temperature. Moreover, we show by temperature dependent experiments that the increment of the pentacene molecules during the transformation is supplied by a two-dimensional gas reservoir that exists on the surface of the saturated brick-wall phase at room temperature.

Keywords: Pentacene; Self-assembly; Scanning tunneling microscopy; Ag terminated Si

1. Introduction

Organic thin films grown on inorganic surfaces have attracted considerable interest in recent years. This is on one hand due to their electronic and optical applications [1–3] such as organic light emitting devices, solar cells and flexible displays, etc., and on the other hand due to the increasing demand for understanding the fundamental physics of organic semiconductor systems.

Pentacene (C22H14), a planar molecule composed of five benzene rings, processes high carrier mobility [4] that renders it one of the most promising materials for fabrication of high-performance organic field effect transistors (OFETs) [5] and related devices. Since the performance of these devices strongly depends on the molecular ordering, orientation and binding with the substrates, much work has been focused on the interfaces involving pentacene on a variety of single-crystalline surfaces. So far, investigations have been carried out on adsorption kinetics, nucleation, film morphology, crystal quality and relevant growth parameters in pentacene thin film. The condition for a given growth mode is determined by a delicate balance of the intralayer and overlayer-substrate interactions. For example, pentacene molecules stand up and form bulk crystalline phase or the thin film phase on insulating or inert surfaces such as SiO2, SiN, Al2O3 and passivated Si [6–8], while they lie down and form varied 2D patterns (strip, brick-wall or herringbone) on noble metals [9–13] or some metallic interfaces [14–16] where the molecule–substrate interactions surpass the molecule–molecule interactions and lead to a planar adsorption geometry.

Scanning tunneling microscopy (STM) is a powerful tool that has been extensively applied not only to the growth morphology and structure studies of organic molecules on surfaces, but also to the manipulation of molecules[17–20], such as moving, tiling molecules, removing or attaching functional groups, and exciting molecules to metastable states. These manipulation experiments are mostly performed locally, or on individual molecules, while tip-induced structure transformation in large area has not been much studied so far. For pentacene, STM tip-induced local structure rearrangement has been recently observed on the Si(111)-(√3 × √3)Ag (referred to as the Ag/Si-√3 surface hereafter) surface by Guaino et al. [15] and on
Ga film surface by Wang et al. [16]. The observation on Ag/Si-\(\sqrt{3}\) raises a puzzling question: where are the excess pentacene molecules from, since the local density of molecules increases significantly after the structure change. Moreover, it is intriguing whether the tip can induce structure transformation in a larger area.

Here, we present a variable temperature STM study on the scanning-induced structure transformation of pentacene on the Ag/Si-\(\sqrt{3}\) surface. We demonstrate that the self-assembled brick-wall structure (phase S) can be completely converted to another ordered striped structure (phase L) by tip scanning within a large area. Furthermore, we found by temperature-dependent experiments that the increment of the pentacene molecules during the conversion from the low density phase to the high density phase is supplied by a two-dimensional (2D) gas reservoir that exists on the surface of a saturated S phase at room temperature (RT). When the 2D gas condenses into 3D islands at LT, the structure transformation no longer occurs. The tip effects are analyzed and a mechanism of the tip-induced 2D structure transformation is discussed.

2. Experimental section

Experiments were carried out in a commercial Omicron Multiprobe UHV system with the base pressure at \(5 \times 10^{-11}\) mbar. The substrate was cut from a n-type Si(111) wafer (phosphor-doped, \(\rho \sim 2 \Omega \text{ cm at room temperature}\)). The surface was cleaned by flashing the substrate up to 1550 K repeatedly until a nice \(7 \times 7\) reconstruction was formed. Ag was deposited from a tungsten wire evaporator while the substrate maintained at about 800 K. The sample was annealed at the same temperature for extra 3 min to obtain a well-ordered \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure at the Ag/Si(111) interface. Then pentacene molecules were dosed from a Knudsen-cell with the substrate at RT. We held the deposition rate constant and controlled the molecule coverage by varying the evaporation time. The STM images were recorded in constant current mode with an electrochemically etched W tip. LT STM measurements were performed by cooling the sample to about 120 K with liquid nitrogen through a continuous flow cryostat after RT measurements.

3. Results and discussion

At the molecule coverage of \(8.7 \times 10^{13}\) mol/cm\(^2\), about 11% of the atomic density of a bulk-terminated Si(111) \(1 \times 1\) surface, a long-range ordered structure is formed with a brick-wall configuration, as labeled S in Fig. 1a. Because dosing more pentacene onto the surface does not affect the structure observed in STM, we suppose this coverage a saturated one and define it as one molecule monolayer (ML). This phase has been discussed in detail in our previous work [21]. The structure is commensurate with the substrate. The primitive unit cell is outlined in the inset of Fig. 1a, with the lattice parameters of \(a = 13.3\) Å, \(b = 17.6\) Å, \(\gamma = 79.1^\circ\) and related to the Ag/Si(111) substrate vectors by the matrix \(\begin{pmatrix} 3 & -1 \\ 0 & 2 \end{pmatrix}\).

Apart from the S phase, we found the formation of another chain-like structure during the STM scanning, denoted by L as shown in the middle of Fig. 1a. Along the chains pentacene molecules closely align in parallel, with their long molecular axes perpendicular to the chain direction. A rectangular unit cell is drawn. The inset shows the 2D Fourier transformation pattern illustrating the rectangular periodicity of the surface lattice.
are \( a = 6.6 \pm 0.3 \, \text Å \) and \( b = 14.9 \pm 0.3 \, \text Å \). For comparison, the dimension of a single isolated pentacene molecule is \( 14.2 \, \text Å \times 5 \, \text Å \) and the van der Waals length in \( b-c \) plane of the bulk crystal is estimated to be \( 16 \, \text Å \times 6 \, \text Å \) [22]. Therefore, the phase L has a pretty compact configuration, its packing density being \( 1.02 \times 10^{14} \, \text mol/cm}^2 \), 1.16 times of that of phase S. We note that this chain-like structure is very similar to the structures of pentacene adsorbed on noble metal surfaces, where the strong interaction between the empty d orbital of the novel metal substrate and the \( \pi \) orbital of pentacene forces the adsorbed molecules to lie down. For examples, on Cu(110), pentacene molecules are found aligned side-by-side perpendicular to the chain direction [9], and adjacent molecules are separated by 7.2 Å in the regular chain pattern. The chain is 15.6 Å wide with the inter-chain separation of 28 Å. On Au(111), pentacene form a number of ordered structures in the striped form: Kang and Zhu observed five phases by STM, two of which having unit cells of 15.1 Å \times 7.5 Å, 96° and 15.5 Å \times 6.4 Å, 82°, respectively [12]. Parkinson et al. reported a high density phase with a unit cell of 15 Å \times 5.76 Å, 90° [11]. These pentacene structures are similar to the L phase in our observation. However, it is hard to determine whether the molecules are lying with their planes parallel to the surface or not from STM images. For such a close packing, the molecules are likely to tilt their short axis from the substrate to reduce the steric interaction of hydrogen atoms. For example, using elastic recoil detection analysis Suzuki et al. [23] obtained a 13° tilting of the molecular short axis from the Au(111) surface, while X-ray absorption spectroscopy data indicates a tilting angle of less than 5° for the monolayer [24]. In addition, we found that the contrast of the two phases, S and L, can be changed significantly or even reversed by changing the sample bias in STM image, suggesting that phase L is not an adlayer on phase S.

![Fig. 2. (a) A 200 \times 200 \, \text nm² STM image with pentacene dose of 1.2 ML. In phase L, the chains are mostly aligned straight along the [112] directions of the Si(111) surface. (b) (40 \times 40 \, \text nm², -2.4 \, \text V, 0.09 \, \text nA). Some of the chains are curved to follow local surface morphologies (step edge) as marked by the ellipse. (c) (23 \times 23 \, \text nm², -1.5 \, \text V, 0.1 \, \text nA) Three domains of phase L are marked by 1, 2 and 3, respectively. The double-headed arrows indicate the chain directions. It is along the [112] direction in domain 1, at an angle of 35° with [112] in domain 2, and 15° in domain 3. (d) (15 \times 15 \, \text nm², -1.5 \, \text V, 0.1 \, \text nA) An unusual arrangement observed with local defects. Domain a is the normal phase L; while domain b has a slightly different configuration with the frustrated regions marked by the dotted ellipses.](image-url)
A large number of STM images reveal that pentacene chains in the L phase follow predominately the three rotationally equivalent $[\frac{1}{2}1\bar{1}]_C\bar{2}2/C138$ directions of Si(111) surface, as shown in Fig. 2a. However, some of the chains are observed to curve near step edges of the substrate, defect sites or the ends of the molecular chains (Fig. 2b). The situation is similar to pentacene adsorption on Au(111) [11,12] and Au(100) [25]. Apart from the three predominant directions, there is a broad distribution of relative angles between the molecular chains. For example, in Fig. 2c,
three domains of phase L are present. The double-headed arrows indicate the row direction. Domain 1 is along the [112] direction. The angle between domains 1 and 2 is \(~35^\circ\), and \(~15^\circ\) between domains 1 and 3. Statistical analysis shows that about 20\% of the pentacene chains have orientations deviating from [112] and varying arbitrarily. This clearly reveals that phase L is incommensurate with respect to the substrate.

In addition, a slightly different type of arrangement can be found around some defect regions, as shown in Fig. 2d. Two domains, labeled a and b, are found coexisting in the image. Domain a is the normal type having the configuration of phase L as described above, while domain b is slightly different. The molecules are staggered in the chain direction, and the long molecular axis is not perpendicular to the chain. The periodicity along the chain remains \(6.6\ \text{Å}\) while the inter-chain distance no longer retains the same value. This unusual quasi-one-dimensional structure might be induced by some defects that frustrate the molecular assembling (highlighted in Fig. 2d). This fact indicates that the molecule–substrate interaction in the L phase is relatively weak and the potential barrier for the in-plane rotation of pentacene molecules is quite low on the Ag/Si-\(\sqrt{3}\) surface.

It is the most interesting that during STM scanning, the total area of the pentacene chains increases step by step, and the L phase develops gradually. This process is demonstrated in the time-sequential images in Fig. 3a–f, which are taken on an \(80 \times 80\ \text{nm}^2\) area with the same tunneling condition. As seen in Fig. 3a most of the area is covered by phase S that appears bright with only a few dark chains identified as phase L. After 46 min scanning, almost 80\% of the entire area is covered by the new phase L with some small regions remaining unchanged, as shown in Fig. 3f. The transformation normally starts from domain boundaries, defect sites and step edges, which can be understood as these sites are energetically more unstable and there are more free space for the molecules to rotate and move to form chains.

Experiments performed under different conditions reveal that the structure transformation is not spontaneous, and it may occurs only with the help of tip scanning. A surface covered by phase S has been kept in the UHV chamber for a long time (over 10 h) and no change is detected. The obtained structure is not influenced by the deposition rate and the sample preparation temperature. Annealing can not transfer phase S to phase L either. We also investigated the effect of the scanning parameters and found that the transformation is irreversible and independent of the scan direction, but the rate is proportional to the scan speed. The transformation can occur in a wide bias voltage range (\(-4\ \text{V} \to +4\ \text{V}\)). With the same tip the rate of the transformation does not depend on the polarity or amplitude of the bias voltages or the tunneling current, as shown in Fig. 4. But it depends significantly on the tip condition. This indicates that the structure transformation is more likely induced by the electric field between the tip and the surface, which depends strongly on the shape and condition of the tip, while it is not a direct result of the tunneling electrons.

Since phase L has significant higher molecule density than phase S, it is puzzling where the excessive pentacene molecules come from and how they join into the chain structure. We noticed that phase S appears to be a saturation structure. Pentacene dosage within the range of 1–8 ML has been deposited on the surface, and there is no noticeable change of the S structure observed by STM at RT. Therefore we suppose that there is a 2D molecule gas [26,27] of mobile pentacene on the surface of the S phase, which is the pentacene source during the structure transformation from S to L. To verify this we cooled samples with different pentacene dosages to about 120 K for STM observations. For the sample covered by 1 ML pentacene, there is no noticeable change after cooling. The surface is still clean and fully covered by the brick-wall structure. While for surface with higher dosage, we found the formation of scattered big 3D islands after cooling (as shown in Fig. 5), and tip-induced structure transformation no longer occur at LT. This observation clearly demonstrates the existence of a mobile molecule gas on the surface of the S phase at dosage larger than 1 ML, which is condensed into 3D islands at LT. As the height of these pentacene islands can reach a few tens of nanometers, the formation of them requires collection of pentacene molecules within a large area of the surface. Therefore, the mobility of pentacene molecules should be very high on the surface of the S phase. Such a scenario can be described as that at RT and with pentacene dosage higher than 1 ML, the surface is phase separated: the self-assembled S phase and the 2D gas phase on top of it. The residual 2D molecular gas can also be detected as the occasional streaks in the STM images at ambient temperature.

For a 2D mobile gas phase, the density of molecules in the gas phase is limited by the critical coverage (\(\Theta_c\)). Above...
the excessive molecules will form agglomerates. For example, Ag adatoms form 2D gas on the Si(111)-\(\sqrt{3} \times \sqrt{3}\)-Ag surface with \(\Theta_c \approx 0.03\) ML, and excess Ag atoms deposited on the surface form scattered big 3D agglomerates which can be observed directly by scanning electron microscopy (SEM) [28,29]. Such 3D agglomerates are usually too scattered to be observed in STM images due to the limited scanning size. In our case, at RT because of the relatively big thermal energy, individual pentacene molecule migrates rapidly on the surface of the S phase to form the 2D gas phase. Further deposition of pentacene exceeding the critical coverage (somewhere between 1 and 2 ML) would produce big agglomerates which are too large and scattered to be observed in STM. Apart from the large agglomerates, there is always a 2D gas phase, which is in thermodynamic equilibrium with the solid S phase and the 3D agglomerates. Since both the 2D gas phase and the 3D agglomerates are not observable in STM images, one sees no change in the STM images for pentacene coverage above 1 ML. When cooled down, the mobility of the molecules in the 2D gas phase is drastically reduced and the molecule gas condenses into 3D islands which are observed in STM at LT.

The lack of 2D molecular gas at LT explains the absence of the tip-induced phase transformation at LT. Therefore, the residual 2D gas plays a crucial role in the structure transformation, acting as a molecule reservoir to supply the additional pentacene molecules needed for the transformation from a lower density phase to a higher density phase.

The transformation from phase S to L suggests that a surface consisting of pure phase L is energetically more favorable than a surface with separated phases of S phase and 2D gas phase. Since the film growth is a kinetic process, metastable phases like the S phase can form at small coverage range where it is more stable than the L phase. In the commensurate structure of phase S the molecule–substrate interaction dominates the self-assembly of pentacene molecules at the coverage below 1 ML. With the coverage increase, the molecule–molecule interaction increases and overwhelms the molecule–substrate interaction. A surface consisting of separated phases (S phase and 2D gas phase) becomes thermodynamically less stable than a pure L phase, yet an energy barrier has to be overcome in order for the system to enter the lower energy configuration (L phase), which can be triggered by the tip scanning.

4. Summary

In conclusion, we have studied the scanning-induced structure transformation of pentacene on the Ag/Si-\(\sqrt{3}\) surface. The self-assembled pentacene molecule layer transforms from a brick-wall structure to a higher-density chain structure in a large area (μm size) during STM scanning. The transformation is only observed at RT and pentacene dosage more than 1 ML. We proved that a 2D gas phase of pentacene exists on the surface of the solid S phase with the pentacene coverage above 1 ML, which acts as a pentacene source to compensate the increment of the pentacene molecules in the transformation. After cooling the surface to about 120 K the 2D gas phase condenses into large agglomerates leaving the whole surface covered by a pure S phase, and no tip-induced structure transformation occurs at LT.

Acknowledgments

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References