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## Self-assembly of semiconductor/insulator interfaces in one-step spin-coating: a versatile approach for organic field-effect transistors

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Self-assembly of interfaces is of great interest in physical and chemical domains. One of the most challenging targets is to obtain an optimal interface structure showing good electronic properties by solution-processing. Interfaces of semiconductor/semiconductor, semiconductor/insulator and insulator/ insulator have been successfully manipulated to obtain high-performance devices. In this review we discuss a special class of interface, semiconductor/insulator interface, formed by vertical phase separation during spin-coating and focus on the versatile applications in organic field-effect transistors (OFETs). The formation of such an interface can be finished within tens of seconds and its mechanism is related to the materials, surfaces and dynamics. Fascinatingly, such self-assembly could be used to simplify the fabrication procedure, improve film spreading, change interfacial properties, modify semiconductor morphology, and encapsulate thin films. These merits lead to OFETs with high performance and good reliability. Also, the method is very suitable for combining with other solution-processed techniques such as patterning and post-annealing, which leads to facile paper electronics, *in situ* purification and single crystal formation. Research on this topic not only provides an in-depth understanding of self-assembly in solution processing, but also opens new paths towards flexible organic electronics.

## 1 Introduction

#### 1.1 Organic semiconductors and spin-coating

Commercial organic light-emitting diodes (OLEDs) have impressed consumers due to their slim size, light weight, flexibility and low-power consumption, and have the potential to be incorporated in the video displays of most electronic devices. Potentially, OLEDs are also very likely to be inexpensive in the future because they use low-cost organic semiconductors (OSCs) as active layers. The low cost of OSCs stems from the low thermal budget in film deposition for device fabrications.<sup>1,2</sup> Due to weak van der Waals forces that hold molecules, no strong covalent bonds need to be broken and so only a small energetic input is needed for the manipulation of OSCs.<sup>2</sup> Most OSCs evaporate below 300 °C and many can be processed at room temperature with solution-processing, in contrast to the

high temperatures required to fabricate, oxidize and dope inorganic Si wafers (~1000 °C).<sup>3,4</sup> This advantage dramatically reduces the cost of industrial electronics, where the cost of the end product is determined by fabrication and packaging rather than by the intrinsic cost of raw materials.<sup>5</sup> The high cost of producing radio-frequency identification (RFID) tags out of silicon limits their use to high-end products, but RFID tags made of OSCs might be produced cheap enough for commodities at the consumer package level.<sup>6,7</sup> Semiconducting behavior with only weak molecular forces holding molecules together is also the basis for another merit of OSCs: flexibility. Soft OSCs can be placed on cheap, flexible substrates such as plastic films, metal foils, or common paper to build complicated circuits.8-10 For instance, with OSC active-matrix backplane, a 3.5  $\times$  3.5 cm display can be bent to a radius of curvature of 1 cm for 50 times without image degradation.<sup>11</sup> A recent work further demonstrated that transistors with OSCs operate reliably while being folded into a bending radius as small as 100 μm.<sup>9</sup> Thus OSCs are accelerating the development of "flexible electronics".<sup>12</sup>

Organic semiconductors are also much better than their inorganic counterparts with respect to tailoring structure and function. Adding a functional group during organic synthesis

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can finely tune band gaps, charge density, thermal properties, solubility, or assembling properties.<sup>13-15</sup> During film deposition, blending different materials can improve mechanical, optical or electronic properties in devices.<sup>16,17</sup> Moreover, an active polymer film can be electrochemically switched to work in different devices in parallel, including transistors, batteries, and displays.<sup>7</sup> Although there are also efforts to tailor properties of inorganic semiconductors by adjusting elements, OSCs are apparently easier to be manipulated as long as their inorganic equivalents rely on crystalline substrates or high temperature processing.

To realize low-cost deposition of thin-film OSCs for devices, numerous processing methods have been developed, *e.g.* spin-coating, inkjet-printing, zone-casting, *etc.* Many unconventional, chemical approaches related to general thin film fabrication have also been invented very recently.<sup>18–21</sup> Among these,

spin-coating is still the most commonly used and one of the very few that has been implemented in a manufacturing environment for organic electronics.5 Compared to solution methods derived from drop-casting, such as inkjet printing, zone-casting and shearing,<sup>22-24</sup> spin-coating alone can provide uniform films over a large area. In inkjet printing, internal Marangoni micro-flow produces concentration gradients and different drying speeds in spatially distinct areas in a single drying ink droplet.<sup>25,26</sup> Consequently, when droplet sizes are large (e.g. in centimeters), the resulting films tend to be non-uniform (a famous outcome is the "coffee-ring" effect) unless the deposition surfaces have been modified or substrate temperature is controlled.<sup>27</sup> However, spin-coating can produce wafer-scale, uniform films rapidly (in minutes), and does not require a complicated set-up.<sup>28</sup> Moreover, the spin-coating process is compatible with traditional pre- or post-patterning processes.<sup>29</sup>



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Because of these advantages, spin-coating is highly competitive as a simple, facile fabrication method.

#### 1.2 Self-assembled interfaces for organic field-effect transistors

The formation and function of self-assembled interfaces are discussed broadly in physics, chemistry and biology.<sup>30–33</sup> With a large number of new materials emerging rapidly, how to assemble them in nano-scale to create specific functionalities is exceptionally attractive and challenging, and many discoveries have provoked considerable excitement.<sup>34–36</sup> To build special interfaces that exhibit good electronic properties requires advances in both interface science and electronic technology.<sup>16,37–39</sup>

Regarding self-assembly in OSCs, building a molecular interface via solution-processing proves an easy way to manipulate the microstructure to obtain high-performance devices.<sup>5,22,24,40-42</sup> Solution-processed organic electronics, including OLEDs, organic photo-voltaic (OPV) and organic field-effect transistors (OFETs), have been advanced largely by studying the semiconductor/semiconductor, semiconductor/ insulator or insulator/insulator interface.<sup>17,43-46</sup> OFETs are cherished as a powerful tool to investigate the electronic process at an interface,47-54 and valued for being low-cost, flexible and robust in commercial electronics.55-57 Yet compared to general applications in OLEDs and solar cells, in OFETs, blends of materials are much less used and control of their interface is much less studied. The scope has been hampered by the fact that in OFETs, charge transport is blocked by an energy barrier between different materials and tends to occur within a single material.58 For high carrier mobility OFETs, if a two- or multi-component blend does not show phase separation on a large scale, a low percolation threshold for carrier transport is preferred;<sup>59</sup> or if a blend exhibits a large scale phase separation, a well-defined horizontal interface is required.<sup>60</sup> The formation of such interfaces usually requires special combination of materials and delicate control during processing.

In this review we focus on the application of a special class of interface: the semiconductor/insulator interface formed by vertical phase separation during spin-coating. This interface is formed by spin-coating a two-component blend of semiconducting and insulating polymers onto a substrate; during spin-coating the components phase separate vertically, or outof-plane with respect to the substrate, into two distinct layered films on the substrate.<sup>60</sup> The resulting structure appears similar to the structure achieved with multiple single component depositions from orthogonal solvents (Scheme 1). In the following discussions, we show that the outstanding advantages of this approach in OFETs extend far beyond just simplifying the fabrication procedure; vertical phase separation can also improve the interfacial properties,<sup>61,62</sup> solve dewetting problems during film deposition,<sup>61,63</sup> modify intermolecular morphology,<sup>64</sup> and enhance device stability.<sup>65</sup> Moreover, when this method was combined with other techniques such as patterning and post-annealing, even more versatile device applications and interesting studies in physical chemistry have been inspired.62,63,66,67



**Scheme 1** A semiconductor/insulator double layer is made by one-step spincoating. Here only one possible structure is shown for simplicity. Under slightly different conditions or with different molecules, the layers could be inverted. In this paper, the components in a multiple layer structure are listed from the top to the bottom, *i.e.* "semiconductor/insulator" denotes a bi-layer structure with the semiconductor on the top and the insulator at the bottom.

# 2 Self-assembly of semiconductor/insulator interface

#### 2.1 Mechanism

Phase separation in bulk mixtures commonly leads to an isotropic, disordered morphology of coexisting phases.<sup>68</sup> In spin-coating blends of organic materials, typically spinodal decomposition or nucleation results in laterally phase-separated regions in the solidified film.<sup>69</sup> Even though a transient vertical stratification may occur in the liquid state during spinning, usually the interface between the stratified layers will be disrupted and finally deforms.<sup>70</sup> In some cases the vertical phase separation will remain after solvent evaporation, but such separation is observed only in a few combinations of materials and on specific substrate surfaces.

Vertical phase separation in a system of solutes, solvent and substrate is driven by interactions. These interactions can be roughly divided into three categories: solute–substrate, solute–solvent and solute–solute interactions.<sup>45,71,72</sup> Although these interactions in addition to liquid–substrate and liquid–air interactions operate simultaneously during spin-coating, it is generally believed that centimeter-length scale phase separation is mainly dominated by one of the first three. Theoretical analysis that describes and proposes explanations of general spinodal decomposition can be found in some early literatures<sup>73,74</sup> and also in recent reviews.<sup>45,75</sup> In this context, we briefly discuss the mechanism for vertical phase separation along with representative experimental examples related to OFETs.

The solute–substrate interaction is a common driving force for vertical phase separation. In this case, one of the two solutes preferentially adheres to the substrate surface during spinning, and thus as the solvent evaporates the solution separates into distinct phases.<sup>76</sup> This is because components have different surface free energies, which controls how well different solutions or molecules will wet a surface and can be characterized by water contact angle measurements.<sup>72</sup> Preferential adsorption on a substrate can be easily observed in spin-coating blends of non-conjugated, insulating polymers.<sup>76–78</sup> As an example, a blend of polystyrene (PS) and polyvinylpyridine (PVP) was spin-coated onto a pre-treated gold surface. Half of the gold surface was pristine and thus polar and hydrophilic, while the other half was covered by a hydrophobic, nonpolar On bare Au surface



On hydrophobic SAM

**Fig. 1** (a) A film of PS–PVP blend spun-cast onto Au surface. The top half is bare Au surface and the bottom half was made hydrophobic by coating with a SAM of octadecylmercaptan before spin-coating. A topography image by AFM shows a different morphology for the top half (uniform top surface) and the bottom half of the sample (lateral phase separation). In (b) and (c), the PS (light grey) and PVP (dark grey) phase distribution in the film is visualized by a superposition of cross-sections at the locations indicated by lines in (a). Reproduced with permission from ref. 78. Copyright (1998) Nature Publishing Group.

self-assembled monolayer (SAM) of octadecylmerctaptan before spin-coating (Fig. 1). As a result of the difference in surface properties, a spin-coated film of PS and PVP featured distinct morphologies in the two regions: a vertical phase separation on bare Au and a lateral separation of phases on the SAM. This happens because more polar PVP sticks to the Au substrate, whereas no preferential adsorption takes place on the nonpolar SAM surface.<sup>78</sup>

Similar phenomena are observed in blends of a semiconductor and an insulator, usually a blend of hydrophobic semiconductor and a significantly less hydrophobic insulator.<sup>60,61,79,80</sup> For example, when semiconductor poly[5,5'-bis(3-dodecyl-2thienyl)-2,2'-bithiophene)] (PQT-12) was blended with insulator poly(methyl methacrylate) (PMMA) and spin-coated on a hydrophobic substrate, *i.e.* octyltrichlorosilane (OTS)-coated SiO<sub>2</sub>, a bi-layer film was formed with a PMMA/PQT structure.<sup>79</sup> The reason is presumed to be that hydrophobic PQT-12 preferentially adsorbs onto the OTS-modified substrate. Convincing evidence for the importance of solute-substrate interaction is observed by spin-coating the same mixture on bare SiO<sub>2</sub> surface: the same blend did not form a bi-layer film with vertical phase-separation, but instead exhibited a lateral phase separation. Such surface-induced vertical segregation has also been observed between PMMA and other hydrophobic semiconductors, including both polymers [e.g. poly(3-hexylthiophene) (P3HT)]<sup>80</sup> and small molecules [e.g. triethylsilylethynyl anthradithiophene (TESADT)<sup>81</sup> and benzothienobenzothiophene derivatives (Cn-BTBT)].<sup>61</sup> Therefore, in order to obtain a vertical phase separation or verify the mechanism of phase separation, one could spin-coat certain solute components onto varied surfaces with different surface free energies,77,78,82,83 or vice versa, spin-coat solute components with various surface free energies onto a certain substrate surface.59,80,84 It is noteworthy that annealing treatment can change the surface free energy, which will modify the phase separation.<sup>72,85</sup> In fact, tuning the vertical phase separation by engineering surface affinity is a widely used strategy to control charge transport in

OFETs, or to manipulate localization and separation of excitons in OLEDs and solar cells.<sup>86–88</sup>

Another important driving force for phase separation is solute-solvent interaction, which is mainly affected by the solubility of solutes and trajectory speed of solvents.45,60,64 The latter is determined by the evaporation rate of solvent and spin speed.<sup>60</sup> We discuss the impact of solubility first. As the solvent evaporates, the content of solvent near the solventair interface is reduced. Consequently, the less soluble solute becomes less concentrated in the top and more concentrated in the bottom where solvent content is rich. Such a concentration gradient drives the de-mixing and can lead to a vertically separated phase.<sup>45,75</sup> Hence, using solvents with different solubility will modify the morphology of phase separation.<sup>77,89,90</sup> While solubility affects the overall film geometry, trajectory speed has a critical impact on the quality of the semiconductor/ insulator interface.60,64 In a study of the bi-layer film with semiconducting poly(9,9-dialkylfluorene-alt-triarylamine) (TFB) and insulating bisbenzocyclobutene derivative (BCB), it was shown that either too high or too low a trajectory speed can lead to a gradated interface between the two components.<sup>60</sup> This is detrimental to OFETs that rely on charge carrier hopping between molecules separated by nanometer-scale distances.91 Quantitative study on BCB/TFB films further revealed that a few nanometer increase of interfacial roughness led to a decrease of carrier mobility by one or two orders of magnitude.<sup>60</sup> Therefore, controlling trajectory speed to obtain a smooth, defect-free and molecularly abrupt interface is extremely important for high performance OFETs. Additionally, the evaporation rate of solvent also significantly influences the crystallization of the semiconductor.64,92 In a study of a TESADT-PMMA bi-layer film (Fig. 2), a moderately low solvent evaporation rate formed the vertical phase separation, and at the same time, led to a uniformly crystallized semiconductor film with larger grain sizes, fewer boundaries and preferable molecular orientation.<sup>64</sup> Tuning the solute-solvent interaction in spinning can avoid chain entanglement across the interface that creates obstacles for charge hopping and thus improve film quality for high performance OFETs.

The solute-solute interaction is often investigated in blends of materials that tend to crystallize.<sup>58,93-95</sup> Both the order in which each component crystallizes, as well as the flow of solution, amorphous, or crystalline states influence the final structure. Therefore, it is possible to obtain large scale vertical segregation by manipulating the rheology of transient states during spinning or by controlling crystallization. For example, spin-coating a blend of crystalline semiconductor 6,13-bis-(triisopropyl-silylethynyl)-pentacene (TIPS-PEN) and polymer dielectric poly(a-methylstyrene) (PaMS) resulted in a triplelayer film: TIPS-PEN/PaMS/TIPS-PEN.65 Found in several separate works, the self-assembly of a tri-layer proves robust and reproducible.<sup>81,85,96,97</sup> This interesting structure can be explained by the following process that occurs during spincoating: firstly TIPS-PEN form crystallites, which are expelled to the top and bottom by the spinning liquid and trap the PaMS below it; and then subsequently the remaining solvent



spin-coated from TESADT–PMMA blend in various solvents (left: low boiling point solvent, right: high boiling point solvent). Reproduced with permission from ref. 64. Copyright (2012) Wiley-VCH Verlag GmbH & Co. KGaA.

evaporates from the PaMS. Even more complicated than such a crystalline-amorphous system, a blend of two crystalline components can exhibit different layer structures depending on which component crystallizes first. Taking the blend of P3HT and polyethylene (PE) for instance, P3HT will form a continuous layer coating the substrate (also on the top) if P3HT crystallizes before PE does; this sandwich structure provides an efficient percolation path for charge transport at the bottom channel.58 When the crystallization order is reversed, *i.e.* if PE crystallizes before P3HT does, then P3HT cannot crystallize efficiently and cannot form a continuous layer, but instead P3HT is distributed uniformly throughout the vertical direction in the film, which leads to poor FET performance. Hence, to achieve appropriate vertical segregation in a crystallite-crystallite system, the sequencing of crystallization should be regulated by controlling thermal conditions or by selecting the appropriate solvent.94

The commonly observed vertical phase separation mentioned above is summarized in Scheme 2. In summary, to achieve vertical phase separation, the two solutes should have a large difference in surface affinity, solubility, or crystallization temperature. However, in order to ensure large-scale, high-quality separation, or instead to understand why it is not achieved, one must take all of the above factors into account.

#### 2.2 Characterization methods

To examine whether large-scale vertical phase separation has been obtained, common surface measurements can provide



**Scheme 2** Schematic representations of several vertical phase separations discussed in this context.

information on the overall structure. Then, a detailed, quantitative compositional profile as a function of depth can be drawn by either invasive or non-invasive measurements.

For preliminary investigations, surface water contact angle measurement can be used to detect the top layer component when the two components have large difference in surface energy, e.g. in the blend film of semiconductor P3HT ( $\sim 103^{\circ}$ ) and dielectric PMMA ( $\sim 73^{\circ}$ ).<sup>80,98</sup> In some cases, a direct observation of the structure can be made by physical or chemical etching. Physically, making a scratch on the samples can sometimes tear off the top layer and expose the underlying layer to air.<sup>66,99</sup> Alternatively, one can use orthogonal solvents to dissolve a part of the top layer without destroying the underlying film.<sup>61,78,100</sup> Then, spectroscopic analysis such as energy dispersive X-ray spectroscopy<sup>79</sup> or UV-vis absorption spectroscopy<sup>61</sup> can be performed on the etched or un-etched regions to detect elements or components. Also, as solvent etching exposes the surface of the under-layer, the roughness and morphology of the interface can be directly observed by atomic force microscopy (AFM).<sup>62,78,100,101</sup> The aforementioned phase separation between PS and PVP (Fig. 1) was revealed exactly by this method, where the PS phase was selectively removed by cyclohexane solvent and the remaining PVP layer was then scanned by AFM to characterize the interface between the two phases. Therefore, a handful selective etching technique enables direct compositional characterization, particularly when the phase separation is large in scale and has an abrupt interface.

Detailed depth profiling is needed when the two components diffuse into each other without having an abrupt interface. A most common and effective approach is to use an ion beam to gradually sputter the target film and simultaneously analyze the component of either the sputtered fragments or the remaining film. The analysis can be done by dynamic secondary ion mass spectrometry (SIMS), where the secondary ions from the sputtered area are collected in a mass spectrometer to be identified and counted, according to their mass-to-charge ratios (m/q).<sup>102</sup>

The technique can provide a three-dimensional depth profile of each component.<sup>65,96,102–104</sup> Alternatively, while the target film is gradually etched, the surface of the remaining film is analyzed by X-ray photoelectron spectroscopy (XPS).<sup>98,105</sup> In the spectra, the characteristic electron binding energy peaks indicate the identity of each element and the relative intensity of peaks allows deduction of an approximate elemental composition.<sup>106</sup> For instance, in the spin-cast film of TESADT–PMMA, the sulfur and silicon peaks were the markers for the semiconductor TESADT and so their relative ratios indicate the distribution of TESADT (Fig. 3a). After the sample was treated by solvent vapor annealing (SVA), their signals decreased in the area where TESADT and PMMA coexist (Fig. 3b).



**Fig. 3** (a, b) Measurement results from Ar sputtering with XPS (TESADT–PMMA blend film): relative ratios of sulfur and silicon atoms as a function of the depth for (a) an as-cast TESADT–PMMA blend film; (b) a 1,2-dichloroethane vapor annealed film (closed circles: Si<sub>2p</sub>, open circles: S<sub>2p</sub>). (c, d) Scheme of film structure deduced from XPS measurements: (c) as-cast, (d) after vapor annealing. Reproduced with permission from ref. 105. Copyright (2009) Wiley-VCH Verlag GmbH & Co. KGaA.

This result indicates that TESADT moved towards the film top after SVA (Fig. 3c and d), directly revealing the structural evolution. Besides, in the case that only the film bottom needs analysis, one can de-laminate the film from the substrate and measure near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to determine the composition ratio.<sup>107–109</sup> The above techniques damage the surface of the target film and thus are referred to as "invasive" methods.

Besides invasive analysis methods, there are non-invasive probing methods that detect scattering, reflection or absorption signals to deduce a compositional depth profile. In Rutherford backscattering spectroscopy (RBS) measurements, the incident ion beams are scattered by atomic nuclei in the target film and the loss in their energy indicate the elements contained in the target film.<sup>58,110</sup> In variable-angle spectroscopic ellipsometry (VASE), the change in polarization of light reflected from the target material is measured, from which the optical constants of the material can be calculated.<sup>81,86,111,112</sup> Armed with the optical constants of each material, the spectroscopic data for the sample can be fitted to different structural models to find the best model based on the quality of the fitting.<sup>111</sup> In addition, neutron reflectivity (NR) measurement is also capable of reconstructing depth profiles of composition with nanometer resolution. It detects the variation in scattering length to determine the composition of the target film.<sup>113</sup> In order to obtain a larger spread of scattering lengths, deuterated materials are often used; this enhances the NR contrast.<sup>81,99</sup> In Fig. 4, a study by VASE and NR on the bi-layer film with 2,8difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TESADT) and PMMA is presented. Apparently, though the investigated film structure is very similar to that presented in Fig. 3, VASE and NR signals are much more complicated compared to those produced by XPS. Instead of directly depicting the compositional profile, the data were fitted according to the proposed model of the film structure (inset in Fig. 4a and b). Note that we intentionally use the similar examples (TESADT-PMMA) adopted from different works (shown in Fig. 2-4) specifically for ease of comparison. In all, compared to the invasive methods, these non-invasive methods can be performed repetitively on one specimen, but most of them rely on an accurate model to deduce compositional distributions.



**Fig. 4** Compositional analysis on film of diF-TESADT–PMMA by (a) VASE and (b) NR. In (a) and (b), the open circles represent the VASE or NR data and the solid lines are the best model fitting. Insets show the derived depth profile for the diF-TESADT volume fraction. Reproduced with permission from ref. 81. Copyright (2013) Wiley-VCH Verlag GmbH & Co. KGaA. (c) Scheme of the film structure.

The above characterizations significantly advance material and interface science by the study on how the combination of materials and spin-coating dynamics affect the final interface structure. These techniques have also been combined with the OFET fabrication and measurements, and reveal how the interface structures influence charge transport properties. To this end, firstly we introduce how these self-assembled interfaces benefit OFETs fabricated by spin-coating alone. Then we discuss the further investigations on OFETs by applying patterning and post-annealing techniques.

## 3 OFET application 1: direct spin-coating

The field-effect transistor (FET) uses the gate electric field to modulate the number of mobile carriers at the semiconductor/ insulator interface and hence the conductivity of a channel.<sup>114</sup> Generally, high carrier mobility ( $\mu$ ), which characterizes a high speed of carriers when pulled by a certain electric field, requires a contaminant-free semiconductor/insulator interface and a good packing order of semiconductor molecules. Therefore, the requirements for making high performance OFETs are manifold, including a uniform semiconductor film free of pin-holes, a clean surface of insulator without contamination, and good protection of active channels from damage. Correspondingly, we will highlight the advantages of the described self-assembled multi-layer in the aspects of solution spreading, interface modification, film encapsulation, *etc.* 

#### 3.1 Better spreading: solve dewetting

In spin-coating, especially when the surface is non-wettable, dewetting may occur, i.e. the thin film of solution ruptures and then separates into droplets during spinning.<sup>115–117</sup> As a result, only separate small domains of functional materials-instead of a uniform film-are left after the solvent evaporates. Such dewetting often takes place when the solute is a small molecule, when the solvent has a high boiling-point and low-viscosity, or when the substrate surface is hydrophobic.<sup>92,118,119</sup> It is noteworthy to mention that a lot of commonly used self-assembling monolayers (SAMs), which eliminate interfacial traps or modify film morphology, are of low surface energy and thus hydrophobic, easy to cause dewetting.<sup>120,121</sup> However, blending a polymer into solutions provides an answer to overcome dewetting, because many common polymers have better adhesion to hydrophobic surfaces and are easily deposited by spin-coating. Solute-substrate interaction dominates this phase separation, and the more adhesive polymer dielectric acts like a "glue layer" between the substrate and semiconductor layer.

An example is shown in the case of spin-coating Cn-BTBT molecules.<sup>61,63</sup> When using a high boiling-point solvent such as chlorobenzene or anisole, the film only spread on areas smaller than a square millimeter. Using low boiling-point solvents such as chloroform improved film spreading but still left large pinholes in large-area films. But when the blend of Cn-BTBT and PMMA was spin-coated, a uniform thin film was obtained without any pinholes (Fig. 5). Because a high boiling-point solvent was enabled in spin-coating the blend, crystallinity of



**Fig. 5** Spin-coating of Cn-BTBT in anisole (top): the spot on the right is a dried droplet; the rest of the film dewetted. A film spin-coated from Cn-BTBT–PMMA blend in anisole (bottom): the entire surface. Reproduced with permission from ref. 63. Copyright (2012) Elsevier B.V.

the Cn-BTBT layer was improved, as characterized by larger crystal sizes. Therefore, using a blend to produce a vertically phase-separated film can simultaneously overcome dewetting and improve the crystallinity of the semiconductor layer.

#### 3.2 Self-assembly: form two layers in one step

Simultaneously multiple distinct organic layers can obviously simplify the device fabrication process. For example, the blend P3HT-PMMA with adequate weight ratio could self-assemble into a well-defined bilayer structure with P3HT-PMMA.<sup>80</sup> As the interface between the two materials is continuous and uniform, it is suitable to act as the charge transport interface without further modification. This feature allowed direct formation of FET devices without depositing additional dielectric layers. Also, as the bottom layer was less than 100 nm thick, the operation voltage was sufficiently low. The performance of a typical device with P3HT-PMMA (weight ratio = 5:95) is shown in Fig. 6. For a narrow window of operation (gate voltage 1.0 to -2.0 V), the on-off ratio was about 10<sup>3</sup> and the gate leakage current remained 10 times smaller (Fig. 6b). The extracted saturation field-effect mobility  $\mu_{\text{FET}}$  was 3  $\times$  10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This work together with other demonstrations well-illustrates the easy-process of one-step formation of a semiconductor/insulator bilayer film and the promising potential in fabricating low-voltage, high-performance OFETs.<sup>46,47</sup> It is notable that to form a smooth, defect-free dielectric interface for charge transport, several practical factors of the deposition process need to be considered: compositional ratio, solvents, spin-coating speed and vapor pressure during spin-coating, as discussed in section 2.

#### 3.3 Self-modification: enhance carrier mobility

In self-assembly, the polymer dielectric replaces the bare substrate surface and can act as an interfacial modifying layer



Fig. 6 Performance of low-voltage-driven FETs based on P3HT–PMMA blends. (a) Output characteristics of P3HT–PMMA (5:95) FET on a bare silicon substrate (PMMA layer thickness is about 60 nm). (b) Transfer characteristics and gate leakage current. Inset: device configuration. Self-separation simplifies the fabrication process for OFETs. Reproduced with permission from ref. 80. Copyright (2008) Wiley-VCH Verlag GmbH & Co. KGaA.

which benefits the charge transport. First, by modifying the chemical structure of the insulating interface, some pre-existing contaminants that contain mobile ions and chemical impurities that are detrimental for carrier transport, can be eliminated by the polymer insulator.<sup>122</sup> Second, crystallization of the semiconductor during spin-coating is also improved, because the solution drying rate is reduced and the underlying surface is modified.<sup>92,123</sup> These features can lead to enhancement of carrier mobility in FET and provides an alternative of depositing SAMs before coating films.<sup>98</sup>

The advantages of surface modification are manifest in the OFETs spin-coated from a blend of semiconductor 2,7-didodecyl[1]benzothieno[3,2-b][1]benzothiophene (C12-BTBT) and PMMA.<sup>61</sup> After the spin-coating, a bi-layer structure with C12-BTBT-PMMA was obtained. In bottom-gate, top-contact FETs, although the PMMA layer decreased the total capacitance, the device with self-organized C12-BTBT-PMMA film exhibited a current level over 5 times higher than that of the single layer film of C12-BTBT (Fig. 7). The average mobility of the bi-layer device was  $\mu_{\text{FET}} = 0.63 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , compared to  $\mu_{\rm FET}$  = 0.11 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for the single layer devices. The significant enhancement is attributed to better crystal formation and also modification of the dielectric interface.<sup>124</sup> The latter is supported by the analysis of hysteresis in the transfer curve. The bi-layer film exhibited a much reduced hysteresis window (difference of  $V_{\rm th}$  between the forward and backward scan),  $\Delta V_{\text{th}} = -2.9$  V, compared to  $\Delta V_{\text{th}} = -17.4$  V in the single layer film. Correspondingly, the density of the effective trapped charges was reduced by 88% in the bilayer film when compared to the single layer film on bare SiO<sub>2</sub>.<sup>91</sup> As the charge traps generally come from impurities or water contamination, this result indicates that using a less polar dielectric and forming the interface by one-step spin-coating instead of two successive steps is much less susceptible to charge trapping.125

An increase in FET mobility was also found when spincoating the blend diF-TESADT and  $P\alpha MS.^{81}$  The blend forms a tri-layer structure, TESADT/ $P\alpha MS$ /TESADT, probably due to solute-solute interaction as discussed above. The bi-layer film



**Fig. 7** (a) Device configuration. (b) Transfer characteristics of FETs made with C12-BTBT and PMMA (dots) and C12-BTBT only film (squares). The transistor on the underlying layer is shown for reference (triangles), indicating good insulating properties. (c) Square root of drain current of C12-BTBT and PMMA (dots) and C12-BTBT-only film (squares). Self-modification of the interface and crystallinity enhances mobility. Reproduced with permission from ref. 61. Copyright (2012) Elsevier.

exhibited a channel length independent mobility of  $9.4 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , nearly three orders of magnitude higher than that of single layer devices ( $1.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). Shin *et al.* suggest that a larger proportion of desirable crystal directions are formed in the blend films compared to neat diF-TESADT film, which could be the source of the enhanced performance.

#### 3.4 Self-sealing: improve device stability

In addition to the structure of semiconductor/insulator, it is also possible to form a reverse structure, insulator/ semiconductor, by tuning surface energy to drive phase separation. In this case, the electronically inert insulator layer separates organic semiconductors from ambient air, which will serve as a barrier to water and oxygen and alleviate the problem of oxidation under illumination. Taking advantage of this feature, several studies report improvement of stability under air exposure, thermal annealing or illumination.<sup>58,65,79,97,104</sup>

Improved environmental stability is firstly shown in the work by Arias et al.79 Spin-coating a blend of PQT-12 and PMMA resulted in a PMMA-PQT-12 bilayer film on the OTS surface, due to the selective adsorption of PQT-12 on the OTS surface as mentioned before. The self-encapsulated OFET exhibited a small shift ( $\sim 7$  V) in the onset voltage after 20 days exposure to air, which was 50% less than the shift observed in one day for the OFET with single layer PQT-12. The insulating PMMA layer sufficiently protected the accumulating layer from fast degradation. Also, a very similar bi-layer film exhibited better stability under bias-stress, according to the letter written by Lee et al.<sup>104</sup> The semiconductor poly(didodecylquaterthiophene-alt-didodecylbithiazole) (POTBTz-C12)<sup>126</sup> and PMMA form a PMMA-PQTBTz-C12 bi-layer on octadecyltrimethoxysilane (ODTS)-treated silicon oxide substrates. When the devices are stressed by  $V_g = 20 \text{ V}$  (OFF-bias) at  $V_d = -10 \text{ V}$  in ambient air, shift of  $V_{\text{th}}$  was much smaller (~5 V) in the device with a bi-layer film compared to that of the device with a single PQTBTz-C12 film ( $\sim$  15 V) (Fig. 8a). Presumably, the reduced V<sub>th</sub> shift is because the strong negative dipoles of the carboxyl groups of PMMA suppress the hole accumulation that is induced by the OFF-bias stress. Hence, the bilayer device exhibited an enhanced electrical stability under OFF-bias stress.

In addition, thermal stability can also be improved by having phase separation. In the report by Ohe *et al.*,<sup>65</sup> OFETs with single layer TIPS-PEN and multilayer TIPS-PEN/P $\alpha$ MS/TIPS-PEN were measured after heating on a hot plate under nitrogen atmosphere (Fig. 8b). The performance of pure TIPS-PEN OFETs started to degrade significantly when heated over 120 °C and the mobility decreased from 10<sup>-1</sup> to 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> after heating at 180 °C.<sup>121,122</sup> However, loss of performance was much attenuated in tri-layer OFETs, in which the mobility

remained at 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> even after heating at 180 °C. Despite that the mechanism remains to be understood, clearly the inclusion of insulating polymers P $\alpha$ MS and phase separation had improved thermal stability.

#### 3.5 Improve uniformity: reduce variation

In addition to the properties of individual devices (e.g. mobility, on/off ratio and stability), statistical uniformity in performance also needs to be critically considered for future commercial applications. This includes not only variation among devices on the same substrate, but also variation from batch to batch.<sup>63</sup> Yet, solution processed OFET arrays often show large variations of performance in labs, especially with crystalline small molecules.<sup>63,127,128</sup> Unless solved, the problem of non-uniformity will no doubt limit practical applications in active matrix backplanes for electronic paper or other display media.<sup>11,129,130</sup> The low uniformity in carrier transport and carrier injection mainly comes from variations in crystal morphology (sizes, orientations and qualities) and film thickness.131,132 Recent works have demonstrated that these variations can be reduced by introducing an insulator polymer into the crystallization process of small molecules to form vertical phase separation.<sup>63,65</sup>

A demonstration was shown also in a study of OFETs prepared from vertically phase separated TIPS-PEN and P $\alpha$ MS (Fig. 8c).<sup>65</sup> Pure TIPS-PEN FETs exhibited a large variation  $\sigma_{\rm on}/\langle I_{\rm on} \rangle$  of 52%, where  $\langle I_{\rm on} \rangle$  is the average on-current and  $\sigma_{\rm on}$  is the standard deviation. When adding P $\alpha$ MS into the solution for spin-coating, self-organized films (TIPS-PEN/P $\alpha$ MS/TIPS-PEN) exhibited a lower device variation  $\sigma_{\rm on}/\langle I_{\rm on} \rangle$ , remarkably improved to only 11%. Ohe *et al.* explain that the additional polymer insulator in solution improves the rheology in spin-coating (viscosity and surface tension), giving a physically uniform film. Also, the additional P $\alpha$ MS reduces the drying rate



**Fig. 8** Left panel: PMMA–PQTBTz-C12 based OFET. Threshold voltage shift ( $\Delta V_{th}$ ) with negative gate bias stress (ON-bias) and positive gate bias stress (OFF-bias) of the PQTBTz-C12 based OFET and the PMMA–PQTBTz-C12 blend based OFET after 10 000 s. Reproduced with permission from ref. 104. Copyright (2012) American Institute of Physics. Right panel: OFET made from a blend of TIPS-PEN and P $\alpha$ MS. (b) Dependence of the saturation mobility on heating temperature for 10 min under nitrogen atmosphere. (c) Histogram of  $I_{on}$  of 82 FETs with a TIPS-PEN/P $\alpha$ MS/TIPS-PEN multilayer (filled sticks) and of 82 pure TIPS-PEN FETs (open sticks). It indicates that self-sealing sufficiently improves device stability. Reproduced with permission from ref. 65. Copyright (2008) American Institute of Physics.

of the solution, which consequently leads to larger crystal grains and higher mobility.

### 4 OFET application 2: patterning

In order to meet industrial standards, patterning the spincoated semiconductors in well-defined geometric features is desirable.133-135 Electrical isolation of devices can greatly minimize parasitic current paths. One of the most common patterning technologies for solution-processed organic semiconductors is to selectively deposit hydrophobic SAM for patterning surface wettability, prior to depositing semiconductor solutions.<sup>127,134,136,137</sup> To eliminate the time required for SAM growth (e.g. several hours), a hydrophobic polymer CYTOP (water contact angle  $\sim 110^{\circ}$ ) is spin-coated and subsequently exposed to O2-plasma through shadow mask.<sup>138</sup> The unexposed area remains hydrophobic, whereas the exposed area becomes hydrophilic and wettable for solution. Thus after spin-coating, materials are selectively deposited in the patterned regions. Combining this technique and the vertical phase separation as discussed above has generated several interesting results.

A direct combination is illustrated in Fig. 9a.<sup>63</sup> After spincoating the CYTOP layer and patterning it, a C8-BTBT and PMMA mixture was spin-coated and formed isolated domains. Consequently large plate-like C8-BTBT crystals were formed only in the patterned domain (Fig. 9b), thanks to improved wetting conditions and the prolonged evaporation time in the confined region. Compared to as-spun films, these crystals led to improved OFET uniformity. The average  $\mu_{\rm FET}$  is 0.08 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with a small deviation of 0.03 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and  $V_{\rm th}$  and the sub-threshold slope (*S*) are  $-1.17 \pm 1.00$  V and  $-0.30 \pm 0.06$  V dec<sup>-1</sup>, respectively (Fig. 9c). Such good uniformity in performance among devices is critical for driving displays as mentioned in Section 3.5.

The combination also shows a large benefit in reducing interfacial roughness, because the spin-coating process naturally generates a smooth interface between C8-BTBT and PMMA.<sup>62</sup> Such surface modification enables application in paper electronics, in which the high roughness of paper would otherwise be reflected at the semiconductor/dielectric interface and limit carrier mobility.<sup>139</sup> As shown in Fig. 9e, the bare paper substrate has large root-mean-square (rms) roughness of  $\sim$ 48 nm. A piece of paper coated by parylene as a protective layer to resist water and chemicals still has a surface roughness as large as  $\sim\!16$  nm. But when a CYTOP layer was spin-coated and patterned with selective plasma etching, followed by spin-coating a C8-BTBT-PMMA blend solution for vertical phase separation, the successive spin-coating steps efficiently screened the original roughness and provided a smooth semiconductor/insulator interface (rms  $\sim 3$  nm). The resulting devices yielded high



**Fig. 9** (a) Fabrication process of combining the CYTOP patterning and phase-separation. (b) Optical image of the resulting plate-like crystals formed in the patterned areas. (c) Transfer curves of the transistor arrays based on the C8-BTBT crystals. Reproduced with permission from ref. 63. Copyright (2012) Elsevier B.V. (d) Devices on a piece of paper made from the same process. (e) Device structure and root-mean-square (rms) roughness of the different surfaces from the bare paper substrate to the PMMA layer. Reproduced with permission from ref. 62. Copyright (2012) Elsevier B.V.

electrical performance, exhibiting high  $\mu_{\rm FET}$  (1.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and a large on/off ratio (>10<sup>8</sup>). The performance is among the highest in terms of both carrier mobility and on/off ratio for OFETs on paper substrates thus far, suggesting it to be a simple spin-coating process with great potential for paper electronics.

Another advanced application is the *in situ* purification that can eliminate the impurity influence in OFETs. For organic electronics, impurities frequently appear as by-products of the material synthesis and can induce traps that capture charge carriers and subsequently affect the charge transport.140,141 Removal of impurities from the active materials is thus essential to achieve high performance of organic-based devices, yet the extra processing raises the time consumption and final production cost. Therefore, a solution fabrication technique using low-purity OSCs to fabricate a well-performing device can simplify the process and lower the cost.<sup>142</sup> Surprisingly, such a purification process can occur inherently in the phase separation process described above. When low-purity C8-BTBT was mixed with PMMA and spin-coated on patterned regions, impurities were excluded on top of the active organic crystals, and were visible by optical microscopy as needle-like crystals (Fig. 10). The resulting transistor performances were nearly identical to those references with high-purity C8-BTBT ( $\mu_{\text{FET}}$  =  $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) (Fig. 10c and d). The *in situ* purification can be



**Fig. 10** Cross-polarized microscopy images of typical C8-BTBT crystals in patterned regions from high- (a) and low-purity (b) C8-BTBT solutions blended with PMMA. Transfer curves of the FET arrays based on patterned C8-BTBT crystals from high- (c) and low-purity (d) materials. (e) Left: cross-polarized microscopy image of the small needle-like crystal; right: illustration of the *"in situ* purification" during spin-coating with impurity (red ellipsoids) and C8-BTBT (blue ellipsoids) molecules. Reproduced with permission from ref. 142. Copyright (2013) Royal Society of Chemistry.

explained based on the discussion in Section 2: selective adsorption of PMMA onto the substrate drives a vertical phase separation to form a C8-BTBT–PMMA bi-layer (the solute– substrate interaction); at the same time, spontaneous crystallization of impurity and C8-BTBT expels the impurity molecules to the top of the layer (*i.e.* the solute–solute interaction). As a result, the impurity crystals are separated from active channels between C8-BTBT and PMMA. This finding can stimulate a new strategy of organic electronics to seek the lowest purity and lowest cost material that still provides adequate performance.

#### 5 OFET application 3: recrystallization

Performance of OFETs is closely correlated with the morphology of the semiconducting layers.<sup>123</sup> In particular, high-quality organic single crystals can exhibit large mobility values ( $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), overwhelming the amorphous silicon devices.<sup>128,143</sup> It is interesting that in the self-assembled bi-layer described above, the polycrystalline semiconductor film on the top can recrystallize into the single crystalline state with simple post-treatment with solvent vapor annealing (SVA).<sup>66,67,144,145</sup> This newly discovered re-crystallization highly relies on the conditions of the semiconductor/dielectric interface.

When a C8-BTBT-PMMA bilayer was annealed by chloroform vapor at room temperature overnight,<sup>146–148</sup> the top C8-BTBT layer re-crystallized into rod-like single crystals. These crystals were several hundreds of microns long and exhibited strong birefringence in the cross-polarized microscope (Fig. 11).<sup>66</sup> Time-lapsed optical images indicate that the polycrystalline film was broken and crystals continued to grow on top of the PMMA surface. Such re-crystallization was found to be much more complete on a polymer base film PMMA than on an inorganic substrate such as SiO<sub>2</sub>. In order to probe the mechanism of re-crystallization, a series of polymers and organic solvent vapors were investigated (Fig. 12a). In previous reports on treatment with solvent vapor, the re-organization of the functional materials is critically dependent on the vapor pressure and the similarity between solvent and base film in terms of polarity. However, these factors were not found to be closely linked to the formation of C8-BTBT crystals (e.g. low polarity HMDS or CYTOP surface cannot generate large crystals). Instead, the solubility of base polymer films in solvents highly affected the re-crystallization, *i.e.* single crystals appeared when base polymer layers were soluble in the solvent vapor, while they did not appear in all the opposite cases (Fig. 12a). The results clarify that recrystallization is determined by the miscibility between the solvent and polymer under-layer. Further evidence has been given by a real-time video of the sample surfaces: the poly-crystalline C8-BTBT film dissolved and broke within 1 min, whereby the C8-BTBT film on an insoluble substrate remained unchanged after solvent exposure. The observations unambiguously indicate that the soluble PMMA dramatically enhances the total uptake of chloroform,<sup>149</sup> compared to the case without PMMA (Fig. 12b). Consequently, the absorbed solvent significantly increases the molecular mobility and thus the diffusion rate, which allows the strongly polar



Fig. 11 Process of re-crystallization on semiconductor/insulator interface. Time-lapsed photos of crystal growth are also shown. The dashed squares indicate how two crystals grow and merge with each other. Reproduced with permission from ref. 29. Copyright (2011) Wiley-VCH Verlag GmbH & Co. KGaA.



**Fig. 12** (a) Optical images of vacuum-sublimed C8-BTBT films after vapor treatment for 15 h on different interfaces, taken by a polarized microscope. Crystals were found only when the solvent vapors and the polymer base film were miscible. Reproduced with permission from ref. 67. Copyright (2012) Royal Society of Chemistry. (b) Scheme showing the small molecule semiconductors, solvent vapor, and polymer base film in saturated solvent vapor: non-miscible solvent and polymer (left) and miscible solvent and polymer (right).

C8-BTBT to lower the overall free energy *via* re-crystallization after nuclei formation. Taking advantage of this mechanism, single crystals of several other semiconductors were also obtained.<sup>67</sup>

Compared to the methods to use vapour-transport or droplet drying to obtain a single crystal of OSCs, this new process avoids the need for vacuum and can generate thin crystals directly on polymer dielectrics. Hence, the self-assembled interface provides a new platform to enhance the crystallization degree of the OSCs.

Measurement of bottom-gate, top-contact transistors fabricated from the C8-BTBT crystals produced an average  $\mu_{\text{FET}}$  of  $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the highest  $\mu_{\text{FET}}$  is 9.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Fig. 13), which is among the highest mobilities of OSCs reported to date.<sup>150</sup> To further investigate charge transport properties in these crystals, temperature dependence was measured during heating and cooling cycles in a 200 K wide temperature window. In both directions, the current level and the extracted mobility increased with the lower temperature, while the threshold voltage remained almost constant. Such temperature behavior is in contrast with common solution-processed polycrystalline OFETs, but is similar to the band transport in single crystalline inorganic semiconductors. It implies that disorders in crystals and defects at the self-assembled semiconductor/dielectric interface are sufficiently low that interaction of the delocalized carriers with phonons is very weak.<sup>151</sup> This study highly encourages the method using of vertical phase-separated film and SVA to obtain high-mobility single crystal OFETs.

The crystals just described are unfortunately randomly distributed and oriented, making device fabrication difficult. In order to control the orientation of crystal formation, an approach derived from that described in Section 4 was applied. At first, a CYTOP layer was patterned by photolithography to form an un-wettable region to surround wettable trenches of



**Fig. 13** (a) Schematic of a single crystal OFET. (b) Optical image of the channel region in a device. (c) Transfer characteristics of a typical device operated at a drain voltage of -40 V under vacuum (open squares) and in air (open triangles). (d) Temperature dependence of  $\mu_{\text{FET}}$  and  $V_{\text{th}}$ . Reproduced with permission from ref. 29 and 66. Copyright (2012) Wiley-VCH Verlag GmbH & Co. KGaA.



**Fig. 14** Self-alignment of organic crystal arrays by patterning. (a) Scheme of process: Wettable trenches were formed by patterning a 100 nm-thick CYTOP layer using a standard photolithographic (PL) technique. A solution of C8-BTBT–PMMA in anisole was spin-coated and treated with chloroform vapor. Crystal arrays were then formed with uniform orientation aligned to the trenches. The optical microscope (OM) image is shown on the right. (b) Real-time observation of the crystal growth and alignment process, taken at 1, 2, 5, and 20 min after vapor treatment started. Reproduced with permission from ref. 145. Copyright (2012) Nature Publishing Group.

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bare SiO<sub>2</sub> (tens of microns wide and tens of millimeters long). Then, a semiconductor/insulator blend was spin-coated and annealed with chloroform vapor (Fig. 14a).<sup>145</sup> Afterwards, the C8-BTBT film reorganized into rod-like crystals oriented along the trench directions. The oriented growth was captured by real-time video: crystals initially formed with an arbitrary orientation but gradually aligned along the trench direction with increasing growth (Fig. 14b). The main reason for aligning is that the self-assembly of C8-BTBT molecules is constrained in the narrow trench. For this reason, the crystal formation process is strongly dependent on the trench geometry, *i.e.* length (L) and width (W). Generally, a larger L is better, but for W, an adequate value is needed ( $\sim 20 \ \mu m$ ) to guarantee sufficient space and material in the region. The approach provides a solution-processing technique to align the crystals grown from the semiconductor/dielectric bi-layer film.

## 6 Conclusions

Self-assembly in spin-coating produces a vertical phase separation between semiconductor and dielectric within a short timescale of tens of seconds. Much progress has been made in probing film structure at the nanometer-scale and understanding the dynamic process at the interface, as well as in the bulk phase during phase-separation. The discovery has led to versatile applications in OFETs. Blending with a polymer dielectric not only improves the wetting conditions during film deposition, but also eliminates interfacial traps and changes the functional groups where charges accumulate. All these merits have significantly improved device performance in terms of mobility, stability and uniformity. The method is notably compatible with other techniques related to solution processing such as patterning and post-annealing. These fascinating approaches have achieved facile paper electronics, demonstrated in situ purification and generated high-quality single crystals. The efforts invested in this class of selfassembled interface have provided an extremely rich area of investigation of device fabrication and physics, and also raise a considerable amount of new questions and challenges with regard to self-assembly in solution processes.

The mechanisms and methods as discussed above are not limited to the introduced materials. In the future, exciting progress could be achieved by combining this technique with other novel material systems and processing techniques. Inorganic semiconductors, functional nano-materials, or biological materials with good solubility may also be probable to be used in the spin-coating and self-assembly.<sup>152-155</sup> In particular, for some recently emerging nanomaterials and nanosystems, their molecular systems can be controlled by macroscopic mechanical stimuli such as deformation and translational movements.<sup>156–158</sup> As such stimuli are easily applied to flexible substrates, it will be challenging and interesting to integrate these materials into the self-assembled phaseseparation and fabricate new types of flexible electronic devices. Obliviously there is still much room for theoretical and technical advancement for the precise control of film structure and interface involving the new materials.

## Author Contributions

The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript.

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