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Coverage dependence of the structure of tetracene on Ag(110)

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Abstract

The ordered adsorption structures of tetracene on Ag(110) have been studied by low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. At a low coverage, as calibrated with LEED, both $p(4 \times 4)$ and $c(8 \times 4)$ ordered structures are simultaneously formed on an Ag(110) surface at room temperature. STM images suggest the molecular plane is parallel to the Ag surface with its long molecular axis aligned along the [001] azimuth. DFT optimization reveals a separation of 0.3 nm between the molecular plane and substrate surface while the center of the tetracene molecule is on the long bridge site. Increasing coverage slightly, a $\left(\begin{smallmatrix} 6 & 2 \\ 2 & 5 \end{smallmatrix}\right)$ structure is formed while the adsorbed molecules maintain the flat-lying geometry with adjacent molecules alternating their height relative to the surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the past decades, organic materials have become more and more attractive due to their potential applications in organic light-emitting diodes (OLEDs) [1], organic field-effect transistors (OFETs) [2], solar cells [3] and organic light-emitting (field-effect) transistors (OLETs) [4]. The performance of these devices could be strongly influenced by the structures and the characteristics of organic thin films, and particularly by the interactions at the interfaces between organic–organic, organic–inorganic and inorganic–inorganic layers [5]. The need for understanding this interaction has emerged in order to improve the conductivity and the charge carrier mobility [6] of such devices. The controlled growth of organic materials on metal substrates has proved to give an opportunity for producing hybrid organic–inorganic structures with better electronic properties. Consequently, the study of the ordered organic films on metal surfaces with molecular resolution will help us to further understand the

mechanism for molecular self-assembly and charge transport phenomena with better control of the properties of organic thin films [7].

Tetracene has a planar molecular structure consisting of four linearly fused benzene rings with D_{2h} symmetry. It is one of the simplest and most promising organic semiconductors used as the active layer of OLETs [8–10]. Besides, it has also been considered as a model of organic semiconducting materials, which can easily form well-ordered organic films on single-crystal surfaces. The multilayer films of tetracene have been investigated on many substrates [9–15], but monolayer films have only been studied on Cu(110) [16, 17], Ag(111) [18, 19], Ru(10 $\bar{1}$ 0) [20] Si(100)-(2 \times 1) [21, 22], H–Si(001) [23] and GaSe–Si(111) [24], surfaces. On Ag(110) surfaces, our previous study showed a partially commensurate multilayer tetracene structure [25]. In this work, we report our recent low energy electron diffraction (LEED), scanning tunneling microscopy (STM) and density functional theory (DFT) studies of monolayers of tetracene on Ag(110) with different surface coverages at room temperature.

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2. Experiment

The experiments were performed in a multifunctional ultra-high-vacuum (UHV) VT-SPM system (Omicron) with a base pressure better than 8×10^{-10} mbar. The system has been described in detail elsewhere [24–26]. The clean Ag(110) surface was achieved by argon-ion sputtering for several cycles (500 V, 30 min) and annealing (~ 500 K), and the cleanliness was verified by LEED, XPS measurements and large flat terraces in STM images. Tetracene (Sigma, 99%) was deposited from a resistively heated tantalum boat, at an evaporation temperature of ~ 410 K. Before deposition, tetracene powder was purified by long time out-gassing at a temperature slightly lower than 410 K and the thickness of the deposited layers was monitored using a quartz crystal oscillator and calibrated with the XPS and STM measurements. XPS signals of C 1s and Ag 3d were recorded within the same scanning process. The coverage of tetracene was determined by the intensity ratio of C 1s and Ag 3d. The deposition rate was ~ 0.3 ML min^{-1} with a pressure of $\sim 2 \times 10^{-9}$ mbar. All measurements were performed at room temperature (RT).

3. Results and discussion

When tetracene molecules are deposited on the Ag(110) surface at room temperature, they are expected to be relatively mobile and intend to choose the most stable bonding sites to form an ordered phase. When the coverage is about 0.5 molecules nm^{-2} , the LEED pattern is shown in figure 1(a), recorded at 11 eV. At such a low kinetic energy, all the substrate diffraction spots are located outside the LEED screen. However the fixed geometry of the LEED optics relative to the sample position can still be used to quantitatively calibrate the overlayer LEED pattern against the clean Ag surface diffraction pattern recorded at a higher energy. The unit cell vector can be calculated as follows:

$$a = \frac{h}{\sqrt{2mE} \sin \theta}.$$

Here h is the Planck constant, m is electron mass, E is electron energy and θ is the angle between the diffraction beam and surface normal. Since both basic vectors of the unit cell in the superstructure are four times as long as that in the substrate, the LEED pattern reveals an ordered $p(4 \times 4)$ structure. The STM image of the same surface, shown in figure 1(b), shows the molecular arrangement within the unit cell of the $p(4 \times 4)$ periodicity. This structure assignment is slightly different from the semi-incommensurate structure from our previous analysis [25], which was incorrect and was only based on the STM observation. In the STM image the atomic structure of the substrate cannot be resolved at room temperature; thermal drifting of the scanner and lack of calibration caused the error in our previous analysis.

There is one molecule per unit cell which occupies 16 Ag atoms with a coverage of about 0.54 molecules nm^{-2} . The unit cell has dimensions of 1.15 and 1.60 nm along the $[1\bar{1}0]$ and $[001]$ azimuths, respectively, which is large enough to hold one flat-lying tetracene molecule with its van der Waals dimensions

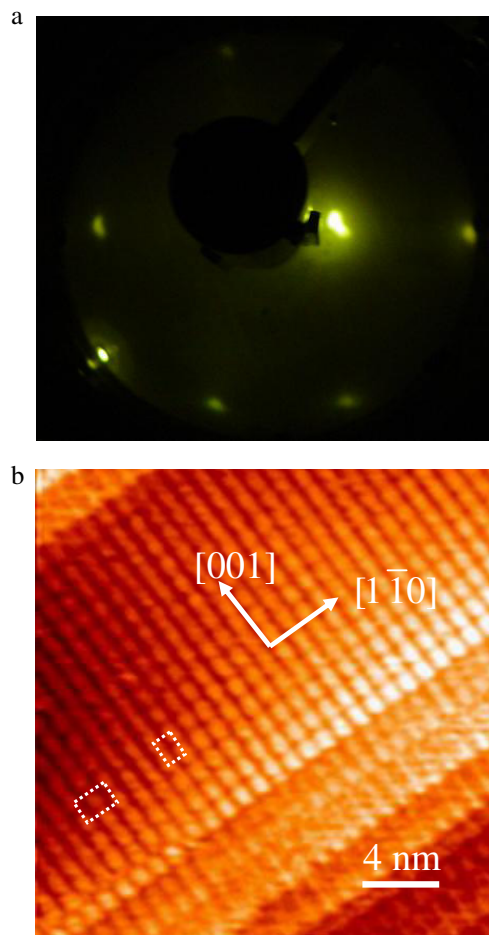


Figure 1. (a) LEED pattern of tetracene on Ag(110) surface at the coverage of 0.54 molecules nm^{-2} , where the beam energy is 11 eV. (b) STM image ($30 \text{ nm} \times 30 \text{ nm}$) of corresponding ordered tetracene on Ag(110) surface with a bias of 0.62 V and tunneling current 0.2 nA.

of $0.70 \text{ nm} \times 1.36 \text{ nm}$. The STM image suggests that the flat-lying tetracene molecules are aligned head to head with their long molecular axis along the $[001]$ azimuth, but side by side aligned along the $[1\bar{1}0]$. With one molecule per unit cell, all tetracene molecules must bond to the equivalent adsorption site.

While dense packing along the $[001]$ azimuth is achieved, a large gap between adjacent molecules along the $[1\bar{1}0]$ is observed, which indicates a relatively weak intermolecular interaction in this direction. Obviously, the overall molecular arrangement is largely affected by the substrate structure. With large intermolecular distance along the $[1\bar{1}0]$ azimuth, it will not cost too much energy to shift the whole molecular rows along $[001]$ by half of the $p(4 \times 4)$ unit cell vector, resulting in a new ordered adsorption structure with a $c(8 \times 4)$ periodicity, as shown in a small area in figure 1(b). With one molecule in a $c(8 \times 4)$ unit cell, all tetracene molecules must bond to the equivalent adsorption site too.

Figure 1(b) also shows the molecular arrangements at some step edges. For a clean Ag(110) surface, normally the step edges appear to be curved. With tetracene molecules on the surface, the step edges are favorite to be aligned along the

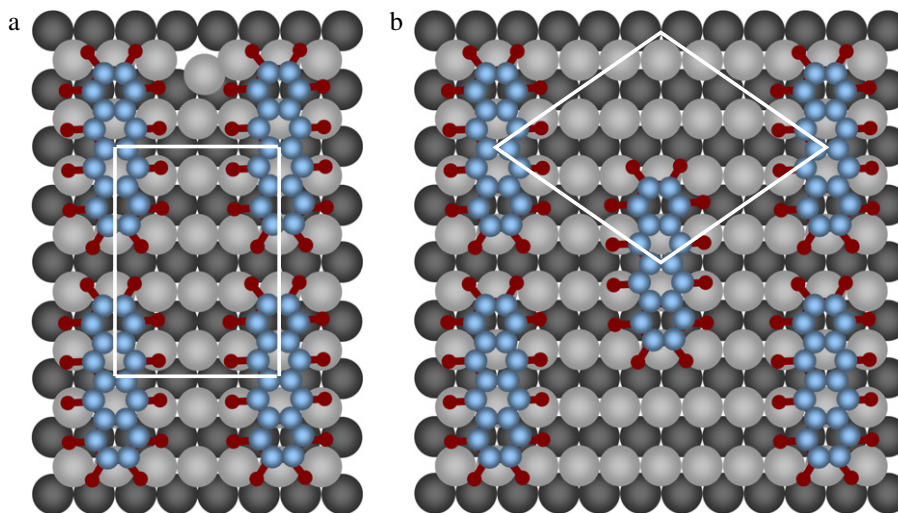


Figure 2. The proposed models of (a) $p(4 \times 4)$ and (b) $c(8 \times 4)$ ordered adsorption structures of tetracene on the Ag(110) surface.

high symmetrical azimuth of the substrate. The pinning of the step edges, governed by the ordered overlayer structures, suggests the presence of attractive interactions between the tetracene molecules and the substrate Ag atoms. It should also be recognized that the molecules at lower terraces are perfectly aligned along the [001] azimuth, which probably not only confirms the attractive interaction between tetracene and substrate, but also, more importantly, suggests the existence of a long range attractive intermolecular interaction that defines the periodicity along the [001] azimuth crossing the substrate atomic steps.

The proposed models of these two adsorption structures are shown in figures 2(a) and (b), respectively. Since the area of the $c(8 \times 4)$ unit cell is double that of the $p(4 \times 4)$ unit cell, one flat-lying molecule in the $c(8 \times 4)$ and $p(4 \times 4)$ unit cells occupies the same area of 1.84 nm^2 , equivalent to 16 Ag atoms. More importantly, in both cases all molecules are bonded to the identical sites on Ag(110) with the same molecular orientation. Although LEED and STM can only reveal the relative dimensions of orientations of the adsorbed molecules on the Ag(110) surface, the exact adsorption sites, as shown in figure 2, were determined by the *ab initio* calculations of the adsorption structure (discussed later). It has been noticed that the $p(4 \times 4)$ structure dominates in the monolayer, but only some small areas with the $c(8 \times 4)$ structure.

With increasing coverage of tetracene on the Ag(110) surface, the molecules are still in a flat-lying geometry. Figure 3(a) shows a typical STM image of tetracene molecules on the Ag(110) surface with a higher surface coverage, $0.67 \text{ molecules nm}^{-2}$, which is equivalent to 13 Ag atoms per molecule. Although the long axis of tetracene molecules is also aligned along the [001] azimuth, the molecules are arranged side by side along the (6, 2) vector together with a (2, 5) vector, forming an oblique unit cell.

Clearly, this higher coverage structure appears to be more complicated than that of the lower coverage surfaces. Along the molecular row in the (6, 2) direction, a periodically alternating of brightness indicates that two molecules nearby

are not at the same height above the substrate. The line profile curve in figure 3(b) shows the height of the molecule along the 'A-A' line in figure 3(a), indicating that the brighter molecules are about 0.05 nm higher than their neighboring molecules. The true height measured by STM is a convolution of height profile with electronic states of the sample. By assuming the electronic states of two different molecules to be more or less identical, we can expect the measured height difference reflects the true height difference in this particular case.

The two-dimensional adsorption structure observed in figure 3 can be described in a matrix of $\begin{pmatrix} 6 & 2 \\ 2 & 5 \end{pmatrix}$ with a unit cell area of 2.99 nm^2 . Since there are two molecules in each unit cell, a flat-lying molecule occupies an area of 1.50 nm^2 . This coverage is about 24% more dense than that of the $p(4 \times 4)$ or $c(8 \times 4)$ structures. A closer packing of molecules is formed as shown in the proposed model in figure 3(c). Similar to the low coverage surface, all the molecules are aligned with their long molecular axis along the [001] azimuth. The alternative heights of the adjacent molecules are also established in this azimuth. However, occasionally, this alternative height arrangement is irregular, causing defects in the periodic structure, as can be observed in the lower left part of the STM image in figure 3(a).

To verify the adsorption structure from the experimental STM images and examine the details of the adsorption mechanism, we have carried out the DFT calculations using the Dmol3 package integrated in the Materials Studio program of Accelrys Inc [27]. Fermi smearing of 0.004 Hartree (Ha) (about 0.1 eV) was taken to minimize the errors in the Hellmann–Feynman forces due to the entropic contribution to the electronic free energy [28], and a real-space cutoff of 0.4 nm was used to improve the computational performance. The k points were obtained from the Monkhorst–Pack scheme [29]. For the numerical integration, we adopted the MEDIUM quality mesh size of the program as a balance between time and accuracy. All energies were extrapolated to $T = 0 \text{ K}$ and the experimentally determined lattice constants were initially used for construction of the Ag(110) surface. The slab was repeated periodically with 1.0 nm of a vacuum

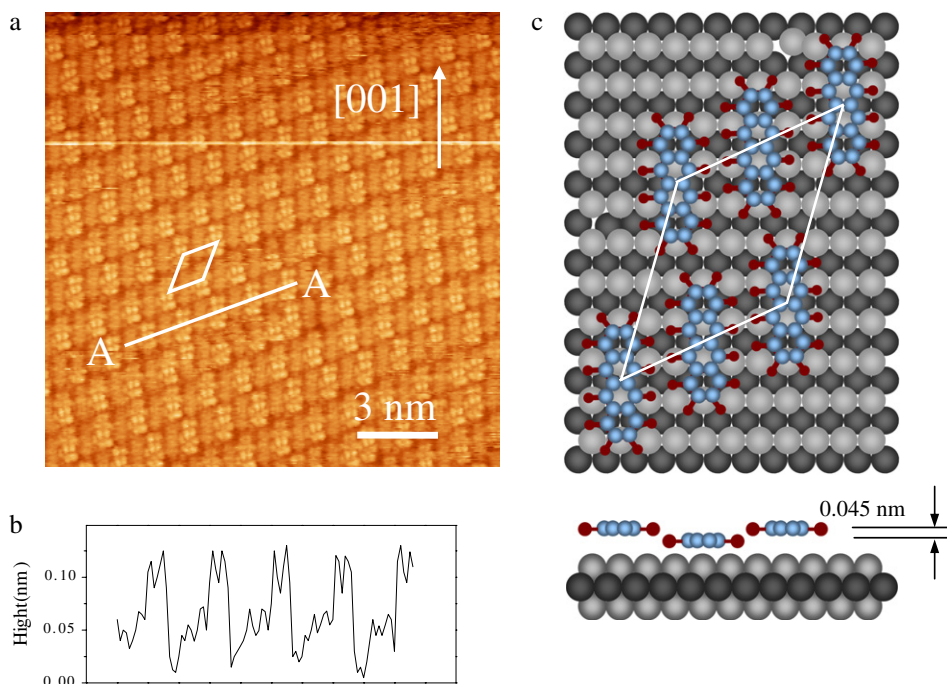


Figure 3. (a) STM image ($20 \text{ nm} \times 20 \text{ nm}$) of tetracene on Ag(110) surface at a coverage of $0.67 \text{ molecules nm}^{-2}$ with a bias of 0.5 V and tunneling current of 0.15 nA . (b) The line profile curve showing the height of the molecule along the 'A–A' line. (c) The top and side views of the proposed model of an ordered adsorption structure which is described by a matrix $\begin{pmatrix} 6 & 2 \\ 2 & 5 \end{pmatrix}$ relative to the Ag(110) substrate.

region between the slabs. A $2 \times 2 \times 1$ k -point sampling was used to ensure the convergence of energies and structures. The tolerances of energy, gradient and displacement convergence were $2 \times 10^{-5} \text{ Ha}$, $4 \times 10^{-2} \text{ Ha nm}^{-1}$ and $5 \times 10^{-4} \text{ nm}$, respectively.

At a low coverage, the calculations were performed with one tetracene molecule in a unit cell. In our model, the top two layers of the substrate together with the adsorbed molecule were allowed to be optimized, while the two bottom layers of the substrate were frozen in the bulk configuration. During the calculation, the long axis of the tetracene molecule was always aligned along the [001] direction and the molecule was set at different heights, from 0.24 to 0.38 nm above the substrate with a step of 0.01 nm . Several highly symmetric adsorption sites, the positions of the molecule center on the substrate surface, for a single tetracene molecule on the Ag(110) surface were selected for comparison, including a top site, long bridge site, short bridge site and hollow site. The adsorption structure was optimized with minimum total energy.

Table 1 summarizes the calculated adsorption energy and the separation between the molecule and the first layer of the substrate for different adsorption sites. The adsorption energy was calculated as follows:

$$E_{\text{ad}} = [E(\text{tetracene}) + E(\text{substrate}) - E(\text{tetracene/substrate})].$$

The calculation results indicate that the molecule is energetically in favor with its π plane parallel to the Ag surface with an optimized separation of ca. 0.31 nm between the molecular and the substrate at all possible high symmetric adsorption sites. The full optimization does not move the

Table 1. The calculated total energy, adsorption energy and the separation between the molecule and the first layer of the substrate.

	Top site	Long bridge site	Short bridge site	Hollow site
Adsorption energy (eV)	1.418	1.837	0.743	0.658
Separation between the molecule and the first layer of substrate (nm)	0.31	0.30	0.32	0.31

molecule away from the initially suggested high symmetric adsorption sites, suggesting that all the selected sites are energetically favorable. Local energy minimization is expected for all these sites and there is a certain energy barrier to be overcome if a molecule transits from one adsorption site to the other. Among these high symmetric sites, only when the center of the tetracene molecule is on the long bridge site with the long molecular axis aligned in the [001] azimuth is the maximum adsorption energy gain achieved, which is 0.42 eV more stable than on the top site, the second most stable adsorption site. With such a significant energy advantage, the molecule will be exclusively adsorbed on the long bridge site even at high temperature. At this most stable adsorption site, the molecule has the smallest gap distance to the substrate which suggests a more attractive interaction between the π orbital and the d band electron of the Ag substrate is responsible for the energy gain. This calculated adsorption configuration is in good agreement with that observed in STM images.

At a higher coverage, the calculations were performed with two tetracene molecules in one unit cell with the

dimensions described by a matrix $\begin{pmatrix} 6 & 2 \\ 2 & 5 \end{pmatrix}$ relative to the Ag(110) substrate. The unit cell vectors are 2.1 nm in the (2, 5) direction and 1.9 nm in the (2, 6) direction, respectively. Similar to the low coverage model above, the adsorption structure was optimized by adjusting the top two layers of the substrate together with the two adsorbed molecules, while the two bottom layers of the substrate were frozen in the bulk configuration. During the calculation, the molecular plane is also in favor of being parallel to the Ag surface and adsorbed on the long bridge site with the long molecular axis aligned along the [001] azimuth, the same as that in the $p(4 \times 4)$ or $c(8 \times 4)$ structures. Starting the calculation, two molecules were set at a height of 0.3 nm. Two molecules were adjusted up and down separately from 0.0 to 0.1 nm with a step of 0.005 nm. The results show that the distances between the molecular planes and the substrate are 0.320 and 0.275 nm, respectively, for the two molecules in each unit cell. One molecule is 0.045 nm lower than the other relative to the substrate, which is in excellent agreement with that observed from the STM images. Moreover, the top molecule is slightly higher than that in the $p(4 \times 4)$ structure at the cost of adsorption energy.

Growth behavior of organic molecules on a metal surface depends on the molecule/substrate and molecule/molecule interactions. When the intermolecular distance is large in the case of low coverage, the intermolecular interaction is weak. At a higher coverage, however, the tetracene molecules are more densely packed with a very small intermolecular distance. Therefore, the intermolecular interaction cannot be ignored. Actually, with a $\begin{pmatrix} 6 & 2 \\ 2 & 5 \end{pmatrix}$ periodicity, molecules almost touch each other if they are adsorbed with the same adsorption height. What is astonishing is we observed in the STM images (figure 3(a)) that, in order to reduce the static repulsion between the adjacent molecules, the molecules self-adjust their adsorption height so that an alternative arrangement is achieved along the (6, 2) direction. This will clearly form a foundation for a growth of multilayers. Nevertheless, all the molecules are still adsorbed on the identical long bridge sites as proven by the *ab initio* calculations. This observation suggests that the energy gain of the adsorption on the long bridge sites is the dominant factor to determine the registry of the adsorbed tetracene against the Ag substrate. The calculated adsorption energy of two molecules on Ag(110) in each unit cell at higher coverage is 3.47 eV, 1.735 eV for one molecule, which is little lower than that of one molecule at lower coverage (1.873 eV). This would explain why the molecules do not move closer at lower coverage.

The π -d interaction between the flat-lying molecule and the substrate is a relatively long range interaction which can be easily adjusted to reduce repulsion due to small intermolecular distance without costing too much in molecular-substrate interaction energy.

Although tilted tetracene on the Ag(111) [18] surface and even upright standing tetracene on Cu(100) [30, 31] have been reported, these adsorption structures were formed at very high coverage, at least four times higher than that in the present work. At such a high coverage, the interaction between the molecules and the substrates can be ignored and the natural herringbone structure of the tetracene crystal

becomes dominant. For the thin film we prepared in the present work, the molecule-substrate interaction guaranteed a flat-lying geometry with an overall balance of intermolecular interactions.

4. Conclusions

In summary, at lower coverage, the ordered adsorption structures of tetracene on the Ag(110) surface with $p(4 \times 4)$ and $c(8 \times 4)$ periodicities are formed. In both cases, each molecule occupies the same area of 1.15 nm \times 1.6 nm. The molecular plane is parallel to the Ag surface with a separation of about 0.3 nm. The center of the tetracene molecule is on the long bridge site with the long molecular axis in the [001] azimuth. When the coverage increases by 24%, the molecules are adsorbed in the flat-lying manner too. They are rearranged by shifting and changing their heights on the surface in such a way as to minimize the repulsion intermolecular interactions. The adsorption configuration can be described by a matrix $\begin{pmatrix} 6 & 2 \\ 2 & 5 \end{pmatrix}$ relative to the Ag(110) substrate.

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