

Available online at www.sciencedirect.com



SURFACE SCIENCE

Surface Science 601 (2007) 3179-3185

www.elsevier.com/locate/susc

# Structural evolution at the initial growth stage of perylene on Au(111)

L. Gao, J.T. Sun, Z.H. Cheng, Z.T. Deng, X. Lin, S.X. Du, H.-J. Gao \*

Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, PR China

Received 16 October 2006; accepted for publication 17 May 2007 Available online 2 June 2007

## Abstract

We report on the structural evolution at the initial growth stage of perylene thin films on Au(111) surface. Scanning tunneling microscopy and spectroscopy have been employed to investigate the structural and electronic properties at 78 K. Rapid molecular diffusion was observed at low submonolayer coverage. Molecules form an ordered structure at monolayer coverage. For the second layer, impinging molecules nucleate into molecular islands with an ordered intermediate structure. © 2007 Published by Elsevier B.V.

Keywords: Aromatics; Gold; Molecular beam epitaxy; Thin film structures; Scanning tunneling microscopy; Low energy electron diffraction (LEED)

## 1. Introduction

The growth of organic thin films on solid surfaces is attracting considerable interest due to their potential applications in organic electronics and optoelectronics [1-5]. In organic devices, carrier transport and luminescent behavior are governed by the orientation and packing of molecules [6,7]. Therefore, enormous efforts have been made to understand and precisely control the formation of organic thin films with various structures. Deposition of organic molecules from the gas phase in ultrahigh vacuum (UHV), sometimes referred to as organic molecular beam deposition (OMBD) or organic molecular beam epitaxy (OMBE), is an ideal means, compared with Langmuir-Blodgett (LB) technique and self-assembly in solution, to achieve monolayer control over the growth of organic thin films with extremely high chemical purity and structural precision. Investigation of the initial growth of the thin films is of great significance, because the initial growth is crucial for the growth of high-quality thin films on the one hand, and the solid/organic interface plays a crucial

role in the performance of organic devices on the other hand.

Perylene  $(C_{20}H_{12})$  is a planar aromatic molecule with rather large intrinsic charge-carrier mobility at low temperatures [8]. Perylene has attracted considerable interest in recent years because of its excellent performance in electronic and light-emitting devices [9]. The formation of perylene adlayers by OMBD has been studied on metal [10-22] and semiconductor [23,24] surfaces. So far, the multilayer growth has been conducted on Si(111) [23], Au(111) [10] and Cu(110) [10,15,20] surfaces. Some previous studies show that perylene molecules pack with the  $\pi$ -plane oriented almost or completely parallel to the substrate in the multilayer regime [15,23]. While other studies show that a planar or near-planar orientation of perylene molecules is limited to the first monolayer, and the transition to bulk structure occurs with increasing film thickness [10,20].

In this work, our main objective is to investigate the structural evolution in the growth process of the first two layers of perylene thin film. Gold, commonly used as a contact material for source and drain electrodes in organic field effect transistors, was chosen as the substrate. Low temperature scanning tunneling microscopy and spectroscopy (LT-STM/STS) and low energy electron diffraction (LEED) were employed to study the structural evolution.

<sup>\*</sup> Corresponding author. Tel.: +86 010 8264 8035; fax: +86 010 6255 6598.

E-mail address: hjgao@aphy.iphy.ac.cn (H.-J. Gao).

# 2. Experiment

All the experiments were performed with an Omicron UHV MBE-LTSTM system with a base pressure below  $3.0 \times 10^{-10}$  mbar. The Au(111) surface was cleaned by repeated cycles of Ar<sup>+</sup> sputtering (1 keV, 5.9  $\mu$ A/cm<sup>2</sup>, 30 min) and subsequent annealing (750 K, 20 min). Then the cleanliness of the surface was checked by LEED and STM. Perylene (Acros, 99+%) materials were effectively purified using the temperature gradient sublimation method and immediately loaded into the sublimation cells. The cells were kept at 338 K for 24 h to be degassed thoroughly before evaporation experiments.

The evaporation experiments were conducted with an MBE-LEED [25,26] that allows in situ recording diffraction patterns in real time during molecular deposition. The molecules were deposited from vapor onto the Au(111) surface with a deposition rate of 0.01 ML/min. The electron energy was set at 12 eV to record the LEED pattern during the adsorption process. The LEED pattern appears like a halo at dilute coverage, changes into a diffuse ring with increasing coverage, then decays into diffuse spots with the coverage close to one monolayer, and finally shows six sharp diffraction spots with a hexagonal distribution at the monolayer coverage. No further LEED pattern transition was observed with further sublimation. In a previous study [13], Seidel et al. observed the further transition of LEED pattern into a final structure with increasing sublimation, which was not observed in our experiment. We speculate that the difference in growth rate leads to the difference in the final monolayer structure. Our work and previous study [13] both show that LEED pattern does not change any more with further sublimation at the monolayer coverage, which is caused by the sharp decrease in sticking coefficient. Only a small number of molecular islands were observed by STM after further depositing molecules onto the first monolayer using the same incident flux for 100 min, the typical growth time for the first monolayer. In our work, we define a monolayer to be a molecular coverage of about  $8.7 \times 10^{13}$  molecules per cm<sup>2</sup>. The molecular coverage is determined by high-resolution STM images. In this paper, the Au(111) substrate was kept at 255 K for the deposition of perylene submonolayer, and at room temperature 300 K for the growth of the first and second layers. All the STM experiments were performed with an Omicron LT-STM system operate at 78 K. A chemically etched tungsten tip was used in our STM measurement. The voltage bias refers to the sample with respect to the tip. All the STM images in this paper were recorded in a constant current mode. dI/dV spectra was measured using a lock-in technique with a modulation signal ( $V_{pp} = 20$  mV, and f = 1 kHz).

#### 3. Results and discussion

The preparation of highly ordered monolayer is the key step in the growth of long-range ordered crystalline organic thin film. It is desirable that molecules form a wetting monolayer on the metal surface, which can effectively suppress the substrate's interaction in the subsequent multilayer growth.

In order to investigate the growth process of the perylene monolayer on the Au(111) surface, we fabricated two submonolayer specimens with different molecular coverage. Fig. 1a is a typical STM image showing the scenario at 78 K after 0.1 ML perylene molecules were deposited onto the Au(111) surface at 255 K. Individual molecules cannot be clearly imaged at this coverage at 78 K due to rapid diffusion over the gold surface. Increasing the molecular coverage up to 0.3 ML, some bright molecular aggregates were observed in our STM measurements at 78 K (Fig. 1b). The molecular aggregates can hardly diffuse over the surface but vibrate locally, thus can be imaged as bright aggregates. The locations of all the aggregates are very selective induced by the surface reconstruction of gold substrate.



Fig. 1. (a) STM image (50 nm × 50 nm, U = -2.3 V, I = 0.08 nA) of molecular diffusion. Molecular coverage is 0.1 ML. (b) STM image (50 nm × 50 nm, U = -1.3 V, I = 0.05 nA) of 0.3 ML perylene molecules on the reconstructed Au(111) surface.



Fig. 2. (a) LEED pattern of Au(111) substrate at 63 eV. (b) LEED pattern of perylene monolayer at 12 eV. (c) STM image (20 nm × 20 nm, U = -0.7 V, I = 0.03 nA) of perylene monolayer. (d) STM image (8 nm × 8 nm, U = -1.0 V, I = 0.05 nA) of perylene monolayer. The sizes of individual molecules are indicated. Molecular long axis is along the [112] direction.

Ordered molecular arrangements form when the coverage increases up to one monolayer. The monolayer superstructure was determined by LEED pattern and high-resolution STM images. In Fig. 2, a and b show the LEED patterns of the clean Au(111) and that of the perylene monolayer, respectively. The LEED pattern of the pervlene monolayer, recorded at 12 eV, shows six sharp diffraction spots that are distributed hexagonally. Thereby, the monolayer superstructure is of a hexagonal two-dimensional Bravais lattice, the same lattice as Au(111) substrate. By comparing the two LEED patterns, we find that the diffraction spots in two patterns have the same azimuthal directions, which indicates that the hexagonal lattice of perylene monolayer has the same orientation with that of gold substrate. Combining LEED results and subsequent STM measurements (Fig. 2c and d), we determined the monolayer lattice as a  $(4 \times 4)$  structure, see the following matrix which was also reported in the previous study [13].

<b>b</b> <sub>1</sub>		4	0		$ \mathbf{a}_1 $
<b>b</b> <sub>2</sub>	=	0	4	•	$\begin{bmatrix} \mathbf{a}_2 \end{bmatrix}$

In the above equation,  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the unit cell vectors of Au(111),  $\mathbf{b}_1$  and  $\mathbf{b}_2$  are the unit cell vectors of the perylene monolayer superstructure. It is obvious that perylene molecules arrange into a commensurate superstructure on the Au(111) surface. The unit cell vectors of the Au(111) substrate are  $\mathbf{a}_1 = 2.88$  Å and  $\mathbf{a}_2 = 2.88$  Å. According to the

above matrix, the unit cell vectors of the perylene monolayer superstructure are  $\mathbf{b}_1 = 11.5$  Å and  $\mathbf{b}_2 = 11.5$  Å with an enclosed angle of  $\Gamma = 60^{\circ}$ . In STM images, individual perylene molecules are ~1 nm in  $[11\overline{2}]$  direction and ~0.6 nm in  $[1\overline{1}0]$  direction, as shown in Fig. 2d. That indicates that the molecular long axis is along  $[11\overline{2}]$  direction, which is in agreement with previous report [22].

First-principles calculations have been carried out to identify the specific adsorption sites.<sup>1</sup> We carried out density functional theory (DFT) calculations of the electronic structure and total energy as implemented in the Vienna *ab initio* simulation package (VASP) [27,28], Perdew–Burke–Ernzerh of generalized gradient approximation for the exchange-correlation energy functional [29], and a plane wave basis set for the expansion of the wavefunction.

<sup>&</sup>lt;sup>1</sup> The perylene/Au(111) system in our calculations was described with a periodic slab model, where each slab was infinite in the *x* and *y* directions and finite along the *z* direction, and then repeated periodically along the *z* direction with a vacuum gap 12 Å (after many tests) to prevent spurious interactions between nearest slab images. In the present calculations, each slab consists of four Au atomic layers with only one perylene layer placed on only one side of the slab to represent a two-dimensional (5 × 5) surface unit cell. Four different adsorption sites were explored, which are fcc site, hcp site, bridge site, and top site. In the structural optimization, the atomic positions of the perylene molecule and the first two layers of the Au slab were allowed to relax while the bottom two Au layers were fixed at their bulk equilibrium positions. The slab has been fully relaxed until the forces experienced by the system were smaller than -0.01 eV/Å.

The interactions between the valence electrons and ion cores were represented by PAW potentials [30,31]. The energy cutoff for plane waves is 400 eV. The number of kpoints is varied until the adsorption energies of pervlene are converged. Molecules adopt lying-flat geometry with the long molecular axis along the  $[11\overline{2}]$  direction, which is verified both by our experimental results (Fig. 2d) and by previous report [22]. Based on that molecular orientation, four possible adsorption sites have been considered in our calculations. Energy optimization results show that the configuration at the bridge site has the highest adsorption energy, which is 3 meV higher than that at the fcc site, 20 meV higher than that at the hcp site, and 22 meV higher than that at the top site. So the possible favorable adsorption site is the bridge site or the fcc site considering there is only a small energy difference between the two adsorption sites in our calculations. Fig. 3 is the supposed model for perylene monolayer on Au(111) surface. We did not observe the compressed monolayer structure reported in previous study [13]. We speculate that the growth rate is responsible for that. The growth rate in our case is around 0.01 ML/min, two orders of magnitude lower than that used in Ref. [13]. The molecules in  $(4 \times 4)$  structure (see Fig. 3) is not close packed, but is reasonable considering the site selective adsorption at perylene/Au(111) interface.

The growth of the second layer is completely different from that of the first layer. When additional molecules are evaporated onto the first layer, two-dimensional molecular islands form with an ordered arrangement, as shown in Fig. 4a and b. The sticking coefficient for the molecules impinging the first monolayer is much lower than that for the molecules impinging the gold surface. Only a small number of molecular islands were observed after further depositing molecules onto the first monolayer using the same incident flux for 100 minutes, the typical growth time for the first monolayer. The apparent height of the molecular islands is 4-5 Å (see the line profile in Fig. 4a), varying with tunneling conditions in STM scanning. Fig. 4b is a typical STM image showing the molecular arrangement of the molecular island. The line profile from C to D in Fig. 4b shows that molecules pack with a dimer-like arrangement in the  $[11\overline{2}]$  direction.

Fig. 5a is a typical high-resolution STM image showing both the molecular arrangement of the first layer and that of the second layer. The substrate orientation can be determined from the first layer. Then the structure of the second layer can be determined as:

$$\begin{bmatrix} \mathbf{c_1} \\ \mathbf{c_2} \end{bmatrix} = \begin{bmatrix} 1.5 & 3.6 \\ -4 & 8 \end{bmatrix} \begin{bmatrix} \mathbf{a_1} \\ \mathbf{a_2} \end{bmatrix}$$

In the above equation,  $\mathbf{c}_1$  and  $\mathbf{c}_2$  are the unit cell vectors of the second layer. The unit cell vectors of the Au(111) substrate are  $\mathbf{a}_1 = 2.88$  Å and  $\mathbf{a}_2 = 2.88$  Å. According to the above matrix, the unit cell vectors of the second layer are  $\mathbf{c}_1 = 13.1$  Å and  $\mathbf{c}_2 = 20.0$  Å with an enclosed angle of  $\Gamma = 46^\circ$ . Molecules form an oblique two-dimensional Bravais lattice with two molecules at each Bravais lattice point. We determine that the molecules in the second layer adopt a tilted configuration, instead of a flat-lying configuration, according to the density calculated in the STM measurements. Fig. 5 is the supposed structural model of the second layer.

The difference in growth mode between the first two layers is ascribed to their different circumstances in the competition between molecule–molecule and molecule–substrate interactions. The dominant force for the growth of the first layer is the molecule–substrate interaction. The growth of the second layer is dominated by molecule–molecule interaction, which results in the growth of ordered molecular islands. The existence of the first layer leads to a remarkable decrease of the interaction between the substrate and the molecules of the second layer.

The first layer prevents the direct bonding between the second layer and the gold substrate on the one hand, and



Fig. 3. Supposed structural model for perylene monolayer on Au(111) surface. Bridge site is selected according to our DFT calculations.



Fig. 4. (a) STM image (90 nm  $\times$  90 nm, U = -0.8 V, I = 0.08 nA) of perylene island on the first layer. Below is the line profile from A to B in the image. (b) STM image (15 nm  $\times$  15 nm, U = -0.4 V, I = 0.04 nA) on the perylene island. Below is the line profile from C to D in the image.



Fig. 5. (a) STM image (40 nm × 40 nm, U = -0.4 V, I = 0.04 nA) showing the molecular arrangements of both the first layer (I) and the second layer (II). (b) The proposed structural model of the second layer. ( $c_1, c_2$ ) are the unit cell vectors of the second layer. Side view is along  $c_1$  direction.

weakens the vertical extension of the electronic states of gold substrate on the other hand. For the dI/dV spectra (Fig. 6) measured on the first layer, there is a gap of  $\sim 2.3 \text{ eV}$  between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), located at 0.9 eV below  $E_{\rm F}$  and at 1.4 eV above  $E_{\rm F}$ , respectively. Our dI/dV results are in agreement with previous study on the perylene/Au interface using ultravio-

let photoelectron spectroscopy (UPS) and DFT calculation [32]. The surface state of the gold substrate was not detected in the dI/dV measurement.

The growth mode for perylene on Au(111) was also observed for many polycyclic aromatic hydrocarbons (PAHs) molecules [10]. Generally the planar PAHs molecules form a monolayer on metal surfaces with the molecular plane parallel to the substrate [1]. In most cases including



Fig. 6. I-V(a) and dI/dV(b) spectra measured on the perylene monolayer on the Au(111) surface.

perylene/Au(111), however, the bulk structure of PAHs does not include a low-index and closely packed plane whose molecular arrangements are the same as the molecular monolayer on metal surface, so from the second layer onward perylene films adopt different packing ways from that of the first monolayer, and get close to the bulk structure. For perylene/Au(111), the molecular island is an intermediate structure, with molecules tilting from the surface and forming a dimeric arrangement. The surface structure of epitaxial crystal perylene multilayer is the herringbone packing of dimeric perylene molecules in the *ab*-plane of the monoclinic  $\alpha$ -perylene single crystal [9,10,33]. Although the structure of the molecular island in the second layer is different from the final multilayer structure, the former has two features of the latter, i.e. dimeric arrangement and tilting molecular orientation.

## 4. Conclusion

We have studied the structural evolution in the growth of the first two layers of perylene on Au(111) with STM/ STS and LEED. Our work indicates that the evolution of molecular arrangements is induced by the variation of the competition between the molecule–molecule interaction and the molecule–substrate interaction with molecular coverage.

#### Acknowledgements

This work was supported in part by the National Science Foundation of China (NSFC), (Grant No. 90406022), National 863 and 973 projects of China, Supercomputing Center, CNIC, CAS, Shanghai Supercomputer Center.

# References

- [1] G. Witte, Ch. Wöll, J. Mater. Res. 19 (2004) 1889.
- [2] G. Horowitz, J. Mater. Res. 19 (2004) 1946.
- [3] S.R. Forrest, Chem. Rev. 97 (1997) 1793.
- [4] (a) H.-J. Gao, K. Sohlberg, Z.Q. Xue, H.Y. Chen, S.M. Hou, L.P. Ma, X.W. Fang, S.J. Pang, S.J. Pennycook, Phys. Rev. Lett. 84 (2000) 1780;
  - (b) H.-J. Gao, Z.Q. Xue, K.Z. Wang, Q.D. Wu, S. Pang, Appl. Phys. Lett. 68 (1996) 2192;
    (c) S.X. Du, H.-J. Gao, C. Seidel, L. Tsetseris, W. Ji, H. Kopf, L.F.
  - Chi, H. Fuchs, S.J. Pennycook, S.T. Pantelides, Phys. Rev. Lett. 97 (2006) 156105.
- [5] S.M. Barlow, R. Raval, Surf. Sci. Rep. 50 (2003) 201.
- [6] W. Gebauer, M. Bässler, R. Fink, M. Sokolowski, E. Umbach, Chem. Phys. Lett. 266 (1997) 177.
- [7] N. Karl, Synth. Met. 133-134 (2003) 649.
- [8] N. Karl, K.-H. Kraft, J. Marktanner, M. Münch, F. Schatz, R. Stehle, H.-M. Uhde, J. Vac. Sci. Technol. A 17 (1999) 2318.
- [9] Y. Toda, H. Yanagi, Appl. Phys. Lett. 69 (1996) 2315.
- [10] G. Witte, K. Hänel, S. Söhnchen, Ch. Wöll, Appl. Phys. A 82 (2006) 447.
- [11] P. Yannoulis, R. Dudde, K.H. Frank, E.E. Koch, Surf. Sci. 189/190 (1987) 519.
- [12] X. Liu, S.H. Mohamed, J.M. Ngaruiya, M. Wuttig, T. Michely, J. Appl. Phys. 93 (2003) 4852.
- [13] C. Seidel, R. Ellerbrake, L. Gross, H. Fuchs, Phys. Rev. B 64 (2001) 195418.
- [14] (a) L. Gao, Z.T. Deng, W. Ji, X. Lin, Z.H. Cheng, X.B. He, D.X. Shi, H.-J. Gao, Phys. Rev. B 73 (2006) 075424;
  (b) Z.T. Deng, H. Lin, W. Ji, L. Gao, X. Lin, Z.H. Cheng, X.B. He, J.L. Lu, D.X. Shi, W.A. Hofer, H.-J. Gao, Phys. Rev. Lett. 96 (2006) 156102.
- [15] Q. Chen, T. Rada, A. McDowall, N.V. Richardson, Chem. Mater. 14 (2002) 743.
- [16] S. Söhnchen, K. Hänel, A. Birkner, G. Witte, Ch. Wöll, Chem. Mater. 17 (2005) 5297.
- [17] D. Wang, L.-J. Wan, Q.-M. Xu, C. Wang, C.-L. Bai, Surf. Sci. 478 (2001) L320.
- [18] M. Eremtchenko, D. Bauer, J.A. Schaefer, F.S. Tautz, J. Mater. Res. 19 (2004) 2028.
- [19] L. Gross, C. Seidel, H. Fuchs, Org. Electr. 3 (2002) 1.
- [20] K. Hänel, S. Söhnchen, S. Lukas, G. Beernink, A. Birkner, T. Strunskus, G. Witte, Ch. Wöll, J. Mater. Res. 19 (2004) 2049.
- [21] B. Lu, H.J. Zhang, Y.S. Tao, H. Huang, H.Y. Li, S.N. Bao, P. He, Q. Chen, Appl. Phys. Lett. 86 (2005) 061915.
- [22] S. Yoshimoto, E. Tsutsumi, O. Fujii, R. Narita, K. Itaya, Chem. Commun. (2005) 1188.
- [23] J. Taborski, P. Väterlein, H. Dietz, U. Zimmermann, E. Umbach, J. Electron Spectrosc. 75 (1995) 129.
- [24] P.J. Unwin, T.S. Jones, Surf. Sci. 532 (2003) 1011.
- [25] C. Seidel, J. Poppensieker, H. Fuchs, Surf. Sci. 408 (1998) 223.
- [26] (a) Y.L. Wang, W. Ji, D.X. Shi, S.X. Du, C. Seidel, Y.G. Ma, H.-J. Gao, L.F. Chi, H. Fuchs, Phys. Rev. B 69 (2004) 075408;
  (b) D.X. Shi, W. Ji, X. Lin, X.B. He, J.C. Lian, L. Gao, J.M. Cai, H. Lin, S.X. Du, F. Lin, C. Seidel, L.F. Chi, W.A. Hofer, H. Fuchs, H.-J. Gao, Phys. Rev. Lett. 96 (2006) 226101;

(c) Z.H. Cheng, L. Gao, Z.T. Deng, Q. Liu, N. Jiang, X. Lin, X.B. He, S.X. Du, H.-J. Gao, J. Phys. Chem. C 111 (2007) 2656.

- [27] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) R558.
- [28] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [29] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [30] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
- [31] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
- [32] S.J. Kang, Y. Yi, K. Cho, K. Jeong, K.-H. Yoo, C.N. Whang, Synth. Met. 151 (2005) 120.
- [33] D.M. Donaldson, J.M. Robertson, J.G. White, Proc. Roy. Soc. 220A (1953) 311.