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Controlled Growth of Ultrathin Film of Organic Semiconductors by Balancing the Competitive Processes in Dip-coating for Organic Transistors

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KEYWORDS Ultrathin film, organic semiconductor, OFET, dip-coating, competitive process
ABSTRACT Ultrathin film with thickness below 15 nm of organic semiconductors provides excellent platform for some fundamental research and practical applications in the field of organic electronics. However, it is quite challenging to develop a general principle for the growth of uniform and continuous ultrathin film over large area. Dip-coating is a useful technique to prepare diverse structures of organic semiconductors, but the assembly of organic semiconductors in dip-coating is quite complicated, and there are no reports about the core rules for the growth of ultrathin film via dip-coating until now. In this work, we develop a general strategy for the growth of ultrathin film of organic semiconductor via dip-coating, which provides a relatively facile model to analyze the growth behavior. The balance between the three direct factors (nucleation rate, assembly rate, and recession rate) is the key to determine the growth of ultrathin film. Under the direction of this rule, ultrathin films of four organic semiconductors are obtained. The field-effect transistors constructed on the ultrathin film show good field-effect property. This work provides a general principle and systematic guideline to prepare ultrathin film of organic semiconductors via dip-coating, which would be highly meaningful for organic electronics as well as for the assembly of other materials via solution processes.

1. INTRODUCTION

Organic semiconductor is the key component of organic electronic devices that possess unique features such as low cost, mechanical flexibility, and large area coverage.\textsuperscript{1-9} Generally, the thickness of organic semiconductor layer in organic electronic devices is in the range of several tens of to hundreds of nanometer (nm), which consists of tens of or more molecular layers.\textsuperscript{10-16} On the other hand, ultrathin film (< 15 nm, Figure 1a) of organic semiconductors represents a kind of nano-scale film consisting of monolayer to few molecular layers (Figure 1b).\textsuperscript{17-23}
According to the surface morphology, ultrathin film includes continuous and microstructured film (Figure 1a), both of which provide excellent platform for fundamental researches and practical applications.\textsuperscript{24-30} For example, in organic field-effect transistors (OFETs), the charge transporting layer (conductive channel) is located at the interface between semiconductors and dielectrics, and its thickness is only about one to several nm, i.e., one to several molecular layers.\textsuperscript{31-35} In the conventional OFETs, conductive channel is buried in the thick organic semiconductor film (tens of nm) and difficult to characterize.\textsuperscript{36} If ultrathin film is utilized in OFETs, the conductive channel is exposed outside, which would be favorable for both the investigation of conductive channel and the application for sensors.\textsuperscript{24-30} However, it is quite difficult to develop a general principle to grow large-area, uniform, and continuous (at least along one dimension) ultrathin film of different organic semiconductors.

Figure 1. (a) Schematic illustration of continuous and microstructured ultrathin film (UTF). (b) Schematic illustration of monolayer to few layers that constitute UTF. (c) Molecular structure of p-type semiconductors (TIPS-pentacene and C8-BTBT) and n-type semiconductors (NDI3HU-DTYM2 and C60).
Until now, several methods have been used for the preparation of ultrathin film of organic semiconductors, such as vapor deposition, Langmuir-Blodgett technique, electro-static assembly, covalent self-assembly, dip-coating, and so on.\textsuperscript{17-30,37-46} Generally, in the ultrathin film regime, vapor deposition usually produces the discontinuous patches or non-uniform film consisting of lots of grains and grain boundaries. Langmuir technique, electro-static assembly, and covalent self-assembly usually need the organic semiconductors with some special functional groups such as hydroxyl, silyl, etc. which may influence the electrical performance.

In our previous work, we realized the controllable growth of monolayer to multilayer ultrathin microstripes of organic semiconductor by tuning the pulling speed in dip-coating process.\textsuperscript{45,46} However, such unique and useful growth behavior seems to be limited to 2,7-dialkyl-Dithieno[2,3-d:2’,3’-d’]benzo[1,2-b:4,5-b’]dithiophene (DTBDT-Cn) compounds, that is, it shows specificity toward certain compounds (i.e., poor molecular generality), which will greatly overshadow the significance of this growth behavior and hinder its further applications in different fields. Until now, a general strategy to prepare ultrathin film of different organic semiconductor via dip-coating has not been developed, which is an important but quite challenging task.

Aiming at this issue, in this work we develop a model to direct the growth of ultrathin film of organic semiconductors in dip-coating. This model consists of the following main aspects: (1) The balance between the three direct factors (nucleation rate, assembly rate, and recession rate) is the key to determine the growth of ultrathin film; (2) The balance between nucleation rate and recession rate is a prerequisite to form the deposition; (3) Under the balance between nucleation and assembly, the solute may grow into ultrathin film via intermolecular self-assembly; (4) Low solution concentration is another prerequisite for the growth of ultrathin film because low
concentration yields less deposition on substrate and thus is favorable to form ultrathin film. Furthermore, the concentration should not be far from the saturation point. With the guidance of this model, the optimization of the experimental conditions can be performed in a reasonable and efficient way. The controlled growth of ultrathin film of four organic semiconductors is realized through the proper combination of common experimental conditions including solvent type, solution concentration, and pulling speed. The field-effect transistors are constructed on the ultrathin film, which show good field-effect property. This work provides a general principle and systematic guideline to prepare ultrathin film of organic semiconductors via dip-coating, which would be highly meaningful for organic electronics as well as for the assembly of materials via solution processes.

2. EXPERIMENTAL SECTION

2.1 Materials and characterizations

6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT), and C60 was purchased from Sigma-Aldrich company and used as received. NDI3HULDTYM2 was synthesized according to the literature. They are dissolved in single or mixed solvent to form solution. The solubility of TIPS-pentacene in toluene and acetone is obtained from product description of TIPS-pentacene (Sigma-Aldrich), which is further confirmed by the experiments. The solubility of TIPS-pentacene in n-octane, ethanol, and isopropanol is obtained from the experiments. The silicon wafer with 300 nm SiO$_2$ layer was immersed vertically into the solution and then was pulled out at controlled speed ($U$). The speed ranging from 10 to 3000 $\mu$m/s is controlled by a high-precision linear motor stage.
The experiments were carried out at ambient laboratory condition (Temperature = 20.0 – 28.0 °C, Humidity = 30.0 - 65.0%).

The morphology, topography and thickness of stripe were measured on Veeco Dimension 3100 in tapping mode. Optical image was obtained on Olympus BX51 optical microscope equipped with CCD under bright field mode. XRD measurement with θ-2θ scan mode was carried out on Bruker D8 ADVANCE diffractometer.

2.2 Device fabrication

The heavily doped silicon wafer and 300 nm thermally-oxidized layer were used as gate and insulator, respectively. After preparation of ultrathin film, gold film was pasted onto the microstripes as electrode via probe station. For the transistors based on TIPS-pentacene and C8-BTBT microstripes, the total width of microstripes was accumulated through optical image and defined as channel width. Field-effect characteristics measurement was performed on Keithley 4200 in air at room temperature. The field-effect parameters were obtained from the standard equation (1) in the saturation region:

\[ I_{ds} = \frac{W}{2L} C_i \mu (V_{gs} - V_t)^2 \]

where \( C_i \) is the dielectric capacitance, \( W \) is channel width, and \( L \) is channel length.

3. RESULTS and DISCUSSION

Firstly, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene, Figure 1c), which is a soluble pentacene derivative and shows good field-effect performance, is selected as a model compound to test whether and how ultrathin film can be obtained through dip-coating. In fact,
the growth of microstructure of TIPS-pentacene through dip-coating has been reported in several literatures, but all those reports produce thick film or microstripes (tens of nm, beyond the range of ultrathin film). In order to get ultrathin film of TIPS-pentacene, at the beginning we use the similar experimental parameters with our previous work. Toluene solution of TIPS-pentacene with different concentration (1, 2, 4 mg/mL) is prepared for dip-coating. The pulling speed ranging from 10 to 2000 µm/s are tried, but no deposition or very sparse dots (Figure S1) can be found on the substrates, indicating almost no TIPS-pentacene nucleates on the substrate. We also try to tune other experimental conditions such as evaporation rate of solvent, environmental temperature and humidity, as well as surface treatment, but all these attempts fail to get uniform and continuous ultrathin film. It seems dip-coating is unsuitable to get ultrathin film of TIPS-pentacene. To circumvent the hindrance, it is necessary to reconsider the growth mechanism of dip-coating, and to find the possible reasons for the unwanted results.
Figure 2. (a) Schematic illustration of the dynamic processes in dip-coating at low speed (left part) and high speed (right part) regime. The abbreviations of Nuc&Ass, Rec, and Evap represent nucleation & assembly, recession, and evaporation, respectively. (b) The key factors influencing the growth of ultrathin film in dip-coating. The bottom position of pulling speed denotes that it has effect on most of other factors. The factors with red frame indicate these experimental parameters are relatively easy to tune.

Figure 2a illustrates the schematic diagram of dip-coating process. When the substrate is pulled out from the solution, meniscus and entrainment forms at the three-phase contact area in low and high speed regime, respectively (Figure 2a). Since the evaporation rate near the contact line is larger compared to the bulk solution, the evaporation of solvent at the contact line will increase the local concentration of solute molecules. When a critical concentration is reached, the solutes start to deposit, leading to the formation of nucleation center. The capillary force will cause solute to flow toward the contact line, and the supplied solute will aggregate onto the nucleation center and form different kind of microstructure.

According to the above statements, it can be found that the self-assembly of organic semiconductors via dip-coating is essentially an evaporation-induced growth process that involves competition at the three-phase contact line between the dynamic processes including substrates movement, solvent evaporation, solution recession, solute nucleation (or precipitation) and solute assembly, as shown in Figure 2a,b. A few factors influence the growth behavior, which may be classified into direct and indirect ones. As shown in Figure 2b, nucleation rate, assembly rate, and recession rate are assigned to be the direct factors, and the balance between them would be the key to get ultrathin film. Nucleation rate mainly depends on the solvent evaporation rate, solution concentration, and solute solubility (saturation concentration).
Assembly rate refers to the capability to assemble into 1D or 2D ordered microstructure via intermolecular interaction, and is closely related to the intermolecular interaction, solute/solvent interaction, and solute/substrate interaction. Recession rate is mainly determined by gravity, solution property (density, viscosity, surface tension, etc.) and substrate surface property. Therefore, the recession rate is generally in a fixed range for certain solution and substrate. The pulling speed determines the geometry of three phase contact area which serves as the platform for the growth of solute, so it may exert elaborate effect on most of other growth factors. It can be seen from Figure 2b that the growth of ultrathin film is influenced by many factors, some of which are fixed at small range or difficult to characterize (such as gravity, solvent/solute interaction, solute interaction, etc.), and therefore are not good candidates to tailor the growth behavior. While solvent evaporation rate, solution concentration, solute solubility and pulling speed are relatively easy to modify, so it would be ideal to tune the growth behavior through these factors. In addition, the viscosity and surface tension of solution are also important factors for the growth of solute in solution processes, but the organic small molecular solvents used in this work generally have similar viscosity and surface tension (Table S1). Therefore, solvent viscosity and surface tension may play a minor role in determining the morphology of ultrathin film, as compared to solvent evaporation rate, solution concentration, and solubility of solute.

The model shown in Figure 2b provides a facile guideline to analyze the growth behavior. In our beginning experiments with the solution concentration of 1-4 mg/mL, almost no deposition forms on the substrate, which means that TIPS-pentacene could not precipitate at the contact line with the evaporation of solvent (toluene). According to the growth mechanism as stated above, to get deposition on substrate, the solution concentration should reach the saturation point for nucleation with the evaporation of solvent. Otherwise, the solute will flow back into the bulk
solution with the recession of solution. In fact, the solubility of TIPS-pentacene in toluene is quite large (over 50 mg/mL), so in low concentration (1-4 mg/mL) solution it will take longer period to reach the nucleation point, and during this period the solute already flows back to the bulk solution. The unbalance between recession rate of solution and nucleation rate of solute may account for no deposition in our beginning experiments. To realize the balance, we increase the solution concentration to 20 mg/mL to enhance the nucleation rate. At this condition, thick microstripes over 50 nm (Figure 3a) are obtained with the pulling speed in the range of 10-1000 \( \mu \text{m/s} \), which is similar to the previous reports.\textsuperscript{51-53} This result is reasonable because the higher concentration leads to more deposition of solute on the substrate and thus thicker microstripes which are however beyond the range of ultrathin film.

**Figure 3.** (a) Optical image of microstripes of TIPS-pentacene obtained in toluene solution with concentration of 20 mg/mL. (b) Relationship between molecular layer number \( (N) \) and pulling speed \( (U) \) in octane solution. The number of “0” denotes discontinuous dots. (c) Optical image and (d) AFM image and section profile (3-5 molecular layers) of TIPS ultrathin film obtained at
1000 µm/s in octane solution. The unit of x,y-axis in section profile (d) is µm and nm, respectively.

Although no ultrathin film is obtained in our beginning experiments (toluene system), two pieces of useful hints are gotten for the growth of ultrathin film: 1) the balance between nucleation rate and recession rate is a prerequisite to get the deposition (Figure 2b); 2) high solution concentration generally produces thick film or microstructures, while relatively low concentration should be favorable to get ultrathin film. The first hint indicates that if the nucleation rate could not match the recession rate (e.g., in 1-4 mg/mL toluene system), generally no deposition forms. Therefore, it is necessary to increase the nucleation rate to get its balance with recession rate, which can be achieved by increasing the solution concentration, accelerating evaporation rate, and/or lowering the solubility of solute (Figure 2b). In view of the second hint, accelerating evaporation rate and lowering the solubility would be the feasible choices to match the recession rate.

Accelerating of evaporation rate may be achieved by using solvent with low boiling point and high volatility. Chloroform and dichloromethane satisfy these requirements. For chloroform, at low concentration below 4 mg/mL, almost no deposition forms on the substrate. Only at high concentration (>10 mg/mL), thick (over 30 nm) microstripes are obtained. This result is similar to toluene system, owing to the good solubility (over 30 mg/mL) of TIPS-pentacene in chloroform. For dichloromethane solution with concentration of 2 mg/mL, discontinuous dots generally form at the speed of tens of to hundreds of µm/s. These results indicate that despite of relatively high evaporation rate of chloroform and dichloromethane, the good solubility of TIPS-pentacene in them still renders the difficulty in getting ultrathin film at low concentration.
Lowering the solubility may be achieved through the utilization of single poor solvent (low solubility) or the mixture of the good (large solubility) and poor solvents. Accordingly, we classify several common solvents into good and poor solvent (referring to the solubility for TIPS-pentacene), in which good solvent includes toluene, chloroform, dichloromethane, and poor solvent includes octane, hexane, ethanol, isopropanol, and acetone. Firstly we try single solvent system with poor solubility. Octane is firstly selected since it has some similar characteristics (boiling point and molecular weight) with toluene, but has a relatively low saturation solubility of about 7 mg/mL for TIPS-pentacene. A solution of 2 mg/mL is prepared for dip-coating, and only short and discontinuous structure appears (Figure S2a) at speed below 1000 µm/s. Significantly, at a speed of 1000 µm/s, thin (less than 10 nm) and dentritic microstripes (a kind of microstructured ultrathin film) are obtained (Figure 3c,d). With the increase of speed, the thickness (> 30 nm, Figure S2b,c) increases as well and goes beyond the range of ultrathin film. The relationship between thickness and pulling speed in octane solution is shown in Figure 3b, which is consistent with the mechanism of entrainment controlled regime (Figure 2a, right part).46

As shown in Figure 3c, the uniformity of ultrathin film obtained in octane system is not very good. The relatively low volatility of octane yields a long assembly period, which gives too much time for the molecules to assemble into the thick and non-uniform microstructures. Therefore, we further try hexane, ethanol, isopropanol and acetone with relatively quick evaporation rate compared with octane. In hexane system, we get some discontinuous dots or thick microstructure (for details, see Supporting Information, Figure S3). Ethanol and isopropanol have very low solubility (< 0.5 mg/mL) for TIPS-pentacene, so no deposition forms.
Remarkably, in the case of acetone (1.0 mg/mL), very uniform ultrathin film are obtained. At low speed of 10 μm/s, uniform and dentritic microstripes form with the thickness of about 15 nm (Figure 4a,b). At 30 μm/s, the thickness reduce to below 10 nm (Figure 4c,d). The thickness uniformity below 30 μm/s is quite good with coverage over hundreds of micrometer. At 50 μm/s, the thickness is similar to that at 30 μm/s, but some discontinuous dots appear (Figure 4e,f). With the increase of speed, the portion of discontinuous microstructure increases as well. Once the speed is higher than 100 μm/s, almost no continuous microstructures are obtained (Figure S4a). This result may be related to the quick evaporation rate of acetone, which leads to the quick nucleation without good intermolecular assembly into uniform microstructure. The inverse proportional relationship between the pulling speed and the layer number (Figure S4b) at low speed indicates that the growth occurs in the meniscus controlled regime (Figure 2a, left part). The growth results in acetone system indicate that the balance between nucleation and assembly is favorable to get uniform ultrathin film (Figure 2b). If the nucleation period is relatively long, then the solute may have enough time to assemble into thick microstructure. On the other hand, too short nucleation period may bring difficulty for the solute to assemble into ordered structure, and yield discontinuous structure.
Figure 4. (a) Optical image and (b) AFM image and section profile of TIPS-pentacene microstripes obtained at 10 µm/s. (c) Optical image and (d) AFM image and section profile (4-6 molecular layers) of TIPS ultrathin film obtained at 30 µm/s. (e) Optical image and (f) AFM image and section profile of TIPS ultrathin film obtained at 50 µm/s. (g) Optical image and (h) AFM image and section profile of TIPS-pentacene ultrathin film obtained at 1000 µm/s. (a-f) acetone solvent, (g-h) the mixed solvent (chloroform:isopropanol). The unit of x,y-axis in section profile (b,d,f,h) is µm and nm, respectively.

Using the single solvent with poor solubility for TIPS-pentacene, ultrathin film can be obtained by tuning the balance between the nucleation, assembly, and recession (Figure 2b). Theoretically, such balance may be achieved via the mixture of solvents with good and poor solubility. The chloroform and toluene are used as good solvent, and ethanol, hexane and isopropanol are selected as poor solvent. After systematic optimization (for details, see supporting information 2), mixed solvent (chloroform:isopropanol, 1:2) is used for dip-coating.
At high speed range (200-1000 µm/s), uniform dentritic ultrathin film with thickness less than 10 nm (Figure 4g,h) forms over large area (over hundreds of µm).

The above results demonstrate that ultrathin film of TIPS-pentacene can be obtained via the rational optimization of experimental conditions under the direction of the model in Figure 2b. As listed in Table 1, proper combination of solvent type, solution concentration, and pulling speed may obtain the balance between the competitive processes in dip-coating (Figure 2b), which would be favorable to get large-area, uniform and continuous ultrathin film.

Table 1. Growth results of TIPS-pentancene under different experimental conditions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration (mg/mL)</th>
<th>Growth result (pulling speed, µm/s)ab</th>
<th>Notesc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>20</td>
<td>Thick microstripe (50-500)</td>
<td>Rec &lt; Nuc</td>
</tr>
<tr>
<td>Chloroform</td>
<td>&lt;4</td>
<td>Sparse dots or no deposition (10-1000)</td>
<td>Rec &gt; Nuc</td>
</tr>
<tr>
<td>Octane</td>
<td>2</td>
<td>Non-uniform UTF (1000)</td>
<td>(Rec ≈ Nuc) ≠ Ass</td>
</tr>
<tr>
<td>Ethanol</td>
<td>&lt;0.5</td>
<td>No deposition (10-1000)</td>
<td>Rec &gt; Nuc</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.0</td>
<td>Uniform UTF (10-50)</td>
<td>Rec ≈ Nuc ≈ Ass</td>
</tr>
<tr>
<td>Toluene:(Hexane, Acetone, or Ethanol)</td>
<td>~ 2</td>
<td>Sparse dots or no deposition (30-1000)</td>
<td>Rec &gt; Nuc</td>
</tr>
<tr>
<td>Chloroform:Hexane</td>
<td>1.6</td>
<td>Discontinuous microstripes</td>
<td>(Rec ≈ Nuc) ≠ Ass</td>
</tr>
<tr>
<td>Chloroform:Isopropanol</td>
<td>2</td>
<td>Uniform UTF (10)</td>
<td>Rec ≈ Nuc ≈ Ass</td>
</tr>
</tbody>
</table>

a) UTF means ultrathin film. b) The pulling speed adopted between 10-1000 is 10, 30, 50, 100, 200, 500, 1000 µm/s, respectively. c) The abbreviations (Rec, Nuc, and Ass) represent recession, nucleation, and assembly, respectively. Symbols (> and <) mean the comparison of relative rate. Symbols (≈ and ≠) denote the balanced and unbalanced status, respectively.

To test the generality of the rule established above, we further try another three organic semiconductors including p-type C8-BTBT, n-type NDI3HU-DTYM2, and n-type C60 (Figure 1c). Using the similar principle, ultrathin microstripes (5-10 nm) of C8-BTBT (Figure 5a,b) is obtained with the mixed solvent (toluene:tetrachlorocarbon, 1:1, 1.1 mg/mL) at a pulling speed...
of 3000 µm/s. Ultrathin film (about 2 nm) of NDI3HU-DTYM2 (Figure 5c,d) is achieved with the mixed solvent (toluene:dichlorobenzene, 1:14, 2 mg/mL) at the pulling speed of 10 µm/s. It can be found from Figure 5 c,d that continuous NDI3HU-DTYM2 monolayer film with few bilayer islands forms. The area of monolayer film almost covers the whole substrate (with area of several cm²). Such growth result means that NDI3HU-DTYM2 prefer to assemble in 2D growth mode, which is quite different from the TIPS-pentacene or C8-BTBT that prefer to the 1D growth mode. 2D and 1D growth mode may give rise to continuous and microstructured ultrathin film, respectively. The ultrathin microstripes (13-17 nm) of C60 (Figure 5e,f) is obtained with the mixed solvent (toluene:tetrachlorocarbon, 1:1, 0.6 mg/mL) at a pulling speed of 3000 µm/s. The coverage of ultrathin film of these three organic semiconductors is over mm², which is large enough for device fabrication. These results clearly indicate that the growth rule established in this work can be applicable for the preparation of ultrathin film of different organic semiconductors.
Figure 5. (a) Optical image and (b) AFM image and section profile of C8-BTBT ultrathin microstripes. (c) Optical image and (d) AFM image and section profile of NDI3HU-DTYM2 ultrathin film. (e) Optical image and (f) AFM image and section profile of C60 ultrathin microstripes. The unit of x,y-axis in section profile (b,d,f) is µm and nm, respectively.
Figure 6. (a) Output and (b) Transfer curves of OFETs on TIPS-pentacene ultrathin film. (c) Output and (d) Transfer curves of OFETs on C8-BTBT ultrathin film. (e) Output and (f) Transfer curves of OFETs on NDI3HUL-DTYM2 ultrathin film. Insets in a,c,e are the images of transistor devices.

The electrical property of ultrathin film is tested with transistor geometry. Figure 6 show the output and transfer curves of transistors based on TIPS-pentacene, C8-BTBT, and NDI3HU-DTYM2 ultrathin film. It can be found from output curves that the ultrathin film show well-defined field-effect characteristics. The molecular ordering confirmed by XRD measurement (Figure S7) may contribute to the field-effect charge transporting. The field-effect parameters (mobility, threshold voltage, and on/off ratio) are derived to be 0.16 cm²/Vs, -20.7 V, and 1.8 ×
10^6, respectively. The corresponding values of C8-BTBT ultrathin film are 1.68, -18.2 V, 1.2 × 10^6, respectively. The mobility, threshold voltage and on/off ration of NDI3HU-DTYM2 ultrathin film are calculated to be 0.005 cm^2/Vs, -4.2 V, and 1.4 × 10^5, respectively. However, the field-effect mobility of ultrathin film is still lower than the reported value of thick film,^{47,51-53,55} which may be due to the following reasons: (1) The ultrathin film is more susceptible to ambient conditions, e.g., oxygen and humidity, while in thick film device, the upper layer will exclude these adverse factors away from charge transport layer; (2) Bare SiO_2 coated silicon wafer is used as substrate, and the interface of SiO_2/semiconductor may have more defect such as hydroxyl group which will act as charge-trapping sites; (3) The assembly rate for ultrathin film is relatively quick compared with thick film, so the molecular ordering in the ultrathin film may be relatively lower. The FETs on C60 microstripes are measured in air and under vacuum (Figure S8), but no field-effect property can be observed probably due to the electron trapping effect of SiO_2 dielectric.^{56}

Finally, several points for the growth of ultrathin film via dip-coating are emphasized here,

i. The growth of uniform and continuous ultrathin film can be achieved through balancing the competitive processes between recession, nucleation and assembly as shown in Figure 2b.

ii. The balance between nucleation rate and recession rate is a prerequisite to form the deposition. If nucleation rate is smaller compared with the recession rate of solution, the solute may flow back into the bulk solution, leading to no or sparse deposition. The opposite condition may leads to thick or discontinuous deposition.
iii. Nucleation and assembly always occurs simultaneously. If the balance between them is achieved, the solute may grow into ultrathin film via intermolecular self-assembly during the continuous solvent evaporation. If nucleation period is too long, the solute will assemble into thick microstructure. The opposite conditions may yield discontinuous microstructure.

iv. Low solution concentration is another prerequisite for the growth of ultrathin film, because low concentration yields less deposition on substrate and thus is favorable to form ultrathin film. In view of the theoretical calculation (for details, see supporting information) and our experimental results, the concentration of 0.5-4 mg/mL would be favorable to get ultrathin film. In addition, the concentration should not be far from the saturation point. Otherwise no deposition probably yields due to the unbalance between nucleation rate and recession rate as stated above. For highly soluble organic semiconductors, the poor solvent or the mixture of good and poor solvent that have saturation solubility below 10 mg/mL are useful choices.

4. CONCLUSION

In conclusion, we demonstrate a general principle to grow uniform and continuous ultrathin film of p- and n-type organic semiconductors via balancing the competitive processes at the three-phase contact line in dip-coating. The solvent type, solution concentration, and pulling speed are used as main parameters to tune the balance between the recession rate of solution, nucleation rate, and assembly rate. Ultrathin films of four organic semiconductors are realized with low solution concentration that is near to saturation point at proper speed range. OFETs constructed on ultrathin film show good field-effect property. The general growth principle
demonstrated here would provide a meaningful tool to prepare ultrathin film organic semiconductors which may serve as an excellent platform for the fundamental research and applications in the field of organic electronics.

ASSOCIATED CONTENT

**Supporting Information.** Growth results of TIPS-pentacene in different solvents. XRD results of ultrathin film. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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A general principle for the growth of ultrathin film (UTF) of organic semiconductors via dip-coating process is developed. The balance between the three competitive factors (nucleation rate, assembly rate, and recession rate) is the key to get uniform and continuous ultrathin film. Under the direction of this principle, ultrathin film of four organic semiconductors are obtained, which show good field-effect property.