Temperature and coverage driven condensation of pentacene on the Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$–Ag surface

2007 J. Phys.: Condens. Matter 19 356005

(http://iopscience.iop.org/0953-8984/19/35/356005)

Temperature and coverage driven condensation of pentacene on the Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Ag surface

Jing Teng, Jiandong Guo, Kehui Wu[1] and Enge Wang

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

E-mail: khwu@aphy.iphy.ac.cn

Abstract
The adsorption and self-assembly behavior of pentacene molecules on the Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Ag surface has been studied by variable-temperature scanning tunneling microscopy (STM). By cooling the surface from room temperature to 120 K we observed the condensation of a two-dimensional molecular gas phase to a new ordered solid phase (P2). The structure models of this phase and the high-density brick-wall phase (P1) are proposed consistently based on a systematic investigation of the morphology, chirality and domain boundary structures of the two phases. The self-assembly mechanism of pentacene molecules driven by temperature and molecular coverage is discussed.

1. Introduction

The performance of organic semiconductor devices depends crucially on the crystal quality of organic thin films. To improve the quality of crystalline films requires a control of the initial arrangement of molecules on solid surfaces. Moreover, the electron transport through the interface between the film and the substrate is significantly influenced by the interface structure, such as the molecular ordering, orientation and their binding with the substrate. Therefore, much effort has been devoted to understand the self-assembly of organic molecules on solid surfaces and its influences on the subsequent growth of thin films [1–5].

Pentacene ($C_{22}H_{14}$) is one of the most promising candidates for organic semiconductor device applications [6–9]. The growth of pentacene on silicon surfaces has received intensive studies due to its potential integration with silicon based technology. For pentacene growth on clean silicon surfaces, the strong chemical interaction between the silicon dangling bonds and the molecules makes the pentacene molecules immobile, resulting in a disordered wetting layer and poor film quality. To solve this problem, silicon surfaces have been passivated by a cyclohexene buffer layer [10–12] or by metals that form superstructures to improve the

---

[1] Author to whom any correspondence should be addressed.

molecule mobility and hence the crystal quality of pentacene films. More interestingly, the orientation of pentacene molecules on the silicon substrate can be controlled by tuning the surface metallicity. On strongly metallic surfaces such as Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Au the pentacene molecules are found lying flat on the surface, while on semimetallic surfaces such as Si(111)-(5 × 2)–Au they are found standing up [13]. Such tunability provides an opportunity to grow pentacene films with different interface structures and accordingly different transport properties for particular device functionalities.

Si(111)-($\sqrt{3} \times \sqrt{3}$)R30°–Ag (referred to as the Ag/Si-$\sqrt{3}$ surface hereafter) is a typical metallic surface, which has attracted much interest for pentacene growth. Pentacene molecules are found lying flat with their long molecular axis parallel to the surface. In the previous scanning tunneling microscopy (STM) studies by Guaino *et al* [14, 15], several solid phases formed at room temperature (RT) were reported, including a densely packed brick-wall phase and a few other submonolayer phases. However, the structures of these phases, as well as the self-assembly mechanism, have not yet been fully understood. In this paper, we report a systematic coverage and temperature dependent STM study of the self-assembly behavior of pentacene molecules on the Ag/Si-$\sqrt{3}$ surface. At RT we found two phases, a 2D molecule gas phase at low coverage and a brick-wall solid phase at high coverage, while at low temperature (LT) we found a new ordered solid phase with a low packing density, three-quarters of the brick-wall phase. The two solid phases are essentially similar and their structure models are proposed consistently based on the detailed STM studies of the periodicity and the registry of the molecules. The condensation process of pentacene molecules from the 2D gas phase to the solid phases driven by temperature and pentacene coverage is discussed.

2. Experiments

Experiments were carried out in a commercial Omicron Multiprobe UHV system with the base pressure of 5×10^{-11} mbar. The substrate was cut from a n-type Si(111) wafer (phosphor doped, ∼2 Ω cm at RT). The surface was cleaned by flashing the substrate up to 1550 K repeatedly until a nice 7×7 reconstruction was formed. Ag was deposited from a tungsten wire evaporator while the substrate temperature was maintained at about 800 K. The sample was held at the same temperature for an extra 3 min to obtain a well ordered Ag/Si-$\sqrt{3}$ surface. Pentacene molecules were then dosed from a Knudsen cell with the substrate kept 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 a tungsten tip. LT STM measurements were performed by cooling the sample to 120 K with liquid nitrogen through a continuous flow cryostat after RT measurements.

3. Results and discussion

3.1. Room-temperature phases

At room temperature, a long-range ordered phase is formed with a closely packed brick-wall geometry at the pentacene coverage of 8.7×10^{13} mol cm^{-2}, about 11% of the atomic density of the bulk-terminated Si(111)-1 × 1 surface (see figure 1), consistent with the result by Guaino *et al* [14, 15]. We found this coverage to be a saturated one and defined it as one molecule monolayer (ML) for pentacene adsorption on the Ag/Si-$\sqrt{3}$ surface. Pentacene dosage up to 8 ML has been deposited onto the surface and the STM observations reveal no prominent change.

Figure 1(a) shows a typical filled state STM image of this 1 ML solid phase, named P1. In this phase, pentacene molecules align their long axes along the [1$\bar{1}$0] direction relative to
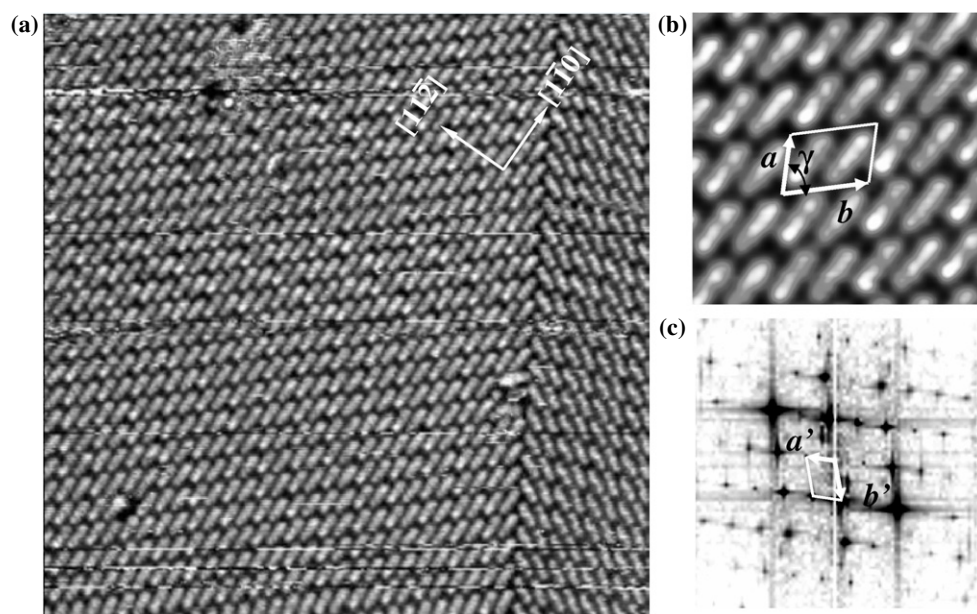
Figure 1. (a) A 21 nm × 21 nm filled state STM image of phase P1 (−1.8 V, 80 pA). (b) A zoom-in image (6.2 nm × 6.2 nm) showing the different contrasts of the two ends of the pentacene molecules. Each unit cell contains two molecules forming a pair. (c) The 2D FFT of (b), which reveals the parallelogram periodicity of the surface lattice.

the Si(111) substrate, forming an array of molecule rows. Along these rows, the two ends of the molecules are not equivalent, with one end brighter than the other end in the filled state STM images, as shown in figure 1(b). The orientation of the molecules lines up alternatively in a bright–dark–dark–bright... sequence. Moreover, the distance between adjacent molecules diverges along the rows, the dark–dark spacing being narrower than the bright–bright spacing. In such a manner, the pentacene molecules pair up along the [1$\bar{1}$0] direction, leading to a periodicity of 34.6 ± 0.2 Å. Across these rows, the intermolecular spacing is 6.7 ± 0.2 Å, close to the van der Waals interaction length of the pentacene molecules in their benzene plane perpendicular to the long axes. These values are consistent with the flat-lying configuration which would maximize the overlap of the aromatic π-system with the substrate orbitals. In figure 1(b), the unit cell of this structure is marked with the lattice parameters of $a = 13.3$ Å, $b = 17.6$ Å, and $\gamma = 79.1°$. Along the b direction, the bright–dark orientation of individual molecules is alternately ordered, leading to the dipolar configuration for the two adjacent molecules within one unit cell.

We propose a structure model of the P1 phase based on the following observations: (1) the underlying Ag/Si-$\sqrt{3}$ layer is retained after dosing the molecules (we observed the $\sqrt{3} \times \sqrt{3}$ periodicity in the low-bias image of the 1 ML pentacene surface); (2) the periodicity along the [1$\bar{1}$0] surface direction is 34.6 Å, exactly three times the long diagonal of the Ag/Si-$\sqrt{3}$ unit cell (11.5 Å); (3) the inter-row spacing is 6.7 Å, which corresponds to the short diagonal of the Ag/Si-$\sqrt{3}$ unit cell; (4) the two ends of the molecule show different contrasts in STM images, implying their asymmetry in the charge-density distribution. We name the benzene rings of the molecule from the dark end to the bright end 1–5, respectively, as indicated in figures 2(a) and (b). The proposed model is superimposed onto the high-resolution STM image
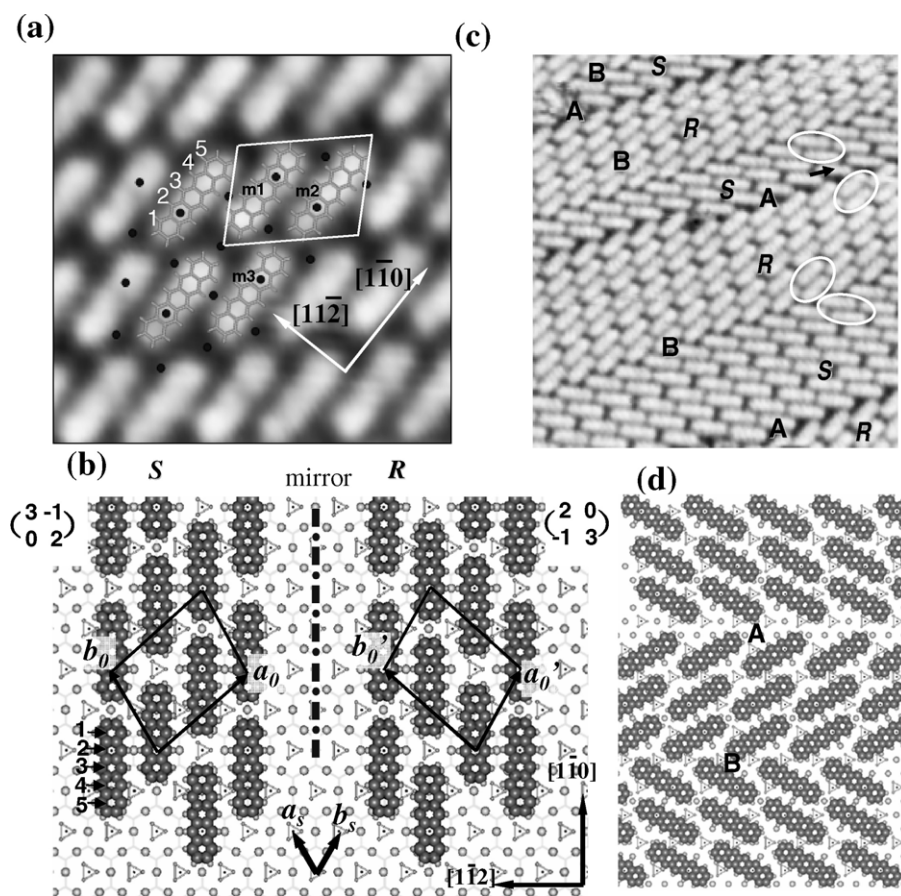
3

Figure 2. (a) A proposed model of phase P1 overlapping on an STM image (5 nm × 5 nm, −1.7 V, 80 pA). Molecules align along the [1$\bar{1}$0] direction of the substrate, with their second benzene ring situated at the center of a Si trimer (black dots). (b) The structure model of pentacene molecules on the Ag/Si-$\sqrt{3}$ substrate. For the substrate, the dots are Ag atoms and triangles are Si trimers. Two chiral structures, labeled 'S' and 'R' respectively, are shown. The unit cell vectors a_0, b_0, a'_0, b'_0 and the substrate vectors a_s, b_s are included. (c) (16 nm × 17 nm) Two types of domain boundaries in phase P1; the molecule pairs are marked with ellipses and an unpaired molecule is indicated by an arrow. 'A' represents the looser boundary as compared with the denser type of boundary 'B'. Their models are schematically drawn in (d).

in figure 2(a), where the dots represent the centers of the Si trimers of the underlying Ag/Si-$\sqrt{3}$ lattice. The paired molecules in a unit cell are marked as m1, m2, respectively, while the neighboring molecule of m2 within a row is marked as m3. In this model, m2 and m3 are reflectively symmetric with the mirror plane along the [11$\bar{2}$] direction. Every molecule aligns the center of its second benzene ring on top of a Si trimer. Correspondingly, the fifth benzene ring is located almost exactly on top of a Ag trimer, while the first ring is just on the edge of a Ag trimer. Such a configuration is consistent with the different brightnesses of the two ends of a pentacene molecule in the filled-state STM images, since the two ends of the molecule are on different adsorption sites.

Besides, the above model can well explain the domain boundary structures observed in our experiments, as shown in figure 2(c). There are two types of domain boundaries (labeled

as A and B). Type A is significantly less densely packed than type B, with a molecule pair (i.e. m1 and m2) on one side and one unpaired molecule on the other side as indicated in the image. In contrast, the type B boundary has molecule pairs on both sides. The structures of the two types of domain boundaries are illustrated in figure 2(d) based on the structure model described above. We find that our model is the only one that generates the two types of boundaries. Translating the molecules to any other possible adsorption sites would result in boundary structures which contradict our experimental observations.

Moreover, the paring of pentacene molecules (m1 and m2) induces two mirror configurations (named R and S) which form two mirror domains with respect to the $[1\bar{1}0]$ surface direction, as shown in figure 2(b). Either configuration can be rotated 60° or −60°, producing another two spatially equivalent domains respectively, amounting to six different domains in total. The unit cell vectors a_0, b_0 of structure S are related to the substrate vectors a_s, b_s by $\begin{pmatrix} a_0 \\ b_0 \end{pmatrix} = \begin{pmatrix} 3 & -1 \\ 0 & 2 \end{pmatrix}\begin{pmatrix} a_s \\ b_s \end{pmatrix}$, while structure R is $\begin{pmatrix} a_0' \\ b_0' \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ -1 & 3 \end{pmatrix}\begin{pmatrix} a_s \\ b_s \end{pmatrix}$. In each domain, the threefold symmetry of the substrate is no longer preserved. This symmetry-breaking effect is clearly displayed in the domain boundary structure as shown in figure 2(c), where all the boundaries are formed by two distinguishable mirror domains. It should also be noted that the inherently non-chiral nature of the pentacene molecule results in an equal probability of forming the mirror domains and the coexistence of these domains makes the overall surface non-chiral and racemic.

For submonolayer coverage at RT, large numbers of data are collected and we found only a 2D gas phase where the pentacene molecules are highly mobile on the substrate and STM is unable to register the moving molecules [16–18]. The high mobility of pentacene molecules on the Ag/Si-$\sqrt{3}$ surface indicates that, although the interaction between the molecule and the substrate is strong so that the molecules are found lying flat, the diffusion barrier must be small enough to facilitate the movement of molecules on the surface. The reason why we have not observed the other solid phases at RT reported by Guaino *et al* [14, 15] is not known yet. It could be that those phases were formed via a kinetic process during the sample preparation and they are merely metastable at RT.

3.2. Low-temperature phases

We cooled the sample to about 120 K for STM measurement. At coverage above 1 ML we still observe phase P1 identical to the RT observations, while at 0.75 ML we find that the gas phase observed at RT is now condensed into a new ordered structure, phase P2, which fully covers the surface as shown in figure 3(a). In this phase pentacene molecules are arranged in a loosely packed brick-wall pattern. All molecules appear identical and so is the intermolecular spacing, as shown in the high-magnification image in figure 3(b). Therefore, each unit cell includes only one pentacene molecule in this phase.

Compared with phase P1, phase P2 possesses a higher symmetry, retaining all mirror planes of the Ag/Si-$\sqrt{3}$ substrate. As a result, only three equivalent rotational domains exist, oriented at 120° with respect to each other. The molecular long axis is also along the $[1\bar{1}0]$ direction and the inter-row separation remains 6.7 Å, the same as that in phase P1, but the intermolecular distance within a row becomes 23 Å, exactly twice the long diagonal of the Ag/Si-$\sqrt{3}$ unit cell. Such alignment makes the molecular density precisely three-quarters of that of phase P1, in good agreement with the experimentally determined coverage of 0.75 ML. Figure 3(b) shows the hexagonal unit cell with the lattice parameters of $a = b = 13.3$ Å, and $\gamma = 60°$, related to the substrate vectors by $\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}\begin{pmatrix} a_s \\ b_s \end{pmatrix}$. Therefore, phase P2 can be denoted as Ag/Si(111)-($2\sqrt{3} \times 2\sqrt{3}$)-pentacene including one molecule per unit cell.
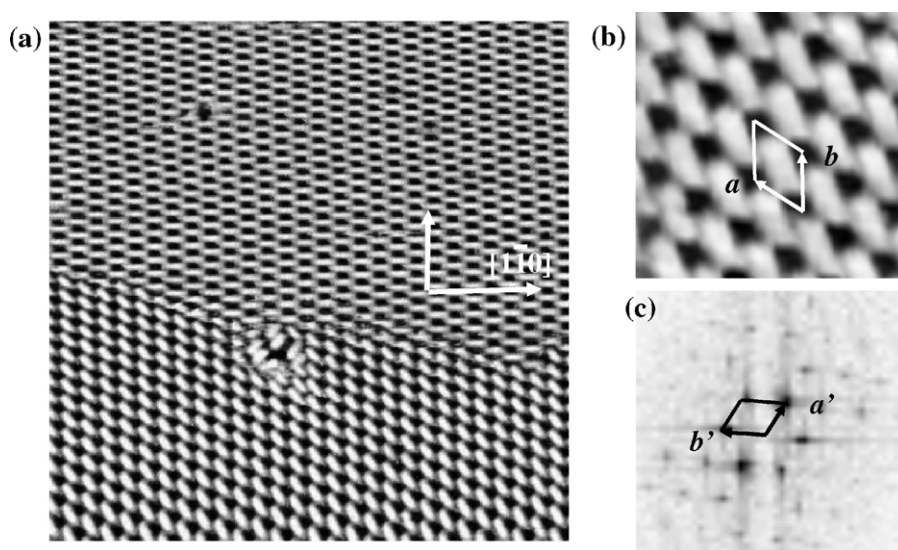
Figure 3. (a) A typical STM image of phase P2 recorded at 120 K (31 nm × 31 nm, −2.5 V, 80 pA). (b) A close-up view (6.5 nm × 6.5 nm) shows the equality of all molecules. A unit cell is outlined, corresponding to the 2D Fourier transform of (c).

The registry of the molecules with respect to the Ag/Si-$\sqrt{3}$ lattice is clearly revealed by the bias dependent STM image as shown in figure 4(a). It has been considered that the bias voltage is a tunable parameter to image either the molecular adlayer or the substrate underneath [19–23]. Because of the energy gap between the highest occupied and lowest unoccupied molecular orbitals, the STM tip is transparent to the molecular adlayer if a small bias voltage within the gap voltage range is applied (−0.6 V in the current case). Consequently, it is possible to image the substrate lattice, as shown in the lower part of figure 4(a). When a larger bias is applied (−3.6 V), the molecules are imaged as shown in the upper part of figure 4(a). By switching the bias voltage during scanning the periodicity of the underlying substrate can be obtained in the same image with the pentacene layer, which makes it possible to determine the registry of pentacene molecules relative to the substrate lattice. In the lower part of figure 4(a), the honeycomb structure with a $\sqrt{3} \times \sqrt{3}$ periodicity is clearly imaged, where the center of each hexagon corresponds to the position of a Si trimer, as marked by the dot arrays. The positions of these dots overlap perfectly with the center of each pentacene molecule, indicating that each pentacene molecule adsorbs on the surface with its central benzene ring on top of a Si trimer, as shown in figure 4(b).

Moreover, the absence of molecule pairs in phase P2 results in only one type of domain boundary. This is confirmed by our experimental observations shown in figure 4(c). The image consists of two domains, with the corresponding structure model illustrated in figure 4(d).

At pentacene coverage between 0.75 and 1 ML, phase P2 coexists with the high-density phase P1 at LT (figure 5). As the pentacene density increases from 0.75 ML, phase P2 starts to grow around defect sites such as domain boundaries or vacancies. The molecules form pairs along the rows in order to accommodate more pentacene on the surface. A complete film in phase P1 is formed when the monolayer coverage is reached.

At pentacene coverage lower than 0.75 ML, we could observe no ordered pentacene structure even at 120 K. The situation appears to resemble the RT case with pentacene coverage below 1ML; that is, the pentacene molecules exist in a 2D gas phase but with a low density.
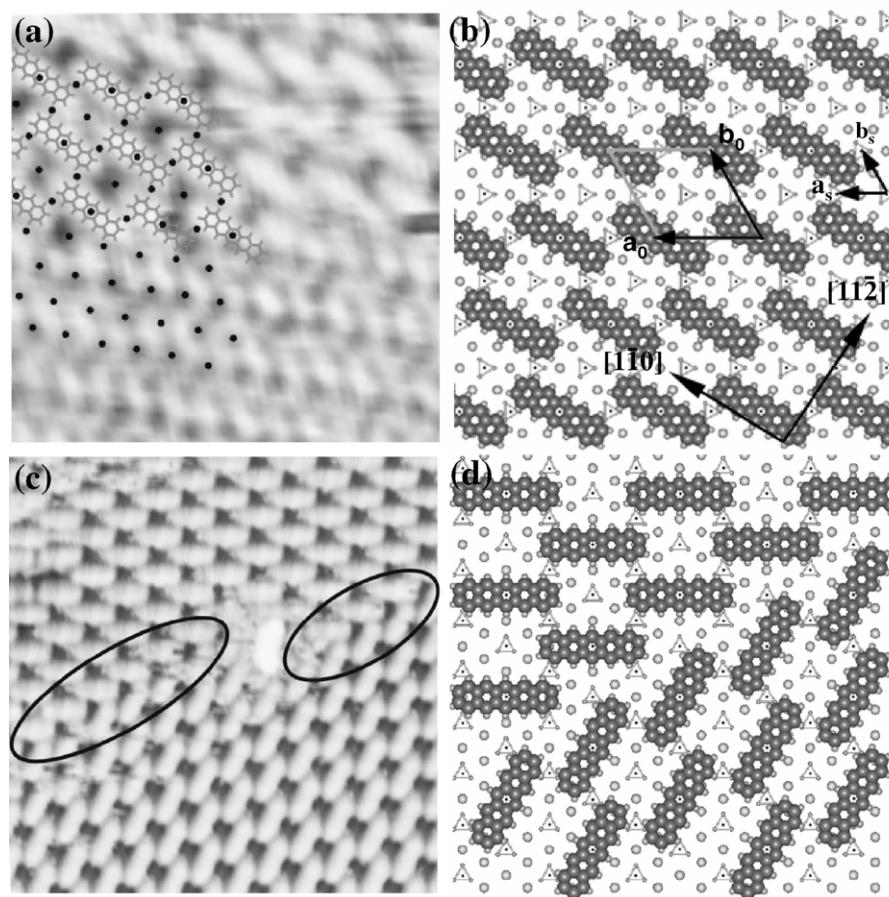
Figure 4. (a) An LT-STM (120 K) image (8 nm × 8 nm) of a phase P2 imaged at low bias (−0.6 V) in the lower part of the image and at high bias (−3.6 V) in the upper part. The positions of Si trimers (dots) aligned perfectly with the centers of pentacene molecules. (b) Schematic drawing of the registry of the molecules with respect to the ($\sqrt{3} \times \sqrt{3}$)–Ag lattice. (c) Domain boundary of phase P2 (15 nm × 15 nm), with the model shown in (d).

3.3. Discussions

We note that the two ordered solid phases, P1 and P2, are inherently similar. They are both commensurate structures, indicating that their molecular arrangements are both mediated by the substrate–molecule interactions. Their long molecule axes are both aligned along the [1$\bar{1}$0] direction of the substrate, with just different periodicities, three times and two times the periodicity of the substrate, respectively. They also have identical inter-row spacing. Moreover, we observe a mixture of these two phases at LT and coverage between 0.75 and 1 ML, suggesting that they are quite close to each other in energy. Since in phase P2 the central benzene ring locates atop the Si trimer, which is evidenced from the bias dependent image, it is logically reasonable to suggest that in phase P1 the pentacene molecule also interacts with the substrate through its π orbit and the Si trimer. In contrast, in the previous P1 model proposed by Guaino *et al* [14, 15] the central benzene ring of pentacene is on top of the Ag trimer. In fact, their model encounters difficulty in that (1) the different brightnesses of the two ends of
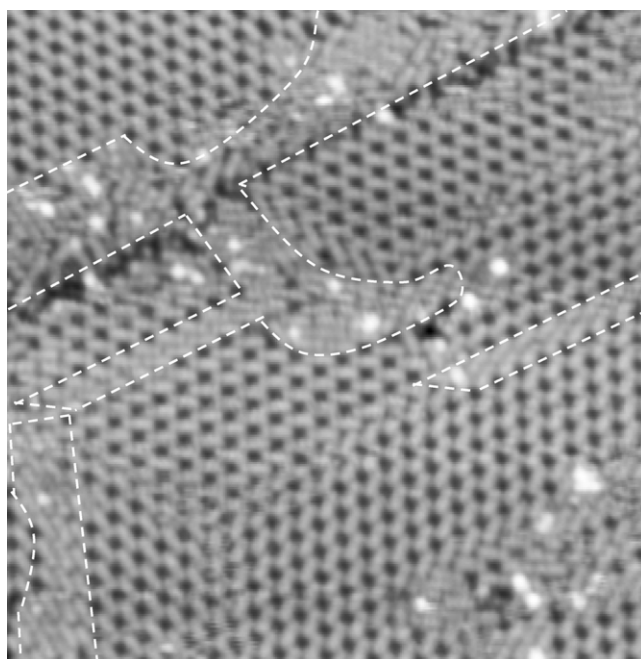
Figure 5. A LT-STM image (31 nm × 26 nm) taken at the coverage about 0.85 ML, where both phases, P1 and P2, are found to coexist. The high-density P1 phase is outlined in the marked regions.

the molecules can not be explained; (2) it does not give the two types of domain boundaries observed in experiments; (3) the intermolecular distance along the molecular long axis (15.3 Å) is shorter than the length of the pentacene molecule, 16 Å, which would induce too high a strain in the flat-lying geometry. In contrast, our model is consistent with all these observations.

The adsorption of molecules on a surface is generally governed by the interplay between the molecule–substrate interaction and the molecule–molecule interaction. In the case of pentacene, it has been found that the molecule–substrate interaction increases with the metallicity of the underlying template [13]. In our system, the molecule–substrate interaction should be strong in that (1) all pentacene molecules are found in a 'flat-lying' configuration and (2) the two ordered phases, P1 and P2, are both commensurate with the substrate, indicating that they are both substrate mediated structures. This is consistent with the strong metallic nature of the Ag/Si-$\sqrt{3}$ substrate [23]. In addition, on the Ag/Si-$\sqrt{3}$ surface, both the lattice corrugation and the lateral variation of the potential energy surface are small [24, 25]. Therefore pentacene molecules are allowed to diffuse freely on the surface to form self-assembly structures with long-range orders.

On the other hand, without any functional group attached to the pentacene molecules, the intermolecular interaction is dominated by the van der Waals force. The interaction is attractive since the interspacing of molecules in our observed structures is larger than the equilibrium distance in the bulk phase. At high coverage (∼1 ML) when the intermolecular interaction is relatively strong, condensed solid phases are favored, and the densely packed brick-wall structure P1 can be stabilized even at RT. At low coverage (∼0.75 ML) when the intermolecular interaction is weak, the thermal activation energy dominates at RT, resulting in the gas phase, in which the molecules are moving fast on the surface. But at LT, as the thermal energy is reduced, the gas phase condenses into the loosely packed brick-wall structure

P2, corresponding to another thermodynamic equilibrium state. At coverage between 0.75 and 1 ML, the RT gas phase condenses to a mixture of the two brick-wall structures, suggesting that these two phases are quite close to each other in energy. This is consistent with the fact that the molecules are allowed to diffuse on the Ag/Si-$\sqrt{3}$ template to establish different orders. The formation of fully covered phase P2 at 0.75 ML, instead of a phase separated Ag/Si-$\sqrt{3}$ substrate and partly covered phase P1, indicates a good wettability of pentacene molecules on the Ag/Si-$\sqrt{3}$ surface. This offers us the controllability of different self-assembled phases by tuning the temperature and coverage. We speculate that other solid phases, with coverage lower than 0.75 ML, might be stabilized at even lower temperatures.

4. Summary

In conclusion, we have performed temperature and coverage dependent studies on the adsorption and self-assembly of pentacene on the Ag/Si-$\sqrt{3}$ surface. A new LT solid phase, P2, is reported, and its adsorption model is proposed consistently with the RT solid phase P1, based on a detailed STM investigation of the geometry, chirality and domain boundary. The two phases are both flat-lying, commensurate structures, indicating that they are substrate mediated phases. In spite of the strong molecule–substrate interaction, the smoothness of the substrate surface and hence the high diffusivity of molecules on the surface play important roles in the molecule self-assembly driven by temperature and coverage changes.

Acknowledgment

References

[1] Hillier A C and Ward M D 1996 *Phys. Rev.* B **54** 14037
[2] Hooks D E, Fritz T and Ward M D 2001 *Adv. Mater.* **13** 227
[3] Schreiber F 2004 *Phys. Status Solidi* a **201** 1037
[4] Witte G and Wöll C 2004 *J. Mater. Res.* **19** 1889
[5] Mannsfeld S C B and Fritz T 2006 *Mod. Phys. Lett.* B **20** 585
[6] Dimitrakopoulos C D, Purushothaman S, Kymissis J, Callegari A and Shaw J M 1999 *Science* **283** 822
[7] Klauk H, Halik M, Zschieschang U, Schmid G, Radik W and Weber W 2002 *J. Appl. Phys.* **92** 5259
[8] Dimitrakopoulos C D and Malenfant P R L 2002 *Adv. Mater.* **14** 99
[9] Lee S, Koo B, Shin J, Lee E, Park H and Kim H 2006 *Appl. Phys. Lett.* **88** 162109
[10] Hamers R J, Coulter S K, Ellison M D, Hovis J S, Padowitz D F, Schwartz M P, Greenlief C M and
     Russell J N Jr 2000 *Acc. Chem. Res.* **33** 617
[11] Meyer zu, Heringdorf F-J, Reuter M C and Tromp R M 2001 *Nature* **412** 517
[12] Ruiz R, Nickel B, Koch N, Feldman L C, Haglund R F, Kahn A and Scoles G 2003 *Phys. Rev.* B **67** 125406
[13] Thayer G E, Sadowski J T, Meyer zu Heringdorf F, Sakurai T and Tromp R M 2005 *Phys. Rev. Lett.* **95** 256106
[14] Guaino Ph, Cafolla A A, Carty D, Sheerin G and Hughes G 2003 *Surf. Sci.* **540** 107
[15] Guaino Ph, Carty D, Hughes G, Moriarty P and Cafolla A A 2003 *Appl. Surf. Sci.* **212** 537
[16] Dunphy J C, Sautet P, Ogletree D F, Dabbousi O and Salmeron M B 1993 *Phys. Rev.* B **47** 2320
[17] Stranick S J, Kamna M M and Weiss P S 1994 *Science* **266** 99
[18] Stranick S J, Kamna M M and Weiss P S 1995 *Surf. Sci.* **338** 41
[19] Mizutani W, Shigeno M, Sakakibara Y, Ono M, Tanishima S, Ohmo K and Toshima N 1990 *J. Vac. Sci. Technol.*
     A **8** 675
[20] Kanai M, Kawai T, Motai K, Wang X D, Hashizume T and Sakurai T 1995 *Surf. Sci.* **329** L619
[21] Dekker C, Trans S J, Oberndorff B, Meyer R and Venema L C 1997 *Synth. Met.* **84** 853
[22] Upward M D, Beton P H and Moriarty P 1999 *Surf. Sci.* **441** 21
[23] Uhrberg R I G, Zhang H M, Balasubramanian T, Landemark E and Yeom H W 2002 *Phys. Rev.* B **65** 081305
[24] Nakajima Y, Uchida G, Nagao T and Hasegawa S 1996 *Phys. Rev.* B **54** 14134
[25] Sato N, Nagao T and Hasegawa S 1999 *Phys. Rev.* **60** 16083