Structural evolution of pentacene on a Ag(110) surface

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Structural evolution of pentacene thin films on Ag(110) crystal, during molecular deposition and during a subsequent change of substrate temperature, was investigated *in situ* by a molecular beam epitaxy low-energy electron diffraction technique. The pentacene molecules exhibit high mobility on the Ag(110) surface at room temperature and the adsorbate shows a structural evolution from disorder in the submonolayer to an ordered structure when it reaches one monolayer. Heating the substrate to 145 °C results in no further structural transition. The ordered monolayer structure on Ag(110) has two domains mirrored at the crystal axis of the silver substrate. Molecular mechanics calculations indicate that the pentacene molecules lie flat on the Ag(110) surface, which is in good agreement with the experimental results. The calculation also gives the favorable position; i.e., the orientation of pentacene on the Ag(110).

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I. INTRODUCTION

Organic thin film transistors (OTFT's), which offer the possibility of applications for flexible displays, all-plastic smart cards, as well as organic light-emitting devices, have received widespread attention in recent years.[1–9] The prospective applications of organic-inorganic devices are a further challenge to study selective organic molecules on well-defined substrates. Pentacene ($C_{22}H_{14}$), an aromatic molecule composed of five benzene rings, is currently attracting much interest among scientists and engineers.[5–18] Pentacene thin films can be used as the channel layer of OTFT's[5–11] because the charge mobility of pentacene in OTFT's has reached or even surpassed that of amorphous Si in Si-TFT's.[10,11] Previous studies on the pentacene thin films include x-ray,[3] atomic force microscopy,[4] and scanning tunneling microscopy[16] as well as theoretical studies of the adsorption of a single pentacene molecule on different surfaces.[17] It is well known that charge mobility and injection in pentacene organic crystals depends strongly on molecular orientation and packing.[18] Thus, in order to improve the performance of pentacene devices, monitoring and controlling the structural growth of pentacene in the thin-film growth process from submonolayer to monolayer is absolutely crucial for its applications.[7,8,19]

In this work, we use a homemade molecular beam epitaxy (MBE) low-energy electron diffraction (LEED) system[20] to investigate the growth of the pentacene thin films on the Ag(110) substrates. The observed structures are further analyzed by molecular mechanics calculations.

II. EXPERIMENT

The experiments were carried out in a UHV chamber equipped with a homemade MBE-LEED. Detailed information about this technique can be found in Ref. 20. The LEED pattern of the samples can be observed *in situ* both during deposition and after deposition. The digitized intensities can be displayed and processed on the monitor. The substrate temperature was monitored by a Cromel Alumel thermocouple, which was in contact with the substrate.

The background pressure of the chamber was better than 1.0×10^{-9} mbar. The Ag(110) crystal was cleaned by standard sputtering with argon ions for 15 min at the pressure of 5×10^{-6} mbar followed by annealing at 350 °C for 3 min. After that, the cleaned Ag(110) crystal surface was checked by LEED before deposition. Cleaning the pentacene molecules was conducted by carefully outgassing inside a Knudsen crucible at 120 °C in the ultrahigh vacuum chamber. The crucible temperature was monitored by a Cromel Alumel thermocouple, which was in contact with the crucible bottom. The deposition time was about 65 sec. The typical deposition rate was ~1 ML/min.

III. RESULTS AND DISCUSSION

The structural transition of the pentacene on Ag(110) from a submonolayer to a monolayer is observed from the LEED patterns. The LEED pattern of the cleaned Ag(110) surface is shown in Fig. 1. The diffraction spots are at positions (01), (0-1), and (10), while the spot at (-10) is shuttered by the electronic emitting gun. During molecular deposition, the substrate is held at room temperature. Figure 2 shows the changing process of the LEED patterns with increasing molecular coverage. When the crucible temperature increases from room temperature to 140 °C, there is no change in the LEED pattern, indicating no additional molecules are deposited on the Ag(110) surface. When the crucible temperature rises gradually to 145 °C, very few molecules deposit onto the substrate. At this stage the LEED pattern looks similar to a halo, as shown in Fig. 2(a). As shown in Fig. 2(b), with further deposition the diffraction intensity is enhanced and the halo assumes an elliptical pattern. The ellipse finally decays and some spots appear in Fig. 2(d), indicating a periodic structure of the adsorbate on the substrate. Figures 2(e) and 2(f) show sharp diffraction spots, corresponding to a well-ordered structure of pentacene on the Ag(110) surface. This diffraction pattern progression indicates that the pentacene

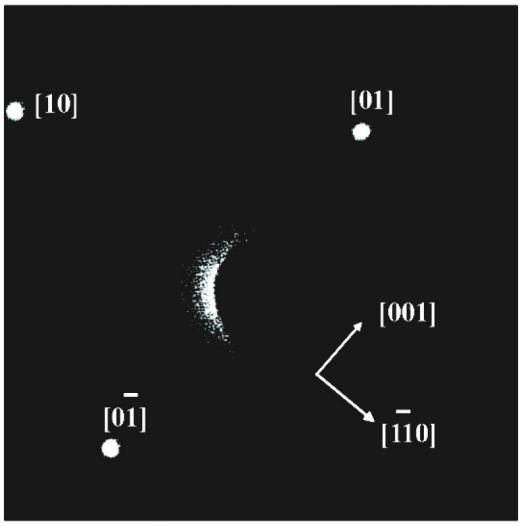

FIG. 1. LEED pattern of Ag(110) substrate before deposition—beam energy of 29 eV, substrate temperature of 20 °C—showing the good crystalline surface structure of the Ag(110).

molecules are highly mobile on the Ag(110) surface at room temperature before nucleation and growth. With increasing molecular coverage, the diffraction pattern is as shown in Fig. 2(f), which is the same as that in Fig. 2(d). It can be seen that there is no structural transition. Where structural transitions are observed for many other kind of molecule[21] with the increasing molecular coverage, no dose-induced structural transition occurs in this molecular system, suggesting that domains grow laterally without change of their internal structure. Figure 2(g) is obtained with higher electron energy of 34 eV, which gives more diffraction spots including the diffraction spots from both substrate and the molecular thin film and the crystalline relationship. Two different structures in Figs. 2(e)–2(g) can be observed, which can be explained by two domain orientations mirrored at the crystal axis of the Ag(110) substrate. This structure is similar to the earlier results that a monolayer of either DPP-PTCDI (Ref. 22) or PTCDA (Ref. 23) on Ag(110) possesses two domain orientations symmetrical to the crystalline axis of the Ag(110) substrate.

Next we analyze the structural properties of the pentacene molecules on the Ag(110). As shown in Fig. 3(a), the molecular structure has two domain orientations mirrored at the crystalline axis of the Ag(110) substrate. Based on this LEED pattern, we propose the schematic diagram of the molecular structure shown in Fig. 3(b). The unit cell vectors $(\mathbf{b}_1, \mathbf{b}_2)$ of the pentacene are indicated together with the base vectors of the substrate $(\mathbf{a}_1, \mathbf{a}_2)$. The unit vectors of the Ag(110) are $\mathbf{a}_1 = 2.889$ Å, $\mathbf{a}_2 = 4.086$ Å. The structural relationship between the molecular structure and the Ag(110) substrate is shown in Fig. 3(b), and it can be described in matrix as

$$\text{Pentacene} = \begin{pmatrix} 3 & -1 \\ -1 & 4 \end{pmatrix} \text{Ag}(110).$$

According to this matrix, the unit vectors of the pentacene are calculated to be $\mathbf{b}_1 = 9.582$ Å, $\mathbf{b}_2 = 16.597$ Å with an enclosed angle of $\Gamma = 125.26°$. The enclosed angle between $\mathbf{b}_1$ and the first substrate vector $\mathbf{a}_1$ is $\phi = 25.24°$. It is found that the pentacene adsorbed on Ag(110) with the molecular plane

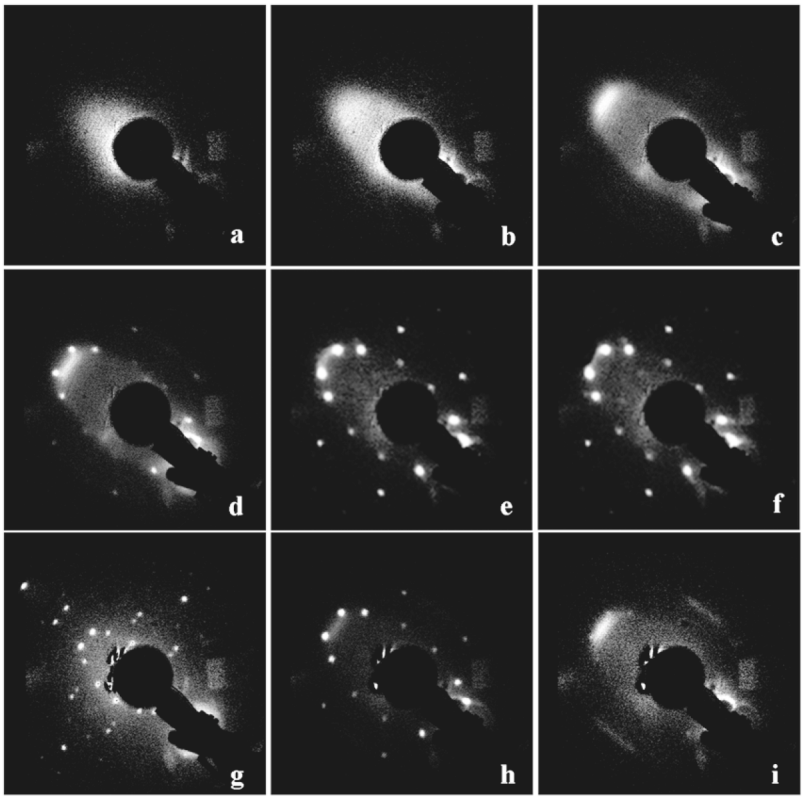

FIG. 2. *In situ* LEED patterns of pentacene on Ag(110) during molecular deposition, showing the structural evolution of the pentacene molecules on the Ag(110). (a) Beam energy $E = 13$ eV, substrate temperature $T_s = 20$ °C, evaporation temperature $T_v = 145$ °C, deposition time $t = 20$ s; (b) $E = 13$ eV, $T_s = 20$ °C, $T_v = 150$ °C, $t = 30$ s; (c) $E = 13$ eV, $T_s = 20$ °C, $T_v = 151$ °C, $t = 40$ s; (d) $E = 13$ eV, $T_s = 20$ °C, $T_v = 152$ °C, $t = 50$ s; (e) $E = 13$ eV, $T_s = 20$ °C, $T_v = 153$ °C, $t = 60$ s; (f) $E = 13$ eV, $T_s = 20$ °C, $T_v = 154$ °C, $t = 65$ s; (g) $E = 34$ eV, $T_s = 20$ °C, $T_v = 154$ °C, $t = 65$ s; (h) $E = 13$ eV, $T_s = 140$ °C; (i) $E = 13$ eV, $T_s = 145$ °C.

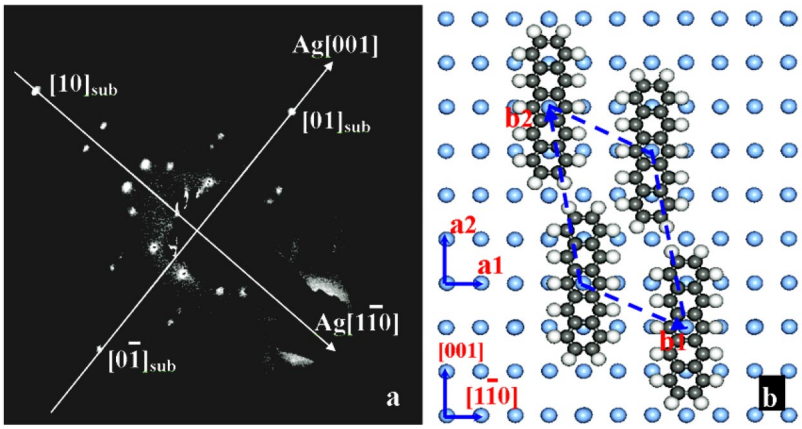

FIG. 3. Pentacene on Ag(110) forms an ordered structure. (a) LEED pattern with beam energy of 34 eV, showing two domain orientations mirrored at the crystal axis of the silver substrate. (b) The structural model in real space $\mathbf{b}_1=3\,\mathbf{a}_1-\mathbf{a}_2$, $\mathbf{b}_2=-\mathbf{a}_1+4\mathbf{a}_2$, $\mathbf{b}_1=9.582$ Å, $\mathbf{b}_2=16.597$ Å.

parallel to the substrate surface, which is similar to pentacene on Cu(110),[16] Si(001),[17] and other aromatic molecules on a Ag(110) surface.[19,24] In this schematic of the structural relation, the adsorption sites of the pentacene molecules relative to the substrate Ag atoms are arbitrarily chosen. The favorable positions and orientations of the main axis of the pentacene molecules on the Ag(110) substrate is to be further determined by the following theoretical calculation.

After the deposition mentioned above we try to increase the substrate temperature to see if any structural transition takes place in the pentacene. We heat the sample slowly, and when the substrate temperature is increased gradually from room temperature to 140 °C, the position and the intensities of the diffraction spots do not change significantly. The diffraction pattern shown in at 140 °C is similar to that in Fig. 2(f) at room temperature, indicating that no structural transition occurs during the heating process. However, when the sample temperature increases to 145 °C, which is close to the temperature used for normal film preparation, the LEED spots slowly become dark [Fig. 2(i)] and finally disappear, indicating the evaporation of the molecules from the substrate. Generally speaking, the desorption temperature of a molecule on silver is higher than the molecular sublimation temperature if there is a covalent bonding of the molecule with the substrate.[21,23] Here the desorption temperature of about 145 °C is a little bit lower than the sublimation temperature. Thus, the interaction between molecules is a weak van der Waals interaction, rather than a chemisorption of O atoms and polar groups on Ag(110).

In order to give further understanding of the experimental results, we use a molecular mechanics calculation to figure out the favorable position and orientation of pentacene on Ag(110).[25,26] The MM+ force field, which is improved from the MM2 force field, is used. In this method, the configuration of the model system in equilibrium is obtained by minimizing the energy. We first calculate one pentacene molecule adsorbed on Ag(110) substrate with different layers of Ag atoms by MM+ force field, and consider six layers of silver atoms for this calculation.[27] Then, we simplify the calculation process and calculate a single pentacene molecule adsorbed on Ag(110) with three possible adsorption modes, standing up, lying sideways, and lying flat [see Fig. 4(c)]. In each of these three modes, the molecule's long axis can assume any one of seven different orientations [see Fig. 4(a)].

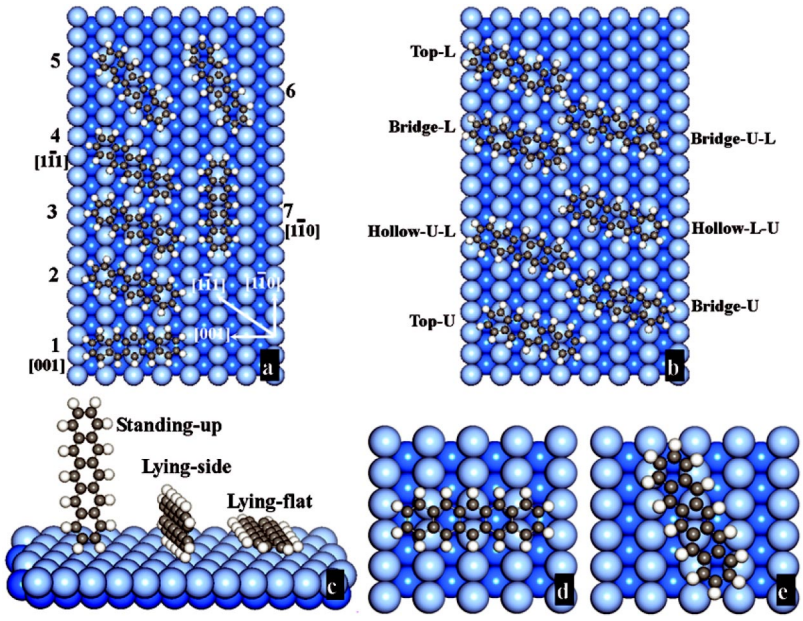

FIG. 4. Schematic diagram for the optimization of a single pentacene molecule on Ag(110). (a) Seven specific orientations are selected: orientations 1, 4, and 7 are along the [001], [1-11], and [1-10] direction of the Ag(110) surface, respectively. (b) Seven specific selected sites. (c) Three specific adsorbed modes. (d) One optimized orientation: the molecular long axis along the [001] direction of Ag(110) surface. (e) Another optimized orientation: the center of the middle benzene ring of the molecule resides at the bridge-*U* site, and the centers of the two benzene rings at the two ends of the molecule are situated at the bridge-*L* sites. *U* and *L* correspond to the upper and lower atoms in the first layer of silver substrate, respectively.

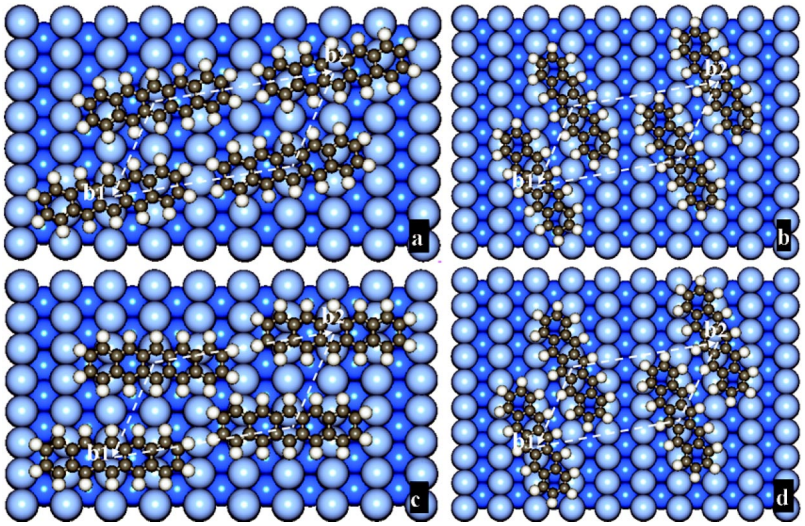

FIG. 5. Schematic diagram of pentacene molecules on Ag(110) in four specific orientations. (a) Orientation A: along the unit vector $\mathbf{b}_2$, (b) orientation B: along the direction of 2 $\mathbf{b}_1$- $\mathbf{b}_2$ of the pentacene monolayer. (c) Orientation C: along the [001] direction of the Ag(110). (d) Orientation D: the center of the middle benzene ring of the molecule resides at bridge-*U* site, and the centers of the two benzene rings at the two ends of the molecule are situated at the bridge-*L* sites.

The center of the molecular plane is located at seven different sites on the substrate [see Fig. 4(b)]. The distance from the lowest carbon atoms of the pentacene to the first layer of the Ag substrate is set to be about 5 Å initially. During the optimization process of the calculation, the Ag substrate is fixed. The single point energy (E_{sp}) and the optimized energy (E_{opt}) are obtained. After optimization, as shown in Figs. 4(d) and 4(e), molecules in either the ''standing-up'' mode or the ''lying-side'' mode finally transfer to the ''lying-flat'' mode. In addition, the optimized results indicate that the center of the molecular plane moves to the bridge-*U* site (between two adjacent topmost Ag atoms) though there are seven different initial sites. Moreover, the molecule's long axis finally rotates to either of two preferred orientations. One is aligning parallel to the Ag [001] direction [Fig. 4(d)]. The other is the centered benzene ring residing at the bridge-*U* site and the two benzene rings at the two ends of the molecule are situated at the bridge-*L* sites (between two adjacent lower Ag atoms in the first layer of substrate) [Fig. 4(e)].

Finally, to precisely determine the favorable molecular orientations of the pentacene in the ''lying-flat'' mode, we calculate 5×5 pentacene unit cells adsorbed on the Ag(110) substrate. Based on the calculated results for a single molecule, we propose four possible molecular orientations A, B, C, and D on the Ag(110) substrate. The lattice parameters $\mathbf{b}_1$, $\mathbf{b}_{2,}$ and the orientation relationship between the molecular unit cell and the Ag(110) unit cell, are deduced from the experimental LEED pattern [see Figs. 5(a) and 5(b)]. The distance between the molecular layer and the first layer of the substrate surface is set to be about 5 Å initially. After the optimization, it is clearly seen that molecules in either the A or B orientation deflect a little bit from their original orientations. Orientation A finally changes to orientation C [see Fig. 5(c)], and orientation B changes to orientation D [see Fig. 5(d)]. The calculated lattice parameters are quite consistent with the parameters deduced from the LEED with an error of $\pm5\%$. In orientations A and B, the distance between the pentacene layer and the substrate surface is finally reduced to 3.3 Å approximately. We have also calculated the E_{sp} and E_{opt} for orientations C and D. The results are the same as for orientations A and B, and the distance between the pentacene layer and the substrate surface is also reduced to 3.3 Å approximately, indicating that orientations C and D are favorable for the molecule on the Ag(110) substrate.

IV. CONCLUSIONS

The structural evolution of pentacene on Ag(110), during molecular deposition and after deposition during the subsequent change of substrate temperature, was systematically investigated by MBE-LEED. The pentacene molecules exhibit high mobility on the Ag(110) surface at room temperature and form an ordered monolayer structure with two domains mirrored at the crystal axis of the silver substrate. It remains stable when the substrate temperature is below the sublimation temperature of pentacene. Molecular mechanics calculations indicate that the pentacene molecules lie flat on the Ag(110) surface and the molecule's long axis aligns along either of two preferred orientations.

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