Air-flow navigated crystal growth for TIPS pentacene-based organic thin-film transistors

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6,13-Bis(trisopropylsilylethylene)pentacene (TIPS pentacene) is a promising active channel material of organic thin-film transistors (OTFTs) due to its solubility, stability, and high mobility. However, the growth of TIPS pentacene crystals is intrinsically anisotropic and thus leads to significant variation in the performance of OTFTs. In this paper, air flow is utilized to effectively improve the TIPS pentacene crystal orientation and enhance performance consistency in OTFTs, and the resulted films are examined with optical microscopy, X-ray diffraction, and thin-film transistor measurements. Under air-flow navigation (AFN), TIPS pentacene drop-cast from toluene solution has been observed to form thin films with improved crystal orientation and increased areal coverage on substrates, which subsequently lead to a fourfold increase of average hole mobility and one order of magnitude enhancement in performance consistency defined by the ratio of average mobility to the standard deviation of the field-effect mobilities.

1. Introduction

In recent years, significant progress has been made in the development of organic thin-film transistors (OTFTs). Due to their ease of fabrication, high performance and cost-effectiveness, solution-processed OTFTs have great potential for applications in large-area flexible integrated systems [1–6]. Among solution-processable organic semiconductors, 6,13-bis(trisopropylsilylethylene)pentacene (TIPS pentacene) is a very promising material because of its high hole carrier mobility and environmental stability [7–15]. However, its tendency to form randomly oriented needle-shaped crystals when crystallized from solution leads to significant performance variations in OTFT performance [16,17].

Drop casting TIPS pentacene (solute) in toluene (solvent) is a widely used method to form polycrystalline TIPS pentacene thin films. When a droplet of solution is in contact with a substrate, its contact lines are pinned and thus restrict the volume change of the liquid content, which is known as the “pinning effect” [18–21]. Consequently, the volume change at the droplet edge is smaller than that in the center. On the other hand, solvent evaporation at the edge is faster than the center of the droplet because of an increased available angle of evaporation at the edge [22,23]. The difference in evaporation rate and volume change between the edge and the center of the droplet causes a radial flow, which supplies the solvent and carries the solute from the center to the edge. The increased density of solute at the edge eventually deposits, forming the so-called “coffee ring”, which adversely affects crystallization and thin-film morphology thereby leading to poor performance of OTFTs. To prevent the “coffee ring” patterns, the pinning effect and excessive center-to-edge solute diffusion should be minimized. In addition, to keep the needle-shaped crystal growth in a consistent orientation, the solution drying direction must be aligned as well. In this paper, external air flow is applied in an effort to facilitate
contact line moving and counteract excessive solute diffusion from the center to the edge of the droplet and keep the solution drying direction identical to that of the air flow. The gas flow approach to control the TIPS pentacene crystallization and morphology has been studied before. For example, Chen et al. used an air flow in vertical configuration (air flow vertical to the substrate plane) to control solvent evaporation and be able to manipulate crystal domain sizes [24]. Also, Kim et al. showed a correlation between the injected gas flow direction and the OTFT performance [25]. In this paper, we systematically investigated the effects of horizontal air flow not only on improving the TIPS pentacene crystal orientation, but also on enhancing the film areal coverage over the whole substrate, which work together to achieve an 11-fold enhancement in performance consistency of OTFTs. The performance consistency here is defined as the ratio of average mobility to the standard deviation of the field-effect mobilities, which is an indication of the mobility uniformity for the OTFT devices over the whole substrate. Optical microscopy and X-ray diffraction were employed to investigate the morphology of TIPS pentacene thin films at different air flow speeds. Our work demonstrates that the employment of external air flow provides a simple, yet effective approach to control solution-processed TIPS pentacene crystal growth, thereby improving the average hole mobility and performance consistency of OTFTs.

2. Experiment

TIPS pentacene was used as purchased (Sigma Aldrich) without further purification. TIPS pentacene powder was first dissolved in toluene with a concentration of 5 mg/ml. Subsequently, TIPS pentacene thin films are formed by drop casting in a solvent rich environment [26]. The experiment was carried out in a plastic chamber to prevent the effect of the air circulation in the chemical hood. For air-flow navigated TIPS pentacene growth, external air flow from a nozzle was turned on simultaneously upon drop casting to facilitate crystal orientation over the whole substrate. Because TIPS pentacene is known for its excellent air stability [11], here we simply used dry air with \(20\%\) humidity for our flow navigation experiments, instead of using an inert gas such as argon or nitrogen. Flow rate was measured for air flow inside the plastic tube by...
using Dwyer VF Visi-Float Flowmeter VFB-65-BV. Since the influence of air flow on the TIPS pentacene growth depends on the distance between air nozzle and substrate and other environmental conditions, the corresponding effects at different air flow rates are based on our in-house experimental setup. Optical micrographs of TIPS pentacene thin films were taken using an optical microscope with a camera built in a Signatone PSM 1000 probe station. Thin film crystallinity and coverage was characterized using Philips X’Pert X-ray Diffraction.

Bottom-gate, top-contact OTFT configuration was adopted in device fabrication. Heavily doped n-type silicon

![Figure 2](image1.png)

**Fig. 2.** Optical images of TIPS pentacene thin films with air-flow navigation. Air-flow direction is from the bottom to the top in each optical image. Panels (a), (b), (c), and (d) correspond to the air flow speed of 1 L/min, 2 L/min, 3 L/min, and 4 L/min, respectively.

![Figure 3](image2.png)

**Fig. 3.** Average misorientation angles in air-flow navigated TIPS pentacene films as a function of air flow speeds.
substrate serves as bottom gate, and 250 nm thermal oxide as gate insulator. After TIPS pentacene growth on the substrate, Au source/drain contacts were thermally deposited through shadow mask with channel length of 100 microns and channel width of 1000 microns. The electrical performance of OTFTs was characterized by current–voltage measurement using an Agilent B1500A semiconductor parameter analyzer. In order to ensure the extracted parameters from the transfer characteristic were consistent, all devices were measured for five times. All measurements were done in the ambient environment at room temperature. From the slope of the transfer characteristic ($I_{DS}^{1/2} - V_{GS}$), field-effect mobility in the saturation regime was extracted.

3. Results and discussion

Fig. 1 illustrates the concept of the air-flow navigation for TIPS pentacene crystal growth. As compressed dry air flows against and over a drop-cast TIPS pentacene droplet (dashed line) on the SiO$_2$/Si substrate, it pushes the front area and contact line forward, minimizing the pinning effect. Also air flow counteracts solute diffusion from center to edge by pushing back the solute away from the edge, preventing solute deposition [25]. As the front contact line moves forward, the solvent evaporates along the air flow path, leading to an orientated crystal growth in the same direction as air flows. As a result, air flow effectively navigates the TIPS pentacene crystallization and improves the crystal orientation over the whole substrate. Fig. 1(b) compares the air flow guided crystal growth at the optimal flow rate with the simple drop-casting crystallization without AFN. If no air flow is applied, the TIPS pentacene thin film exhibits large needle-shaped crystals with random orientation and huge gaps in between. When a proper air flow is applied, TIPS pentacene crystals become well orientated with enhanced areal coverage. The polycrystalline TIPS pentacene thin film obtained at optimum flow rate of 2 L/min yields optimal crystallization in terms of crystal orientation and coverage. Note in Fig. 1(b) that the crystal orientation does not exactly match the air flow direction. This may be partially attributed to the fact that in our experimental setup, some compressed air bounces back from the chamber side wall, causing air disturbances on the substrate edge and affecting crystal growth orientation. Our results also suggest that the air flow is not only able to improve morphology, but also affect film topogra-

![Fig. 4. (a) Plot of average grain width versus flow rate. The TIPS pentacene grain width decreases as air flow speed increases due to enhanced solvent evaporation. (b) Plot of film areal coverage versus air flow speed. The highest film coverage occurs at optimal flow rate of 2 L/min, which corresponds to an optimized TIPS pentacene thin-film morphology. The error bars represent the standard deviation of 10 measurements for both (a) and (b).](image-url)
As shown in Fig. 1(c), without air-flow navigation, the crystal film thickness varies significantly from 30 nm to 770 nm. In contrast, when air flow is applied to navigate crystallization, the TIPS pentacene film demonstrates significantly reduced maximum thickness and less thickness variation. At the flow speed of 2.0 L/min, the thin-film thickness ranges from 13 nm to 35 nm with an average of 20 nm over the whole substrate. The improved uniformity in thickness contributes to an even distribution of nucleation and crystallization events on the substrates because the air flow counteracts the solute diffusion from the center to the edge, resulting in uniform deposition of crystal seeds.

The optical images in Fig. 2 show morphology variations of TIPS pentacene films at different air flow speeds: (a) 1 L/min, (b) 2 L/min, (c) 3 L/min, and (d) 4 L/min, respectively. At a low air flow speed of 1 L/min, the “coffee ring” crystal patterns still persist, with largely improved crystal orientation as compared to the drop-cast TIPS pentacene film. When the air flow rate increases to 2 L/min, the air flow is able to suppress the “coffee ring” effect, leading to the best TIPS pentacene crystal orientation and needle-crystal growth as shown in Fig. 2(b). The TIPS pentacene crystal domains are long needle-shaped [27,28] with the long axis along the [210] direction as well as short axis of \( \frac{1}{2}C_{22} \). As the air-flow speed is further increased to 3 L/min, the toluene solvent evaporates rapidly, resulting in the initiation of some round-shaped crystal domains that are smaller in size within the crystal needles as shown in Fig. 2(c). Those crystal domains do not fully crystallize because of the reduced crystallization time. Such a phenomenon becomes more significant when the air flow speed is increased up to 4 L/min: the external air flow quickly evaporates toluene and TIPS pentacene is almost directly deposited on the substrate, presenting extremely small crystals with very little orientation as shown in Fig. 2(d).

The misalignment in crystal direction is quantified by the misorientation angles of crystal needles. The misorientation angle (\( \theta \)) is defined as the angle between crystal long
axis and air flow direction (as shown in inset of Fig. 3). The average $\theta$ and standard deviation of $\theta$ at different air flow speeds is plotted in Fig. 3. Without air flow, average misorientation angle is $41.4^\circ \pm 27.1^\circ$ (based on six measurements) showing significant misalignment between crystals in the TIPS pentacene thin film. When air flow was applied at speeds of 1 L/min, 2 L/min, and 3 L/min, average values of the angle $\theta$ drop to $17.1^\circ \pm 13.2^\circ$, $9.7^\circ \pm 6.9^\circ$, and $7.0^\circ \pm 4.8^\circ$, respectively. It is noted that at air flow speeds of both 2 L/min and 3 L/min, average misorientation angles are below $10^\circ$, which indicates a 4–6 times reduction in the values of $\theta$ as compared to the original drop-cast film. As air flow rate reaches 4 L/min, the long needle-shaped crystals become round-shaped domains as shown in Fig. 2(d). This is the reason why there are no misorientation angles reported at this flow rate.

As observed in Fig. 2, air flow not only effectively navigates the TIPS pentacene crystal growth, but also affects areal coverage as well as individual crystal domain width. Grain width, $W_G$, is defined as domain dimension along the short axis $[1 2 0]$ of the crystal needles. The TIPS pentacene grain width and coverage as a function of air flow speed were quantitatively analyzed and shown in Fig. 4(a) and 4(b), respectively. Without air-flow navigation, the TIPS pentacene film demonstrates largely anisotropic crystal morphology with an average width $W_G$ of $91 \pm 20 \mu m$. (The average grain width at a specific flow speed is calculated based on ten crystal measurements.) As the air flow speed increases, the grain width decreases due to the fact that air flow facilitates toluene evaporation thereby decreasing the crystallization time. As shown in Fig. 4(a), at the flow speed of 2.0 L/min, the average grain width is $17 \pm 4 \mu m$. At the maximum flow speed of 4.0 L/min, the average grain width, which refers to diameter of round-shaped crystals in this case, further reduced to $5 \pm 3 \mu m$. This demonstrates that the improvement of crystal orientation with AFN is at the expense of the reduced TIPS pentacene crystal grain sizes. Fig. 4(b) shows variations of film coverage with the air flow speed. Here the film coverage is defined by area ratio of the covered film to the whole area from the optical micrographs. Good film coverage (>90%) was obtained at the air flow speed ranging from 1.5 L/min to 2.5 L/min. When the flow rate is too small (<1.5 L/min), the air flow is not strong enough to be effective in aligning the crystals, and large gaps between crystals exist. On the other hand, at a high flow speed (>2.5 L/min), the air flow leads to rapid evaporation of the toluene, resulting in small crystal sizes and poor film coverage (<60%). At the optimal air flow speed of 2.0 L/min, the thin-film morphology exhibits uniform and long needle-shaped crystals with least gaps in between, reaching the highest film coverage.

To further study the effect of air flow rate, X-ray diffraction experiment was carried out on air-flow navigated TIPS pentacene films. As shown in Fig. 5(a), the XRD results consistently exhibit strong (00l) type reflections, which match results reported previously for TIPS pentacene films [9]. (Note that XRD spectra are vertically shifted in order to clearly demonstrate the differences in intensity.) For a better comparison, the intensity values of (00l) type reflections were extracted from Fig. 5(a) and plotted as a function of air flow speed in Fig. 5(b). For the cases with air flow speed of 0–1 L/min, the intensities of the reflection peaks are low, which can be reasonably explained by the

![Fig. 6. (a) Schematic drawing of the bottom-gate, top-contact OTFT structure, (b) a typical transfer characteristic of OTFTs with AFN at an optimal air flow speed of 2 L/min.](image)
poor film coverage. When the flow speed increases to 2 L/min, the highest intensities of (00l) type reflections are achieved, corresponding to the highest film coverage in these films. As the air flow speed further increases beyond 3 L/min, the peak intensities are significantly reduced, accompanied with their reduced film coverage and crystal shape transition from needles to circular domains.

After optimization of TIPS pentacene thin film morphology with air-flow navigation, OTFTs were fabricated using TIPS pentacene films obtained at flow speed of 2 L/min. A bottom-gate, top-contact OTFT configuration was used and shown schematically in Fig. 6(a). Since TIPS pentacene crystals are well oriented with optimal air-flow navigation, source/drain contacts are placed along the crystal growth

Fig. 7. (a) Comparison of OTFT performance between devices without and with air flow at a flow speed of 2 L/min. (b) The average OTFT hole mobility with air flow demonstrates nearly fourfold enhancement as compared to the one without air flow. (c) The ratio of average mobility to standard deviation of field-effect mobilities ($\mu_{\text{Ave}}/\mu_{\text{Stdev}}$) for devices without and with air flow at a flow speed of 2 L/min.
direction to yield the best charge transport in the OTFT channel. Fig. 6(b) shows a typical transfer characteristic of OTFTs at an air flow speed of 2 L/min. The field-effect mobility in the saturation region and threshold voltage ($V_T$), determined from the fitted line in the square root plot of transfer characteristic, are 0.12 cm$^2$/V·s and 4 V, respectively. The current on/off ratio obtained from the logarithmic plot is above $5 \times 10^5$. Note that hole mobility was extracted based on overall channel width rather than an individual needle crystal and there was no surface treatment of the oxide substrates before TIPS pentacene growth.

Finally, we studied the performance consistency of TIPS pentacene based OTFTs in term of mobility variations. Fig. 7(a) shows that OTFTs with AFN exhibit much less variation in the hole mobility than those without AFN. Field-effect mobilities of OTFTs without AFN vary by three orders of magnitude (ranging from $8.4 \times 10^{-2}$ to $9.8 \times 10^{-5}$ cm$^2$/Vs), while those with AFN at the optimum flow rate of 2 L/min stay consistently between $1.2 \times 10^{-1}$ and $9.5 \times 10^{-2}$ cm$^2$/Vs, indicating a much enhanced consistency of OTFT performance. The improved OTFT performance consistency is considered to result from both improved crystal orientation and enhanced thin film coverage. In addition, the average mobility and standard deviation are plotted in Fig. 7(b). Without AFN the average mobilities are 0.03 ± 0.03 cm$^2$/V·s (the standard deviation was calculated from six different devices.) The average mobilities are 0.11 ± 0.01 cm$^2$/Vs at the optimal air flow rate of 2 L/min, which is nearly a fourfold enhancement in average hole mobilities. Fig. 7(c) shows the ratio of average mobility ($\mu_{\text{Ave}}$) to the standard deviation of the field-effect mobilities ($\sigma_{\mu}$), which serves as an indicator of OTFT performance consistency. OTFTs without AFN show $\mu_{\text{Ave}}/\sigma_{\mu}$ of 0.9 while those with an optimized AFN show $\mu_{\text{Ave}}/\sigma_{\mu}$ of 10, which exhibits an eleven-fold increase in performance consistency.

4. Conclusion

In summary, air flow is able to effectively guide TIPS pentacene growth and simultaneously enhance overall areal coverage on a substrate, which was clearly demonstrated by optical microscopy and X-ray diffraction results. With air-flow navigation, the factors that normally lead to “coffee rings” are minimized. We demonstrated that the air-flow navigated TIPS pentacene film morphology strongly correlates with the air flow speed applied. A balance of crystal orientation, crystallinity, and film connectivity is achieved at an optimal flow speed of 2.0 L/min. OTFTs based on TIPS pentacene with a proper air-flow navigation show four times increase in average mobility and an eleven-fold enhancement of performance consistency.

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