Two-Step Growth of Large Pentacene Single Crystals Based on Crystallization of Pentacene Monolayer Film

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ABSTRACT: A two-step growth method, namely, initial crystallization from pentacene monolayer grains to nanosized single crystals (nanocrystals) and subsequent physical vapor transport (PVT) growth on the nanocrystals as seeds, is demonstrated to fabricate larger microsized pentacene single crystals. The pentacene monolayer film deposited on a bare SiO2 substrate was found to self-assemble to nanoparticles during a post-annealing process. Selected area electron diffraction demonstrates unambiguously the nanoparticles and the microsized particles grown by the following PVT are both single crystals but with different crystal phases. Such a two-step growth technology maintains the intrinsic interface states between the SiO2 dielectric and the pentacene active layer and provides a more flexible way to in-situ prepare organic single crystals for device fabrication. The detailed investigation of morphology evolution and the discussion of formation mechanism of nanocrystal seeds indicate that the pentacene molecular transport during annealing is controlled by molecular surface diffusion. A crystal growth diagram based on thermodynamic analysis is proposed to qualitatively interpret the molecular transport from the monolayer film to the nanocrystals of pentacene.

INTRODUCTION

Organic single crystal field effect transistors (SCFETs) have attracted increasing attention in recent years owing to their potential application in optoelectrics.1 Especially, SCFETs exhibit immense advantages in exploration of the transport phenomena in organic devices, as well as in clarification of the performance limit of the available organic materials.2 Up to now, many groups have reported on organic single-crystal growth and relevant organic device design. Easy crystallization of rubrene has enabled such pioneers as Rogers et al. to fabricate larger microsized pentacene single crystals. The pentacene monolayer film deposited on a bare SiO2 substrate was found to self-assemble to nanoparticles during a post-annealing process. Selected area electron diffraction demonstrates unambiguously the nanoparticles and the microsized particles grown by the following PVT are both single crystals but with different crystal phases. Such a two-step growth technology maintains the intrinsic interface states between the SiO2 dielectric and the pentacene active layer and provides a more flexible way to in-situ prepare organic single crystals for device fabrication. The detailed investigation of morphology evolution and the discussion of formation mechanism of nanocrystal seeds indicate that the pentacene molecular transport during annealing is controlled by molecular surface diffusion. A crystal growth diagram based on thermodynamic analysis is proposed to qualitatively interpret the molecular transport from the monolayer film to the nanocrystals of pentacene.
on the seed growth by the subsequent physical vapor transport (PVT) method. Note that developing a high quality single crystal in such a two-step method should acquire high quality seed crystals since crystal defects such as dislocations, cracks, and lattice distortions will "transmit" to the final crystal within a certain range. The pentacene nanocrystals acquired in this paper have been carefully characterized, and a detailed analysis of the crystallization mechanism from monolayer film to single nanocrystals is provided also. As the single nanocrystals were acquired directly on the SiO2 surface in this two-step method, the interface between nanocrystal (and the subsequent microsized crystal) and SiO2 dielectric has not been artificially affected. We believe that this study is instructive for fabrication of high quality organic single crystals and facilitate the investigation of the interfacial effect on electrical transport phenomena.

**EXPERIMENTAL SECTION**

**Fabrication of Pentacene Monolayer Film and Crystal.** Thermally oxidized Si wafers with a 300 nm SiO2 layer were chosen as substrates which were cleaned successively in deionized water, ethyl alcohol, acetone, and a solution of ammonia (ammonia:deionized water = 1:6 (by volume)) with ultrasonic cleaning for 10 min each step and were finally blown dry with high purity nitrogen gas prior to deposition of pentacene (Powder, 97%, from Aldrich Chemical Co.) monolayer film. Pentacene thin film was deposited on the cleaned substrate surface by thermal evaporation (AUTO 306, BOC-Edwards Co.) at ambient substrate temperature and under the background pressure of $5 \times 10^{-5}$ Pa. Then, the samples were immediately transferred into an Ar glovebox and annealed under temperature from ambient to 120 °C with a heating plate. Finally, the annealed samples were taken into a tube furnace as soon as possible for the subsequent PVT growth under protection of circulating nitrogen at ambient pressure. During the PVT growth, the pentacene source temperature was kept constant at 220 °C, and the annealed samples were positioned about 10 cm away from the source zone.

**Characterization.** Pentacene monolayer films before and after annealing were characterized by atomic force microscopy (AFM, Nanoscope IIIa MultiMode, Veeco Co.) in tapping mode. Scanning electron microscopy (SEM) was performed on a Hitachi S4800. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a Tecnai G2 F20 U-TWIN (FEI Co.) at an operation voltage of 200 kV. Annealed samples for TEM observation were prepared by depositing pentacene monolayer film onto a carbon-coated copper grid modified with spin-coated polystyrene (PS) and sequentially annealing with the same process as described above. Larger crystals grown by PVT were transferred with the mechanical method onto a carbon-coated copper grid for TEM observation.

**Figure 1.** AFM image ($5 \times 5$ μm$^2$) of pentacene monolayer film (a1) grown on SiO2 substrate with its height profiles (a2) along the white line in panel a1. SEM image of single nanocrystal (b1) formed in postannealing process and relative SAED pattern (b2) as well as SEM image of single microsized crystal (c1) obtained by PVT and relative SAED pattern (c2). The insets in b2 and c2 show the TEM images of the corresponding samples after SAED characterization. Schematic diagrams of the tilt angle of the pentacene molecule with respect to the surface normal (z) for monolayer film (a3), single nanocrystal (b3), and single microsized crystal (c3).
The morphology of pentacene monolayer film was characterized by AFM and SEM. Figure 1a1 shows that the 0.50 ML pentacene film is composed of many separate disk-like grains which are similar to the previously reported disk-like morphology10 but different than the dendritic morphology.10 The height profile of the pentacene grains indicates that the step height is approximately 1.6 nm, as shown in Figure 1a2. These characteristic results indicate that the phase of the pentacene grain is the “monolayer phase” whose grains consist of a single layer of pentacene molecules which tilt around 11° with respect to the surface normal (z).

SEM image of the postannealed film is presented in Figure 1b1. Postannealing makes the pentacene monolayer film transform to nanoparticles with regular shapes, which are similar to the equilibrium shapes of the pentacene single crystal evaluated by a theoretical calculation.11 In fact, pentacene films with the coverage from less than one ML to several ML show the similar molecular redistribution phenomena. However, when the thickness of pentacene film surpasses 5 MLs, the redistribution process is not observed. Besides bare SiO2 substrate, we observed similar phenomena on many polymer dielectrics, such as polycarbonate (PC, polar polymer) and PS (nonpolar polymer) modified SiO2 substrates. The TEM image and SAED pattern in Figure 1b2 show clearly that the nanoparticle as postannealing product is single crystal. Note that the high-energy electron beam can easily destroy the pentacene crystal beyond a critical dose of about 0.035 mC/cm2,12 corresponding to about 3–5 s in our experiments. Although the SAED characterization is restricted by such short time, we found that the SAED patterns of the pentacene nanocrystals can be expressed in the form of Figure 1b2 through a vast amount of characterization experiments. The SAED pattern has been indexed with lattice constants reported previously: a = 0.6124 nm, b = 0.8078 nm, c = 1.5134 nm, α = 76.475°, β = 87.682°, γ = 84.684° for nanocrystal and microsized crystal, respectively.

Table 1. Calculated Angle Values among Low-Index Planes as Well as Measured Angle Values among Side Faces for Single Nanocrystal and Microsized Crystal

<table>
<thead>
<tr>
<th></th>
<th>single nanocrystal</th>
<th>single microsized crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>angle between low-index planes</td>
<td>(010)/(110)</td>
<td>(010)/(110)</td>
</tr>
<tr>
<td>calculated values</td>
<td>130.420°</td>
<td>126.698°</td>
</tr>
<tr>
<td>angle marked in Figure 2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>measured values</td>
<td>127.5°</td>
<td>127.5°</td>
</tr>
</tbody>
</table>

“Angle values are calculated based on lattice parameters of a = 0.6124 nm, b = 0.8078 nm, c = 1.5134 nm, α = 76.475°, β = 87.682°, γ = 84.684° and of a = 0.6266 nm, b = 0.7775 nm, c = 1.4530 nm, α = 76.475°, β = 87.682°, γ = 84.684° for nanocrystal and microsized crystal, respectively.

Figure 2. Marked angles among the different side faces of single nanocrystal (a) and single microsized crystal (b), as well as the corresponding crystal planes indexed by comparing the measured angles with the calculated values.
**DISCUSSION**

Transport of Postdeposition Pentacene Molecules on the SiO$_2$ Surface. Figure 3 shows a series of SEM images to illustrate the detailed crystallization process of the postdeposition pentacene monolayer film annealed at 80 °C with the varying annealing time from 2 to 180 min. The pictures indicate that the redistribution of pentacene molecules indeed occurs on the bare SiO$_2$ surface. Since diffusion and evaporation redeposition are two possible routes of molecular transport, it is valuable to clarify which is the major process in the postannealing process. In our research, the redistribution process appears at a wide annealing temperature range from ambient to 120 °C. The transport process of postdeposition pentacene molecules is generally observed in an enhanced substrate temperature, and the transport rate is accelerated with the increase of temperature. Without an external pentacene source during the postannealing process, we speculate that the redeposition is difficult to commence and maintain in an open system such as the Ar glovebox in our study. The following detailed characterization results for the morphology evolution confirm that the main transport process is indeed the molecular surface diffusion.

The redistribution process of the pentacene molecules takes place only within localized regions near the cores of nanoparticles, as indicated by the red circles in Figure 3. Meanwhile, the redistribution of pentacene molecules for those monolayer films beyond red circles is less changed, such as those regions in yellow circles. As shown in the series of images of Figure 3, a blank region without a nanoparticle inside has never been observed. This correlation strongly suggests that molecular diffusion is the major process of the molecular transport in the postannealing process. In the specific localized regions, i.e., within the red circles, surrounding pentacene molecules were gradually consumed and area of these blank regions enlarges with annealing time. Finally, they are restricted in circles of around 1.8 μm$^2$ by statistic analysis. The diameter of the blank regions seems limited by the mean diffusion length of a pentacene molecule on SiO$_2$ substrate.$^{16}$ It is noted that the amount of pentacene molecules in the nanoparticle is nearly equal to the consumed monolayer film grains by simply comparing the total area of monolayer grains multiplied by the single layer thickness with the volume of the corresponding nanoparticle before and after the postannealing process. In summary, the surface diffusion is the major transport process in the redistribution of pentacene molecules on the SiO$_2$ surface during the postannealing process.

Thermodynamic Analysis of the Pentacene Molecular Redistribution Process. Table 2 shows the evolution of the island size characterized by AFM with increasing annealing time. It indicates that the heights of islands increase with annealing time and tend to reach a saturation value of about 50 nm even with extending annealing time. The lateral sizes of the islands change less than the heights. Since the isothermal postannealing is a quasi-equilibrium process, the related phenomena can be explained with the thermodynamics as follows.

During pentacene molecules diffuse on the SiO$_2$ surface in the postannealing process, they randomly attach to or detach from the edges of the islands and also randomly jump on the exposed terrace or jump off the steps of the islands. There is a dynamic equilibrium between these opposite processes. The Gibbs free energy $G_{\text{sl}}$ for an island of $n$-layer can be expressed as$$G_{\text{sl}} = n_{\langle 001 \rangle} n_{\langle 100 \rangle} n_{\langle 110 \rangle} \mu_{\text{m}} + [2n_{\langle 100 \rangle} + 2n_{\langle 110 \rangle} + 2n_{\langle 110 \rangle} n_{\langle 110 \rangle} + n_{\langle 001 \rangle} n_{\langle 001 \rangle} + n_{\langle 001 \rangle} (\psi_{\text{m}} - \psi_{\text{m}})] \quad (1)$$where $n$ is the layer number of the island, $n_{\langle 001 \rangle}$ is the total number of unit cells in the $\langle 001 \rangle$ plane of the island within one monolayer, $m_{\text{m}}$ is the number of molecules per pentacene unit cell (i.e., $m_{\text{m}} = 2$ for pentacene), $\mu_{\text{m}}$ is the chemical potential of the infinitely large crystal, $n_{\langle hkl \rangle}$ is the number of unit cells along the edges of the island parallel to the directions $[hkl]$ indicated by the subscript, $\psi_{\text{sl}}$ are the specific surface energies per pentacene unit cell of the $\langle hkl \rangle$ plane, $\psi_{\text{m}}$ is the specific interfacial energy per pentacene unit cell with the substrate, $\psi_{\text{m}}$ is the specific surface energy per pentacene unit cell of the island size characterized by AFM with increasing annealing time. It indicates that the heights of islands increase with annealing time and tend to reach a saturation value of about 50 nm even with extending annealing time. The lateral sizes of the islands change less than the heights. Since the isothermal postannealing is a quasi-equilibrium process, the related phenomena can be explained with the thermodynamics as follows.

Table 2. Lateral Sizes and Heights of Nanoparticles Formed in the Post-Annealing Process

<table>
<thead>
<tr>
<th>annealing time (at 80 °C)</th>
<th>lateral size (nm)$^a$</th>
<th>height (nm)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 min</td>
<td>250</td>
<td>1.6</td>
</tr>
<tr>
<td>10 min</td>
<td>230</td>
<td>22</td>
</tr>
<tr>
<td>16 min</td>
<td>240</td>
<td>24</td>
</tr>
<tr>
<td>42 min</td>
<td>260</td>
<td>33</td>
</tr>
<tr>
<td>110 min</td>
<td>250</td>
<td>53</td>
</tr>
<tr>
<td>180 min</td>
<td>255</td>
<td>52</td>
</tr>
</tbody>
</table>

$^a$Values are tested in different samples in the series with different annealing times. Lateral size is the average diameter of the islands regarded as circles. Height is the average thickness of the islands.

![Figure 3. Morphological evolution of pentacene monolayer film annealed at 80 °C with increasing annealing time. The inserts are enlarged morphological images of corresponding islands.](image-url)
substrate. The first item in the right side of eq 1 corresponds to the bulk energy, the second and third ones are the surface energy of side faces which depend on the shape of the island and the surface energy of the top surface, respectively, and the last one is the net energy induced by the interface. An equilibrium shape of single crystal island confined by (010), (110), and (110) surfaces is supposed in eq 1.

Since the lateral sizes of islands change a little during the postannealing process, the variation of the Gibbs free energy from the island of \( (n-1) \) layer and a monolayer grain to the island of \( n \) layer is

\[
\Delta G_{(n-1)L+1L \rightarrow nL} = -n(001)(\psi_{001} + \psi_{\text{f}} - \psi_{\text{i}}) \tag{2}
\]

supposing the island and the grain have the same lateral shape. In fact, the multilayer island tends to present an equilibrium shape which reduces \( \Delta G_{(n-1)L+1L \rightarrow nL} \) further. Bearing in mind that \( \psi_{001} + \psi_{\text{f}} - \psi_{\text{i}} = m_{\text{mol}}\psi_{\text{mol}-(001)} - m_{\text{mol-sub}}\psi_{\text{mol-sub}} \) eq 2 turns into

\[
\Delta G_{(n-1)L+1L \rightarrow nL} = -n(001)(m_{\text{mol}}\psi_{\text{mol}-(001)} - m_{\text{mol-sub}}\psi_{\text{mol-sub}}) \tag{3}
\]

where \( \psi_{\text{mol}-(001)} \) and \( \psi_{\text{mol-sub}} \) are the interaction strengths between one molecule and a neighboring (001) layer and between one molecule and the substrate, respectively.

For our pentacene/SiO\(_2\) system, \( \psi_{\text{mol}-(001)} \) and \( \psi_{\text{mol-sub}} \) can be simply approximated by 0.141 and 0.105 eV, respectively.\(^{18}\) Substituting the values into eq 3, we get \( \Delta G_{(n-1)L+1L \rightarrow nL} < 0 \), in other words, the monolayer grain will dissolve to stimulate the island growth. With the help of the above thermodynamic analysis, a schematic diagram of Figure 4 based on morphological characterizations is given to depict the important stages of the molecular transport process and the scenarios of shape evolution of the island. The pentacene monolayer film (see Figure 4a) is thermodynamically unstable. The pentacene molecule tends to go upon the terrace rather than go down the step in the postannealing process. The excess jump-on molecules will supersaturate and nucleate on the top terrace of the island. And the nucleus will grow to become a second layer with the ongoing migration of pentacene molecules, as shown in Figure 4b. This redistribution process successively proceeds with the nearly constant driving force (see eq 3) resulting in the formation of multilayers of pentacene islands, as shown in Figure 4c, even though there is no incident flux of pentacene molecules as in the case of deposition growth. During the latter period of postannealing there is no excess pentacene molecule attaching to the edge of the island because only rare pentacene molecules lying beyond the mean diffusion length can diffuse to the edge of the multilayer island before they desorb from the substrate. Consequently the monolayer grains will become separate limited 3D islands (see Figure 4d). It is noted that in the quasi-equilibrium conditions, the 3D island is not like a pill but presents a hexagonal equilibrium shape which can be deduced by the Wulff–Kaischew theorem\(^{19}\) or equivalently obtained by partially differentiating eq 1 to \( n \) and \( n_{(1\bar{0}0)} \) and setting those differentials to zero.\(^{17\ast}\) As an approximation, the relative value between the lateral size and the height of the island can be theoretically calculated using the specific surface energies of pentacene.\(^{18}\) The lateral size of 250 nm corresponds to the height of 33 nm which is close to the characterization results shown in Table 2. We found that when the annealing temperature is relatively low or the annealing time is relatively short, the shape of the 3D island is often irregular with few straight side faces (see inserts in Figure 3). After sufficient long annealing time, most island transforms into regular nanocrystal with a hexagonal shape (see Figure 2a and inserts in Figure 3), which is the equilibrium shape of pentacene crystal on an inert substrate as illustrated in Figure 4e.

Microsized crystals grown by the subsequent PVT method on the nanocrystal seeds are based on the migration of pentacene molecules from an external pentacene source. The
extra pentacene molecules would tend to grow on the exposed faces of the equilibrium shape of the nanocrystal to expand the crystal size. If the PVT growth is carried in a quasi-equilibrium condition, the microcrystallized crystal would still keep equilibrium shape (see Figure 2b), as illustrated in Figure 4f.

Note that during the morphological evolution from monolayer grains to microcrystals, the vertical tilt angle of the pentacene molecule increases gradually; therefore, the vertical tilt angle of pentacene molecule tends to stand upright to minimize $\psi_{001}$ and $\psi_b$. However, when the height of the pentacene island increases, the energy item (the first item of eq 1) plays a dominant role gradually; therefore, the vertical tilt angle of pentacene molecule tends to increase to minimize $\mu_{001}$. By choosing different monolayer coverages or other inert substrates with different surface energy, the height of the pentacene island may be controlled, in favor of further investigation of the thickness-driven phase transition from the monolayer grain to the nanocrystal and to the microcrystallized crystal.

CONCLUSION

A two-step growth method utilizing single nanocrystals as seeds to fabricate large organic single crystals is demonstrated by postannealing of pentacene monolayer film. Comparing with traditional one-step growth method, it reduces the annealing time under quasi-equilibrium conditions to produce high quality microcrystallized crystals with equilibrium shape, providing a more flexible way to in situ prepare organic single crystal. TEM, SAED, and SEM indicate both nanocrystals and microcrystallized single crystals are single crystals with an upper surface of (001) plane and side faces of (010), (110), and (110) planes. Morphological evolution and formation mechanism of nanocrystal seeds were explained by thermodynamics. Specifically, the crystallization process is controlled by the surface diffusion which can be decomposed into three major processes: (i) upward interlayer diffusion of the molecule to form multilayer islands, (ii) surface transport of the pentacene molecule from peripheral grains to stimulate the island growth, and (iii) thermodynamic stabilization of molecule occupation leading to hexagonal equilibrium shapes. Since the single nanocrystals was acquired directly on the SiO$_2$ surface, the interface between the nanocrystal (and the subsequent microcrystallized crystal) and the SiO$_2$ dielectric has not been artificially broken which is important to a following electrical transport study.

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Notes
The authors declare no competing financial interest.

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REFERENCES


(18) The interaction strengths between molecules or the specific surface energies vary with pentacene crystal structures. The values used in this paper, such as $\psi_{\text{mol}(001)} = 0.141$ eV, $\psi_{\text{mol}-\text{sub}} = 0.105$ eV, $\sigma_{(001)} = 0.29$ eV/nm$^2$, $\sigma_{(010)} = 0.51$ eV/nm$^2$, $\sigma_{(110)} = 0.52$ eV/nm$^2$, and $\sigma_{(11\bar{0})} = 0.55$ eV/nm$^2$, correspond to a common phase of pentacene with parameters of $a = 0.6265$ nm, $b = 0.7786$ nm, $c = 1.4511$ nm, $\alpha = 76.650^\circ$, $\beta = 87.500^\circ$, and $\gamma = 84.610^\circ$. These values are acceptable approximations for our bulk phase and crystal phase. Please refer to ref 17.

(19) Wulff–Kaischew theorem is

$$\frac{\sigma_{\text{hkl}}}{h_{\text{hkl}}} = \frac{\sigma_s - \beta_s}{h_s} = \text{constant},$$

where $\sigma_{\text{hkl}}$ is the specific surface energy of the (hkl) crystal plane, $\sigma_s$ is the specific surface energy of the contact plane, $\beta_s$ is the specific adhesion energy of the contact plane, $h_{\text{hkl}}$ and $h_s$ is the distance from the Wulff’s point to the (hkl) crystal plane and the contact plane, respectively. For details please refer to Markov, I. V. *Crystal Growth for beginners: fundamentals of nucleation, crystal growth, and epitaxy*; 2nd ed., World Scientific press: Singapore, 2003.