TOPICAL REVIEW

Multiscale assembly of solution-processed organic electronics: the critical roles of confinement, fluid flow, and interfaces

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Topical Review

Multiscale assembly of solution-processed organic electronics: the critical roles of confinement, fluid flow, and interfaces

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Abstract

Organic semiconducting small molecules and polymers provide a rich phase space for investigating the fundamentals of molecular and hierarchical assembly. Stemming from weak intermolecular interactions, their assembly sensitively depends on processing conditions, which in turn drastically modulate their electronic properties. Much work has gone into molecular design strategies that maximize intermolecular interactions and encourage close packing. Less understood, however, is the non-equilibrium assembly that occurs during the fabrication process (especially solution coating and printing) which is critical to determining thin film morphology across length scales. This encompasses polymorphism and molecular packing at molecular scale, assembly of π -bonding aggregates at the tens of nanometers scale, and the formation of domains at the micron-millimeter device scale. Here, we discuss three phenomena ubiquitous in solution processing of organic electronic thin films: the confinement effect, fluid flows, and interfacial assembly and the role they play in directing assembly. This review focuses on the mechanistic understanding of how assembly outcomes couple closely to the solution processing environment, supported by salient examples from the recent literature.

Keywords: multiscale assembly, organic electronics, solution printing

(Some figures may appear in colour only in the online journal)

1. Introduction

Hierarchical materials manifest multiscale structural and chemical organization arising from interactions between nested building blocks at different length scales. Over the past few decades, advances in our understanding of molecular selfassembly and supramolecular chemistry have ushered in the synthetic paradigm of 'materials-by-design', whereby researchers aim to develop application-specific chemistries by tuning molecular structures atom-by-atom. Much ongoing investigation has centered on the non-equilibrium assembly of these fundamental building blocks, wherein the processing conditions intimately couple with the assembly process and sensitively modulate the solid-state properties in the fabricated devices. In this goal, nature provides both inspiration and aspiration: biological systems represent a level of complexity and mastery over the assembly process which is challenging to achieve in the lab. Take, for instance, the dependence of spider silk strength on the nanoscale confinement of its constituent crystallites [1–3], the aggregation of platelets at wound sites due to hemodynamic shear gradients [4–6], and the role of dynamically reconfigurable interfacial templates during biomineralization [7–9]. These elegant examples highlight the critical roles of confinement, fluid flow, and interfaces in directing the assembly process to create highly precise structures. We will discuss the mechanism and recent advances of each topic in the context of organic electronics.

Organic semiconducting small molecules and polymers provide a rich phase space for investigating the fundamentals of molecular and hierarchical assembly. Unlike inorganic



Figure 1. Multiscale assembly of organic semiconductors critically depends on confinement in the meniscus (black), fluid flows (red), and interfacial phenomena (green). Here, a schematic of the printing process at the transition from a liquid meniscus to solid film is shown. The inset at right depicts the semicrystalline mesoscale morphology of conjugated polymer films, while the left inset depicts polymer molecular stacking.

semiconductors (OSC), their structure is not determined by strongly directional covalent bonding, but rather by weaker van der Waals and quadrupole interactions, specifically intermolecular overlap of $\pi - \pi$ electron clouds. These interactions are enhanced by the high rigidity of the π -conjugated backbone and much work has gone into molecular design strategies that maximize intermolecular interactions and encourage close packing. Besides molecular structure, the fabrication process (esp. coating and printing) is also critical to determining the thin film morphology across length scales (figure 1). This encompasses polymorphism and molecular packing at molecular scale, assembly of pi-bonding aggregates at the tens of nanometers scale, and formation of domains at the micron-millimeter device scale. All these morphological features depend sensitively on the non-equilibrium assembly process inherent during device manufacturing. In the later parts of section one, we set out to explain why morphology at each level is critical to semiconducting properties and device performance.

1.1. Charge transport in OSCs and the impact of thin film morphology

Charge transport in OSCs is significantly less understood than conventional, band-like, transport in inorganic systems, and hence is a topic of intense study. Numerous excellent reviews have been produced that detail the current understanding of charge transport in organic systems [10–13] and the relationship between morphology and charge transport [14–18]. In this section, we summarize the prevailing theories in brief

with the goal of establishing the fundamental relationship between morphology and charge transport.

OSCs exhibit pronounced electron-phonon interactions, described using the concept of a quasiparticle 'polaron' [10], as compared to the electronic interactions which dominate for covalently bonded inorganic semiconductors. This phenomenon arises from both the weak van der Waals interactions between organic molecules and their conformational flexibility. Due to strong electron-phonon coupling, molecular vibrations and lattice phonons influence electronic site energy and overlap of molecular orbitals. As a result, the charge transport mechanism sensitively depends on temperature and, for perfectly ordered lattices, lattice phonons. At low temperature, molecular vibrations are weak and charges are delocalized and can transport in a band-like fashion through the organic crystal [19, 20]. As temperature increases, strong molecular vibrations cause charge localization, leading to charge transport via the more commonly observed hopping mechanism. The charge carrier mobility in the hopping regime is given by equations (1.1) and (1.2) below, [10]

$$\mu_{\rm hop} = \frac{ea^2t^2}{k_{\rm B}T\hbar} \sqrt{\frac{\pi}{2E_{\rm pol}k_{\rm B}T}} \exp\left(-\frac{E_{\rm pol}}{2k_{\rm B}T}\right),\tag{1.1}$$

$$E_{\rm pol} = \frac{1}{2} \lambda_{\rm reorg}, \tag{1.2}$$

where *e* is the elementary charge, $k_{\rm B}$ is the Boltzmann constant, *T* is temperature, \hbar is the Planck constant, *a* is the spacing between molecules, *t* is the charge transfer integral (band width), $E_{\rm pol}$ is the polaron binding energy, and $\lambda_{\rm reorg}$ is the reorganization energy. This equation is consistent with the classical



Figure 2. Order and charge transport in organic semiconductors. Red regions denote charge delocalization. Red lines indicate the direction of charge transport for (a) idealized, single-crystalline small molecules, (b) low molecular weight conjugated polymers, and (c) high molecular weight conjugated polymers. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials [21], copyright 2013.

Marcus equation for electron-transfer rate. We note that the aforementioned charge transport theory applies to perfectly ordered lattices, such as those of defect-free small molecule single crystals (figure 2(a)) [21]. In reality, small molecular semiconductors are often deposited as polycrystalline films in which crystalline domain size, grain boundary structures, and degree of crystallinity play a significant role in charge transport [14]. Control of grain boundary orientation and molecular packing can modulate the charge carrier mobility by orders of magnitude [22]. Much work has also gone into minimizing charge traps at the dielectric interface. As we will describe in later sections, researchers have often used confinement, fluid flow, and interfaces to minimize crystal defects and maximize grain size and alignment.

Semiconducting polymers exhibit more complex charge transport for several reasons [21, 23]. First, their inherent disorder leads to the formation of localized states in the bandgap that smear the band edges, which trap charges and reduce mobility. Second, in polymers, the charges can travel both interchain, as in small molecular semiconductors, as well as intrachain-the rate of which is highly dependent on the chain conformation (planarity and chain length) [24]. Thus far, no rigorous charge transport model has been established for conjugated polymer systems. Nonetheless, considering the relative importance of intrachain to interchain charge transport, two phenomenological models were proposed recently (figure 2) [21, 23]. For low to intermediate molecular weight (MW) polymers (most conjugated polymers reported fall under this category), semicrystalline thin films form in which the amorphous bulk is studded with crystalline domains. In this case, the interchain charge transport through the crystalline regions dominates and the mobility is limited by domain boundaries (figure 2(b)). For high MW polymers, the semi-crystalline domains are interconnected by long polymer chains ('tiechains') serving as 'highways' for electrons or holes via intrachain transport. In this case, the mobility is limited by the interchain transport within the semi-crystalline domains (figure 2(c)). In both regimes, charge transport sensitively depends on a range of morphological characteristics. These parameters include conformation (torsion angle), packing (π – π stacking distance), and ordering (paracrystallinity) at the molecular scale [16, 23–30]; crystalline and amorphous domain sizes and domain percolation at the mesoscale [31–34]; and domain alignment, thin film uniformity, and patterning at the macroscale [15, 22, 26, 31, 33, 35–39].

To understand the role of molecular conformation, Sirringhaus et al compared several polymer systems of various backbone conformations in a recent work combining experimental with computational studies and uncovered the importance of backbone planarity for intrachain transport [24]. This study explained the excellent performance of a nearly amorphous high MW polymer (IDTBT). As for molecular ordering, commonly used methods to improve polymer crystallinity include post-deposition thermal or solvent vapor annealing [40] and the employment of high-boiling-point co-solvent additives [41]. Alternatively, nucleation agents have been utilized to accelerate crystallization rate by inducing heterogeneous nucleation [42]. Stingelin, Chabinyc, and coworkers [42] used two 'inert' additives, originally designed for melt solidification of isotactic polypropylene, to effectively induce nucleation of a diverse set of organic semiconductors (OSCs). It was also demonstrated that domain alignment in polymer thin films can enhance charge transport by over an order of magnitude. The methods for attaining alignment not only encompass post-deposition treatments like mechanical rubbing [43-45], but also techniques that manipulate the solution printing and drying process. For instance, unidirectional coating schemes which pull a solution meniscus over a substrate as it dries [36, 37, 46, 47]. Efforts have also been made to use interface-guided approaches. Heeger, Bazan, and colleagues have used diamond scratched surfaces to align the long axis of rigid conjugated polymer of various MWs during slow drop casting [39]. Recent work by Mohammadi et al introduces the use of dynamically reconfigurable ionic-liquid (IL) substrates to improve crystal size and alignment [33]. These, and other works, are reviewed in later sections of this paper in the context of the driving mechanisms of alignment.

1.2. Multiscale assembly of conjugated polymers under nonequilibrium conditions

On the basis of these recent findings, it is clear that controlling molecular conformation, enhancing molecular ordering, attaining domain percolation, and inducing domain alignment are effective means of promoting charge transport. All of these aspects of morphology are directly influenced by the multiscale assembly process for OSCs, which is intimately coupled to the printing process. In particular, through fluid flow, mass and heat transport, dimensional confinement, and interfacial properties. We have begun to unravel the molecular mechanism and elementary steps of conjugated molecule aggregation and assembly in quiescent or near equilibrium conditions [48]. However, the assembly process under non-equilibrium conditions relevant to solution processing is much less understood. Such understanding is urgently needed to enable rational design and systematic modulation of thin film morphology of printed electronics in order to establish the morphology-charge transport relationship and to elucidate charge transport mechanisms.

With regard to printing methods, OSCs are readily deposited via solution-based techniques such as blade coating, pen-writing, and inkjet printing [49-52], which are designed for compatibility with continuous and high speed (up to tens of meters per minute [50]) roll-to-roll fabrication. Under such conditions, in-plane patterning of printed materials and registry of successive layers of functional materials are no easy tasks. Furthermore, molecular assembly processes strongly couple with mass and momentum transport in an evaporating meniscus. During deposition, mass transport within the fluid by convection and diffusion, transport of solvent across the fluid interface by evaporation and subsequent vapor phase diffusion, and the ensuing heat transfer effects all give rise to competing mass and energy fluxes that determine the overall flow pattern, influencing material deposition [53–55]. Unfortunately, many methods that have been developed for morphology control are in the context of spin coating [42], dropcasting [39], or postdeposition processing [56]-commonly used laboratory methods for preparing semiconductor thin films which are impractical for high-throughput manufacturing.

In the ensuing sections, we will discuss three phenomena in detail: the confinement effect, the impact of fluid flows, and interfacial assembly. In each section, we begin with a discussion of the physics underlying the particular assembly process, drawing mechanistic insights broadly from physical and materials chemistry, colloidal and surface sciences, evaporative assembly, fluid mechanics and transport phenomenon, and crystal engineering. These are followed with salient examples from recent literature with relevance to the printing of OSCs, including both small molecules and polymers. This review does not seek to comprehensively survey all recent advancement in this area, but to focus on the mechanistic understanding of how assembly outcomes closely couple with the solution processing environment.

2. Crystallization in restricted geometry: confinement effects

The growth of polymeric and small molecular functional materials under dimensional constraints (the confinement effect) has been widely reported to lead to changes in both intrinsic properties and multiscale morphology [57, 58]. However, depending on the length scale considered, a variety of different phenomena are often discussed under the umbrella of the 'confinement effect'. Nano-confinement of solutions or melts within dimensions approaching the size of nascent nuclei or individual microdomains has been used widely to study and tune the crystallization behavior and molecular packing of polymers [58], organic small molecules [57], pharmaceuticals [59–65], and inorganic species such as water, helium, and noble gases [66]. Larger scale confinement, on the order of microns or greater, has been used to control mesoscale morphology by directing crystallite orientation and growth [67, 68]. In this section, we begin with a discussion of proposed confinement mechanisms, followed by a review of recent advances in applying confinement to directed assembly of printed organic electronics. We note that the reviewed principles in section 2.1 only serve as a conceptual guideline and may not all be directly applicable to printed electronics. Assembly of OSCs is primarily driven by $\pi - \pi$ and quadrupole interactions which are distinct from well-studied inorganic molecule and flexible chain polymer cases. These interactions, together with the 'hairy rod' molecular structure and rigid molecular conformation of common conjugated polymers, certainly may lead to different nucleation pathways. Also, although the typical confined geometry is planar for printed electronics, we keep our discussion on confinement mechanism general.

2.1. Physical insights on the role of confinement in directing crystallization

Here, we discuss the role of confinement on polymorph nucleation, growth orientation, nucleation rate, and morphology while summarizing mechanisms proposed in literature beyond printed electronics. To explain how nanoconfinement modifies crystallization behavior, we begin by briefly reviewing the results of classical nucleation theory (CNT). A more detailed development of CNT and non-CNTs (e.g., two-step nucleation theory) can be found in various standard texts [69, 70] and reviews [71, 72].

CNT posits that nucleation begins with the appearance of small molecular clusters (nuclei) of the new phase with associated Gibbs free energy change $\Delta G_{\text{cluster}}$. This free energy change comprises a change in the volume (bulk) free energy, ΔG_{ν} , due to altered intermolecular interactions within the nascent phase, and surface energy, γ , due to the creation of a new interface between the nucleus and surrounding fluid. When the system is supersaturated, the volume free energy term is favorable to phase transition ($\Delta G_{\nu} < 0$), whereas the surface energy term is always unfavorable ($\gamma > 0$). This balance is expressed in equation (2.1) for a spherical nucleus in the case of homogeneous nucleation, where V is the cluster

volume, A is the surface area, and r is the cluster radius. The surface energy of the nucleus in this equation is assumed constant. In the case of faceted or non-spherical nuclei, more sophisticated expressions accounting for the difference in facet surface energies have been developed [73, 74].

$$\Delta G_{\text{cluster}} = V \Delta G_{\nu} + A\gamma = \frac{4}{3}\pi r^3 \Delta G_{\nu} + 4\pi r^2 \gamma \qquad (2.1)$$

Thus, $\Delta G_{\text{cluster}}$ is a function of cluster size (figure 3(a), left) [69, 75]. By setting the derivative of $\Delta G_{\text{cluster}}$ with respect to radius equal to zero, one can obtain the maximum ΔG_{crit} and corresponding r_{crit} which represent the nucleation barrier and minimum stable nucleus size, respectively, as given by (2.2) and (2.3) [69].

$$r_{\rm crit} = -\frac{2\gamma}{\Delta G_v},\tag{2.2}$$

$$\Delta G_{\text{crit}} = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} = \frac{4\pi\gamma r_{\text{crit}}^2}{3}.$$
 (2.3)

Clusters form stochastically; those below the critical size spontaneously dissolve, while those above the critical size spontaneously grow. For nucleation from solution, the Ostwald–Freundlich relation (2.4) relates the particle size to the solubility via a parameter known as the supersaturation, *S*defined as the ratio of the solubility of particles of a given radius and the equilibrium solubility. Equation (2.4) can then be combined with (2.2) to solve for the volume free energy change, ΔG_{ν} , which can then be used to obtain equations (2.5) and (2.6) for ΔG_{crit} and r_{crit} .

$$\ln(S) = \frac{2\gamma v}{k_{\rm B}Tr} = -\frac{v\Delta G_v}{k_{\rm B}T},$$
(2.4)

$$\Delta G_{\rm crit} = \frac{16\pi\gamma^3 v^2}{3(k_{\rm B}T \ln S)^2},\tag{2.5}$$

$$r_{\rm crit} = \frac{2\gamma v^2}{k_{\rm B}T \ln(S)}.$$
 (2.6)

Here, *T* represents temperature, $k_{\rm B}$ is Boltzmann's constant, and ν represents the molecular volume. Thus, the critical nucleation barrier and cluster radius are determined in part by intrinsic parameters (γ , ν) and in part by processing conditions (*T*, *S*). Equations (2.4) through (2.6) apply only for the case of homogeneous nucleation from solution; analogous derivations for melt crystallization and heterogeneous nucleation can be found elsewhere [69, 78].

The above equations can be applied directly to explain the role of confinement on polymorph selectivity. Crystal polymorphism engenders changes to molecular packing via variation in molecular conformation, orientation, and intermolecular spacing. Each of these factors can lead to differences in the ΔG_{ν} and γ terms of (2.1) through (2.6). As a result, different polymorphs exhibit different energetic profiles (figure 3(a), right) causing stability rankings to vary for different radii. Thus, confined crystallization within porous templates with dimensions on the scale of critical nuclei can be used for polymorph selection. As an example, it has been reported that by confining anthranilic acid to 7.5 nm pores in controlled pore glass, the form II polymorph (metastable in bulk) can exhibit high stability and persist without transformation to the most stable bulk phase (form III) for over one month. Crystallization within a larger pore size of 24 nm exhibited a mixture of form II and III, while 55 nm pores led only the stable form III, a trend attributed to the larger critical nucleus size of form III [79]. Interestingly, a similar size selection process led to stabilization of the amorphous red phase of 5-methyl-2-[(2-nitrophenyl)-amino]-3-thiophenecarbonitrile (ROY) in 20 nm cylindrical pores despite thermal annealing. The authors attribute this unexpected phase behavior to the formation of particles smaller than the critical radius of any of the crystalline polymorphs [79]. Similar size dependent polymorph stabilization has also been observed for acetaminophen [80](metastable form III stabilized in pores of 22-60 nm) and many other compounds, as reviewed recently by Jiang and Ward [57]. We note that this hypothesis does not consider the role of pore wall interactions, nor the role of heterogeneous nucleation. Alternative mechanisms which account for the specific chemical interactions with the confinement wall and kinetics effects have been explored elsewhere [63, 64].

A similar effect, discussed by Hamilton *et al* [75], relates how confinement within anisotropic geometry can select for nanocrystal orientation (figure 3(b)). Noting that crystals tend to grow with their fast growth direction along the unrestricted pore dimension, they proposed that nascent nuclei that grow at an angle $\Psi < \Psi_{crit}$ fail to reach the critical length (volume) required for thermodynamic stability. Th unstable nuclei then re-dissolve and the nucleation process repeats until welloriented crystals are obtained. We note, however, that in the highly kinetically controlled regimes found in solution printing, it is possible that there is not sufficient time for this iterative process to occur.

A further effect of nanoscale confinement is modulation of the nucleation rate. As mentioned earlier, nucleation is a stochastic process: at a given instant, there exists a distribution of molecular cluster sizes both above and below the critical radius. The distribution of cluster sizes is governed by the Boltzmann distribution taking the form of (2.7),

$$n_r = n_0 \exp\left(-\frac{\Delta G_{\text{cluster}}}{k_{\text{B}}T}\right),\tag{2.7}$$

where n_r represents the number of clusters of radius r, n_0 , represents the number of molecules in the system, and $\Delta G_{\text{cluster}}$ is given by (2.1). The observed nucleation rate is dependent on the number of clusters reaching at least the critical nuclear size, which scales directly with the number of particles in the system. Thus, the restriction of total solution volumes through confinement can significantly increase induction times (the delay between supersaturation and formation of the new phase). This phenomenon has recently been applied to controlling nucleation in thin films via thickness variation [81] (addressed in detail in section 2.2).

At a larger scale, restrictions in growth dimension to the order of hundreds of nanometers to microns have been demonstrated to affect mesoscale grain structure during crystallization. Via 'evolutionary selective growth,' crystals



Figure 3. (a) Left: thermodynamics of crystallization as a balance between bulk driving force and surface penalty. Right: difference in the Gibb's Energy curves for different polymorphs cause relative stability of polymorphs to depend on cluster radius. (b) For crystallization confined to cylindrical pores, only those nuclei that orient at angles $\Psi < \Psi_{crit}$ reach the critical length (volume) necessary for stability. Reprinted with permission from [75]. Copyright (2012) American Chemical Society. (c) Left: schematic of the competitive evolution process. Crystals whose fast-growth axis does not align with the channel are obstructed by better-oriented grains. Right: SEM images for gallium nitride vapor deposited without and with lateral patterning. Pole figures demonstrate the transformation from isotropic to single crystal inplane structure. [67] John Wiley & Sons. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) AFM images of PS/PEO layered films matched against a schematic of how structure and morphology evolve for polymers as the confined dimension shrinks from the micro to nanoscale. Reprinted with permission from [76]. Copyright 2009 American Chemical Society. Reproduced with permission from [77]. COPYRIGHT: © Materials Research Society 2012.

grown in high aspect ratio channels are found to transition from formation of randomly oriented polycrystalline domains at the outset, to the creation of large, directed single crystals further away from the initial nucleation site. Using this technique, Leung et al [36] have reported that by systematic reduction of the degrees of freedom in growth direction, single crystalline GaN can be grown onto an amorphous SiO₂/Si(100) template via metal-organic chemical vapor deposition (figure 3(c)). The authors prepared a 'growth tunnel' structure of SiO₂ with a textured AlN seed deep within the tunnel. The template bounded growth both laterally (4 μ m) and vertically (0.65 μ m) and extended over a length of $20 \,\mu\text{m}$. The authors propose that initially, growth from the seed occurs via 'evolutionary selection' or 'survival of the fastest,' whereby nuclei with their fast growth axis aligned along the channel grow rapidly and obstruct growth of misaligned nuclei (figure 3(c), left) They observe that unrestricted growth led to randomly aligned crystallites (in-plane), while confined growth led to single crystals as demonstrated by optical and electron microscopy, pole diagrams, and x-ray analysis (figure 3(c), right). A follow up study by Kachkanov et al [68] demonstrated that the length scale of confinement played a key role: tunnels with lateral widths of 2.6 and 4.5 μ m favored the evolutionary selection mechanism, while larger tunnels of 8.6 μ m did not.

Similar phenomena have been observed in the confinement of polymeric materials, as recently discussed by Michell and Müller [58] in their very thorough review of crystallization of flexible polymers from the melt phase. Mirroring the results of evolutionary selective growth, they review cases where, for nanolayered materials, modulating film thickness affects morphology as shown schematically [77] and via atomic force microscopy of poly(styrene)/poly(ethylene oxide) films in figure 3(d). Shrinking the film thickness from 21 μ m to 25 nm leads to restriction in the degrees of freedom of growth from spherulitic, to lamellar, to finally singlecrystal growth. Furthermore, Michell and Müller note that crystal growth rate for a variety of polymers decreases commensurately with film thickness. They propose three possible reasons: (1) increasing T_g throughout the film means lower chain mobility and lower rate of diffusion, (2) lowering T_g solely at the substrate interface slows down overall rate and (3) a reduction in total number of active nuclei-as discussed above-decreases crystallization rate.

2.2. Vertical confinement effects

In this section, we highlight a few recent publications relating nanoconfinement effects to polymorph selectivity and nucleation rates pertinent to OSC thin films. In these studies, nanoconfinement is imposed in the out-of-plane direction and sensitively depends on film thickness. Therefore, we consider this phenomenon as vertical confinement in one dimension.

Giri *et al* demonstrated vertical confinement in the case of solution shearing of 6,13(bis-triisopropylsilylethynyl) pentacene (TIPS-pentacene) solutions [82]. Using *in situ* micro grazing incidence wide angle x-ray scattering (μ GI-WAXS), they observed the initial appearance of the **Topical Review**

equilibrium polymorph followed by the appearance of the metastable polymorph during solution shearing. As no change in the peak intensity of the equilibrium polymorph was observed over time, they postulated that the two polymorphs crystallized independently, that is: one polymorph did not transform into another. This assertion was supported by high speed in situ polarized optical microscopy; the film's appearance (top surface) was fully determined during the time it took for the equilibrium polymorph to form. Static and in situ μ GIWAXS measurements taken at different incidence angles (depths of penetration) supported this conclusion (figure 4(a), below). This led the authors to propose a stacked morphology (figure 4(a), above) in which the equilibrium polymorph rapidly crystallizes at the air-liquid interface due to high supersaturation. The media below is then confined in a manner similar to the case of nanoconfinement discussed earlier (section 2.1, figure 3(a), right), allowing the metastable polymorph to form. Furthermore, the authors investigated the effect of printing thinner films (confinement into a smaller volume) and found that the fraction of metastable polymorph increased. In a separate study by Xu et al the authors corroborated the μ GIWAXS observations using surface-enhanced Raman spectroscopy comparing molecular packing at top versus bottom interfaces of the TIPS-pentacene thin films [27].

In later work, Diao et al provided direct evidence on the vertical confinement effect also in solution sheared TIPSpentacene thin films [28]. Using in situ grazing incidence x-ray diffraction (XRD) during thermal annealing combined with differential scanning calorimetry, they observed a significant increase in polymorph transition temperature hysteresis going from bulk powder to 30 nm thin films (figure 4(b)), which they attributed to an increase in the kinetic barrier to polymorph nucleation. This finding implies that the relaxation of the metastable form to the stable form will be delayed in thinner films. In other words, the kinetic stability of metastable forms can be markedly enhanced by decreasing film thickness, as to appear stable over the device lifetime despite being in a thermodynamically unstable state. In addition, the authors observed decreased average transition temperatures in thinner films, analogous to the effect of confinement on melting point/glass transition temperature depression as related in the Gibbs-Thompson equation. Investigating the effect of vertical confinement on polymorph kinetic stability, the authors used film thickness modulation of TIPS-pentacene polymorphs [26] (figure 4(c)), to observe the shift from stable (form I) to metastable (form II) with decreasing film thickness. Furthermore, the authors discovered a highly metastable polymorph not observed before (polymorph III) under ambient conditions, by a combination of the confinement effect and rapid crystallization (kinetic trapping) [28].

Recently, Yu *et al* have reported a method to coherently seed nucleation via topographic patterning of amorphous thin films followed by annealing [81]. The authors used both lithographic and mechanical methods to generate patterned thickness variations for various systems and observed a coherent growth front stemming from the thicker regions. Extending CNT to thin film geometries, the authors define a constant homogeneous



Figure 4. (a) From top to bottom: cartoon of the vertical confinement process during solution printing of TIPS-pentacene, where rapid formation of the equilibrium polymorph confines the volume below, potentially causing formation of the metastable polymorph. GIXD taken at a shallow angle (above, few nanometers penetration) and deeper angle (below) reveals that the intensity of the metastable polymorph (red curve) relative to the equilibrium polymorph (blue curve) is greater closer to the substrate. Reprinted by permission from Macmillan Publishers Ltd: Nature Communications, [82], copyright 2014. (b) Effect of vertical confinement on polymorph transition temperature hysteresis for TIPS-pentacene identified via DSC. As the dimension of confinement shrinks, hysteresis increases. Reprinted with permission from [28]. Copyright 2014 American Chemical Society. (c) Comparison of molecular packing for TIPS-pentacene films of varying thicknesses via GIXD. As film thickness decreases, unit cell distortion increases (formation of metastable phase). Reprinted by permission from Macmillan Publishers Ltd: Nature Materials, [26], copyright 2013.

nucleation rate per unit area as follows,

$$R_A = \frac{N}{\Delta t \Delta A} = Rd, \qquad (2.8)$$

where R_A is the areal nucleation rate, N is the number of nuclei formed per unit volume in the time interval Δt and area ΔA . This areal nucleation rate is geometrically related to the film thickness *d*, and the more typically used volumetric nucleation rate *R*. By rearrangement of (2.8) to solve for the first nucleation event (N = 1), the authors propose that induction time is inversely related to film thickness, a conclusion which they verify experimentally via direct observation through polarized



Figure 5. (a) Schematic of the solution shearing process. (b) TIPS-pentacene molecular structure. (c) Schematic of proposed growth scheme with confinement dimensions shrinking from left to right. As the wetting region shrinks, alignment improves as misaligned grains terminate at the lyophobic boundary. (d) Cross polarized optical microscope images show a transition from spherulites to highly aligned crystals as confinement dimensions shrinks from non-patterned to 20 to 0.5 μ m. [83] John Wiley & Sons. © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

optical microscopy. Remarkably, the trend was consistent for thicknesses between 10 and 200 nm for a variety of amorphouspolycrystalline transitions from thermal annealing of rubrene and molybdenum oxide, to solvent vapor annealing of 5,11-Bis (triethylsilylethynyl)anthradithiophene (TES-ADT) despite ignoring the role of heterogeneous nucleation at the interfaces. The authors used this observation to generate 'bespoke' microstructures via patterned thickness variation on the thin film prior to annealing for TES-ADT, vacuum deposited rubrene, molybdenum oxide, solution-processed poly(ethylene oxide), and solution processed PbI2 hybrid perovskite solvated films. In each case, rapid spherulitic growth within the thicker region seeded slower, highly oriented, polycrystalline growth in the thinner region.

2.3. Lateral and volume confinement effects

Recently, various groups have experimented with using inplane (lateral) patterning of the substrate as well as crystallization within nanoscale channel structures (volume confinement) to control mesoscale crystal grain orientation. Although in some cases the underlying mechanisms of confinement are not addressed in the original work, we draw connections to the physical processes from section 2.1 where appropriate.

Giri *et al* [83] found that solution-sheared crystals of TIPS-pentacene grew via a mechanism akin to evolutionary selective growth (see 2.1) when printed onto a substrate patterned with wetting and de-wetting stripes (figure 5(a)). The authors observed that misaligned crystals rapidly terminate on the lyophobic boundary or are obstructed by crystals with fast-growth directions aligned along the channel, leading to a high degree of alignment and large domain size further down the channel (figure 5(c)). Polarized optical microscopy

demonstrates that the alignment effect is greatly improved as the channel width was decreased from unrestricted (mm scale) to channels ranging from 10 to 0.5 μ m (figure 5(d)). As the fast-growth direction is also the $\pi-\pi$ stacking direction (direction of fastest charge transport), they also observed a concomitant increase in charge carrier mobility from $1.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (10 μ m stripes) to $2.70 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (0.5 μ m stripes). In later work [84], they demonstrate that there is no similar alignment effect for patterns of width greater than 100 μ m.

Nano- to mesoscale confinement effects have been used extensively in the nanoimprint lithography literature for crystallization of functional polymers from the melt phase [85–88] and, recently, from solution [89–91]. Wei et al [90] developed a technique known as 'solvent-assisted roomtemperature nanoimprint lithography' to print the donoracceptor polymer poly[2,5-bis(2-octyldodecyl) pyrrolo-[3,4c]pyrrole-1,4(2H,5H)-dione-alt-2,2':5',2":5",2"'-quaterthiophene] (PDQT) in well-aligned nanostrips. The authors spincast a thin (initially 50 nm) wet film of PDQT onto a substrate before compressing it under a mold with 300 nm deep trenches and drying (figure 6(a)). Upon removal of the mold, well isolated nanostrips are produced with heights depending on the ratio of width of the trenches to their periods (figure 6(b)). Using grazing incidence wide-angle x-ray scattering (GIWAXS), the authors determined that nanostripes exhibited much stronger anisotropic alignment of π -stacks along the stripe length. The authors further quantified the average angle distribution of nanocrystallite p-stacks using cross-polarized optical microscopy, finding that the average degree of orientation (proportional to ratio of maximum: minimum intensity) increased as strip length decreased from 290 to 160 nm (figure 6(c)). This trend was supported by device

measurements with the conductive channel oriented along the



Figure 6. (a) Schematic of the solvent-assisted room-temperature nanoimprint lithography method which generates arrays of polymer crystals with p-stacking along the long axis. (b) AFM images of films that are unprocessed (left) and 290 nm wide, 160 nm tall (right). (c) and (d) Ratio of maximum cross-polarized optical microscopy reflection intensity and charge mobility increase as confinement dimension shrinks. [90] John Wiley & Sons. © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (e) Schematic of the liquid bridge nano-transfer molding process. [92] John Wiley & Sons. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. [93] 2015 © Park et al.; licensee Springer. 2015. With permission of Springer. (f)–(i) SEM and selective area electron diffraction images for TIPS-pentacene nanowires of 50 nm, 100 nm, 500 nm, and 10 μ m widths, respectively. Crystallinity improves as width decreases. Adapted from [93] under Creative Commons Attribution license 4.0.

 π -stacking direction. Mobility increased monotonically with decreasing strip width, to an ultimate value of $0.082 \pm 0.015 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a 20-fold improvement over the unpatterned film (figure 6(d)). The authors attribute the increased domain alignment to 'entropic or graphoepitaxy effects'. We note that it is also possible that evolutionary selection and/or energy minimization via the domain reorganization during slow crystallization play a role.

Using a form of transfer printing from polyurethane acrylate (PUA) molds, Park et al [92-94] printed singlecrystalline nanowires and polycrystalline microribbons of both small-molecule 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) and the polymer poly(3-hexylthiophene) (P3HT). In their process (figure 6(e)), organic ink solutions with high boiling points (>200 °C) are filled into the channels of the mold before being slowly dried under mild heating. Then, the templates are inverted and placed onto a substrate coated in a thin liquid layer which pulls the two OSC surfaces into contact with the substrate as it dries. Using a mold with channels of width 90 nm (unconstrained in depth and length), the authors produced arrays of single-crystal TIPS-pentacene nanowires (90 nm width, 139 nm height) and P3HT (90 nm width, 132 nm height), which was attributed to 'the confinement effect'. Crystallinity was characterized via selective-area electron diffraction and XRD. They noted that the both the TIPS-pentacene and P3HT nanowires grew with the π -stacking directions oriented along the channel [92]. In later work, they systematically investigated the effect of channel width and determined that a lateral dimension of less than 100 nm is required for single crystal formation (figure 6(f)-(i)) [93].

3. Fluid flow driven evaporative assembly

Printing of solution-based organic electronics represents an attractive high-throughput fabrication scheme. A key challenge arises, however, from the coupling between molecular assembly processes and mass and momentum transport in an evaporating meniscus. During deposition, competition between mass transport within the fluid by convection and diffusion, transport of solvent across the fluid interface by evaporation and subsequent vapor phase diffusion, and the ensuing heat transfer effects all give rise to competing mass and energy fluxes that determine the overall flow. In this section, we begin by discussing the flows which arise naturally in both sessile droplets and the moving ink solutions relevant to drop-based printing and meniscus-guided coating/ printing techniques. We then review several recently developed techniques which exploit these flow characteristics to guide molecular assembly.

3.1. Physical origins of fluid flow

Fluid flow within sessile evaporating droplets has been studied extensively and is of critical interest for functional material deposition via inkjet printing [95], spray coating [96, 97], and in various evaporative assembly techniques [98]. The flow field within a droplet is complex (figure 7(a)) and can be viewed as a composition of the chiefly radial evaporation-induced capillary flow, the circulatory Marangoni flows, and buoyancy driven flows (generally neglected). The relative strengths of these depend on a wide variety of parameters, including contact line pinning and the evaporation profile [99], solute particle shape [100, 101], solute concentration [102], surface contamination [100, 103], contact angle with the substrate [104], and thermal conductivity difference between the liquid and substrate [105]. Here, we examine each flow mechanism in turn, beginning our discussion with capillary flows 3.1.1 and Marangoni flows 3.1.2. We then extend the discussion from evaporating droplets to moving menisci, focusing on transport processes in meniscusguided coating/printing 3.1.3.

3.1.1. Capillary flow in an evaporating drop. Beginning in 1997, Deegan *et al* proposed that the primary cause of the formation of ring stains (the 'coffee-ring effect') was due to radial transport of fluid from the interior of a droplet to the pinned edge [55, 99, 109]. When the contact line is not pinned, the evaporation of fluid from the free surface causes the droplet to shrink while maintaining a constant contact angle. In the case of a pinned droplet, the edges of the droplet cannot move, and there must be radial outflow from the center of the droplet to replace evaporating fluid. This radial flow carries non-volatile solute particles to the edge of the pinned drop with increasing velocity, leading to deposition as shown in figure 7(e).

The coffee-ring effect, and more generally evaporation of pinned and non-pinned droplets, has been widely studied both theoretically and experimentally over the years. While the assumptions made, mathematical approaches, and quantitative results of these various approaches differ somewhat, the qualitative flow dynamics are widely agreed upon. In the following discussion, we outline the analytical development of Hu and Larson for an evaporating water droplet of contact angle $<90^{\circ}$ under isothermal conditions [110] to introduce the factors that impact the internal capillary flow profile. We remark on alternative modeling approaches and conclusions where appropriate; extensive commentary on these have been made elsewhere [53, 111–113].

The strength (fluid velocity) of the capillary flow is determined by the non-uniformity of the evaporative flux over the surface of the droplet. Here, mass transport across the free interface is limited by diffusion of the solvent vapor away from the interface. If we furthermore assume that the interface velocity is slow compared to the timescale of establishing the concentration gradient (true unless near the critical point) [112], we obtain equation (3.1): Laplace's equation for vapor concentration in air, C.

$$\nabla^2 C = 0. \tag{3.1}$$

The shape of the droplet is taken to be a spherical cap. This can be justified through calculation of the Bond number (ratio of



Figure 7. (a) Schematic of flows within an evaporating droplet. We note that the direction of Marangoni flows (green arrows) can be reversed. (b) Spatiotemporal flow field in an evaporating droplet measured just above droplet base. Inset demonstrates that velocity vectors point radially. Reprinted figure with permission from [106]. Copyright 2011 by the American Physical Society. (c) Streamlines from finite element models developed by Hu and Larson for flow within droplets with (right) and without (left) Marangoni flow. Reprinted with permission from [103, 107]. Copyright 2005 American Chemical Society. (d) Plot of experimental results (squares/triangles) and theoretical prediction (black line) of Marangoni flow direction at a given contact angle (θ_c) and ratio of substrate to liquid thermal conductivity (k_r). Reprinted figure with permission from [105]. Copyright 2007 by the American Physical Society. (e) From top to bottom: schematic of the role of capillary flow, substrate–solute interaction, and Marangoni flow in solute deposition. Reprinted with permission from [108]. Copyright 2010 American Chemical Society.

gravity to surface tension/capillary forces) and the capillary number (ratio of viscous to surface tension forces). Hu and Larson determined that for small water droplets, the Bond number ranges from 0.03 to 0.04 and the capillary number is around 10^{-8} , justifying the spherical cap assumption [110]. This is generally the case except for very large droplets.

The evaporative flux at the interface, J, can then be given by Fick's Law: equation (3.2).

$$\vec{J}(r,t) = D\nabla C. \tag{3.2}$$

This equation is evaluated using the following boundary conditions in cylindrical coordinates (equations (3.3)), where

r, *R* are the radius of the droplet's base, *h* is the drop height, *z* is the vertical axis, *C* is vapor concentration, and C_v is the saturation concentration, and H_v is the relative humidity (for solvents other than water, the 3rd boundary condition would generally have *c* approaching zero).

1.
$$r < R, z = h(r): C = C_v$$

2. $r > R, z = 0: J = 0$
3. $r = \infty, z = \infty: c = H_v c_v$. (3.3)

At the free surface of the droplet (1), the droplet height is a function of the shape—related by the spherical cap formula to the contact angle. There is no flux through the substrate (2) and far from the droplet the concentration reaches a constant value (here, water droplets were studied so relative humidity H_v is used (3). Hu and Larson then solve for the evaporative flux profile using a finite element method, but provide the analytical approximation of equation (3.4) (similar to that proposed by Deegan [99]), which sharply diverges as the contact line is approached.

$$J \propto J_0(\theta) \left(1 - \left(\frac{r}{R}\right)^2 \right)^{-\lambda(\theta)}$$
$$\lambda = \frac{1}{2} - \frac{\theta_c}{\pi}$$
(3.4)

The singularity of the flux at the contact line is an unphysical conclusion of the lens model; however, the qualitative result of evaporative flux increasing towards the contact line for wetting drops has been supported by experiment (illustrated in figure 7(a)). Using digital holographic interferometry, Dehaeck *et al* [114] measured the local evaporation rate of a droplet of 3 M Novec HFE-7000 (a fluid chosen for its high contrast in their technique). They compare the experimental measurements to the prediction of a variety of models similar to that developed above. While the divergence of evaporative flux is not evident, the qualitative increases in flux towards the droplet edge is observed. Deegan *et al* attribute this edge enhancement to the increased probability of escape of solvent molecules by random diffusion near the edge of the droplet [99].

The evaporative flux can then be coupled to mass and momentum balances on the droplet to determine the velocity profiles within the droplet. In 2005, Hu and Larson [107], provided an analytical solution based on lubrication theory. Presuming low Reynold's number flow, zero shear and the kinematic boundary condition at the free interface, and no slip at the stationary substrate, they provided an analytical expression for the flow field in asymmetric cylindrical coordinates. They confirmed the validity of this result with a finite element model depicted in (figure 7(c), left). Once again, theory predicts an unphysical singularity (here in velocity) at the contact line. Using high-speed microparticle image velocimetry, Hamamoto et al mapped the spatiotemporal evolution of the flow field very near the base of the droplet (height of 30 μ m) as show in figure 7(b). They observed that the velocity is maximized at around 70% of the radius and the velocity near the edge exceeds that at the center by about an order of magnitude.

A number of assumptions were made in the foregoing analysis. The non-uniformity of the evaporative flux is critical in determining capillary flow shape and has been found to depend significantly on the contact angle the droplet forms with the surface. For contact angles $<90^{\circ}$, evaporative flux increases to the edge as shown above, for a contact angle of 90°, the flux is constant over the surface, and for a contact angle $>90^{\circ}$ the flux decreases further from the center of the droplet. This has been demonstrated both theoretically [115] and experimentally [116]. The effects of temperature and presence of nearby droplets also effect the tendency to deposit coffee-rings [117]. Additionally, the above model only applies while the contact line is pinned, although droplet evaporation actually occurs in two stages: constant contact area (pinning), and constant contact angle (depinned) [118]. This latter stage is often assumed to represent a small fraction of total drying time [110]. The competition between droplet evaporation rate and solute movement speed was investigated by Shen et al [119], who found that droplet size can affect coffee ring deposition. Furthermore, solute effects are generally neglected in calculations while in reality they have been shown to significant impact flow patterns, and in some cases suppress the coffee ring effect entirely [101]. The low Reynolds number approximation, while valid for purely capillary flow, can be problematic when faster Marangoni flows are present [53].

3.1.2. Marangoni flow in an evaporating drop. In addition to the chiefly radial capillary flow, recirculating Marangoni flows (figures 7(a), (c)(right)) can have a large impact on the pattern of solute deposition [100, 120]. In the presence of a surface tension gradient, fluid along an interface will flow from regions of low surface tension to those of high surface tension. This gradient manifests as a shear stress along the surface which induces circulating flow in the bulk by mass balance [121]. Surface tension gradients arise naturally due to solute concentration gradients and/or temperature gradients. The strengths of these forces relative to viscous forces are characterized by the Marangoni numbers given in equations (3.5) and (3.6), respectively [122].

$$Ma_C = \left(\frac{\mathrm{d}\gamma}{\mathrm{d}C}\right)^* \frac{d_0 \Delta C}{\mu D_{AB}},\tag{3.5}$$

$$Ma_T = \left(\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right)^* \frac{d_0 \Delta T}{\mu \alpha},\tag{3.6}$$

where γ represents surface tension, d_0 represents the initial droplet diameter, T is temperature, C is concentration, μ is viscosity, α is thermal diffusivity, and D_{AB} is the mass diffusivity of the solute. As the Marangoni number increases, forces induced by the surface tension gradient outweigh viscous resistance and circulatory flow will occur [122]. For most liquids, surface tension decreases with temperature linearly for small perturbations [107]. The effect of concentration is more complex and depends on the nature of the solute-solvent interactions. Note that aqueous droplets are readily contaminated by surfactants that result in strongly weakened Marangoni flow [55, 100, 121].

The direction of circulation depends on the direction of the gradient of driving force. For the well-studied thermocapillary case (temperature-gradient-driven Marangoni flow), Ristenpart et al [105] established theoretically that temperature in a droplet will have extrema at the contact line and the apex of the droplet, a property that, while generally accepted [99, 107], has been challenged early in the evaporation process [123], and very near the contact line [124]. After demonstrating that conduction dominates heat transfer with the droplet, they defined the key parameter $k_{\rm R} = k_{\rm S}/k_{\rm L}$, the ratio of substrate and liquid thermal conductivities to control the direction of circulation. They define three regimes. For $k_{\rm R} > 2$, the heat transfer from the substrate is sufficient to overcome the increased heat loss by evaporation and the temperature is highest at the contact line (so flow near the air interface is directed towards the apex). For $k_{\rm R} < 1.45$, the droplet is coolest at the contact line and flow direction is reversed, inwards along the substrate which can hinder the coffee-ring effect. Finally, in the intermediate region, flow direction depends on contact angle and can reverse during evaporation. These results are plotted in figure 7(d) along with experimental data points using different solvents [105]. Elsewhere it has been demonstrated that the substrate thickness and thermal conductivity both play and role in droplet temperature profiles [125], noted in a more detailed study of the reversal of circulation [124].

Hu and Larson also extended their model to include Marangoni stresses [103], which allowed them to solve for the flow field to find that the direction of recirculation depends on contact angle. From calculation of an inverse Stanton number (ratio of convective to conductive heat transfer effects), they determined that conduction dominated heat transfer and simplified the energy balance to Laplace's equation in temperature (3.7).

$$\Delta^2 T = 0. \tag{3.7}$$

The boundary condition on the free surface equates heat flux to the latent heat of evaporation multiplied by the evaporative flux. Away from the droplet, heat flux is taken as zero, and at the substrate surfaces far from the droplet temperature is taken as constant. Changes to these boundary conditions to match experimental conditions would result in qualitatively similar flow, however the flow direction may change as discussed above. Upon numerically solving for the vapor concentration and temperature fields, Hu and Larson computed the Marangoni stress and applied it as a boundary condition to the Navier-Stokes equations under the lubrication assumption, allowing them to solve for the velocity field within the droplet (figure 7(c), right). In their analysis, they also note flow reversal for low contact angles. They determined that thermocapillary flows are more significant for taller droplets (higher contact angle) due to the larger temperature gradient. It is worth noting that the computed profile represents the quasi-steady state. Other researchers have noted significant instability during the initial stages of evaporation [123].

Marangoni flows have been demonstrated to reverse coffee-ring deposition [100, 126, 127], and lead to uniform or central solute deposition depending on circulation strength, although the exact mechanism is under debate. The Marangoni effect is particularly active in organic solvents whose surfaces are not readily contaminated by surfactants which suppress surface stresses (as is the case for water) [100, 102]. In non-wetting droplets, the large height-to-radius aspect ratio gives rise to an advective component of energy transport that cannot be ignored [104]. Furthermore, the assumption of a spherical cap (lens model) is a poor fit for strong Marangoni flows, which can distort the shape of the free interface [128]. Despite the limited generality of current models of the combined flow, in recent years an abundance of experimental techniques has emerged which balance Marangoni and capillary flows to control morphology, particularly in the inkjet literature as reviewed by Sun et al [129]. Recent work by Bhardwaj et al portrays final deposition shape as an interplay between capillary flow, Marangoni flow, and substrate-solute/solute-solute DLVO interactions (figure 7(e)) [108].

3.1.3. Transport processes in meniscus-guided coating/printing.

Fluid flow in meniscus-guided coating/printing techniques such as slot-die coating, zone casting, and solution shearing differs from the sessile droplet case [49]. Rather than allowing the meniscus to recede slowly under evaporation, with these techniques the experimenter can manipulate the rate at which the meniscus is pulled across the surface. In these coating/ printing techniques, two additional flow driving forces are introduced, capillary action imposed by the print head, and viscous force imposed by the substrate, in addition to solvent evaporation and interfacial stress gradients compared to the case of sessile droplets. Furthermore, the substrate-imposed viscous force is countered balanced with the surface tension effect that drives liquid film dewetting. Interplay of these driving forces can give rise to complex flow patterns and rich instabilities in a moving and drying meniscus. As the coating speed sensitively modulates flow characteristics and printed film morphology, we summarize below analytical and semi-empirical models that determined the dependence of printed film characteristics on coating speed. We note that contact-line engineering, or controlled evaporation of sessile droplets for morphology control has been well reviewed elsewhere [130]. Various dimensionless numbers have been defined to quantify the influence of competing factors; we have earlier mentioned the Bond and Marangoni numbers. For an excellent and thorough review, please see Larson [53]. The capillary number, Ca, is used to relate viscous forces to surface tension forces and is defined as the viscosity of the fluid times its characteristic velocity divided by surface tension. Previous papers have used Ca to map



Figure 8. (a) and (b): Schematics of evaporation and Landau–Levich regimes of film deposition. (c) Experimentally determined film thicknesses with exponential fits. The dotted line represents the theoretical prediction. Reprinted with permission from [133]. Copyright 2009 American Chemical Society.

morphology diagrams for evaporative assembly and determine the onset of contact line instability [131, 132].

As described by Le Berre et al [133], two deposition regimes exist: one in which the meniscus advances at or near the rate of evaporation (evaporation regime—figure 8(a)) and one in which the blade is drawn fast enough to leave a wet film that dries post deposition (Landau-Levich regime-figure 8(b)). The transition between the two regimes reflect the competition in time scales between solvent evaporation and viscous dragout. They report that within each regime, the morphology of deposited phospholipid films is constant, but there is a sharp change in morphology at the transition between regimes. In the ensuing analysis, the authors assumed total wetting, constant evaporation rate, and constant dynamic contact angle. For low speed printing, they derived expressions for the film thickness, h, in the evaporation regime from a mass balance where the solvent evaporation rate and the solute deposition rate are matched by solvent and solute flux towards the meniscus front (3.8). Here, C is the bulk solute concentration, ρ is the solution density, L is the width of the film, Q_{evap} is the solvent evaporation rate, and v is the coating speed. The experimentally determined relationship (h $\propto v^{-1.1}$) was in good agreement with the theoretical prediction. For higher speeds, the researchers extend the previously developed Landau-Levich equation for dip coating (3.9), where κ^{-1} represents the capillary length, Ca is the capillary number (as defined above), and all other constants retain their earlier definitions. In this case, the dynamic meniscus is retained by capillary pressure at the back meniscus as opposed to gravitational forces. The capillary pressure was expressed in terms of the back-meniscus curvature described by θ_1 , θ_2 , and l (figure 8(b)). By assuming this physical picture, they obtained (3.10) for the height of the deposited film in the Landau–Levich regime. Equating (3.8) and (3.10), the critical coating speed separating the two regimes was further obtained.

$$h_{\rm evap} = \frac{C}{\rho} * \frac{Q_{\rm evap}}{L} v^{-1}, \qquad (3.8)$$

$$h_{LL} = 0.94 \kappa^{-1} C a^{2/3} = 0.94 \left(\frac{\gamma}{\rho g^{1/2}}\right) \left(\frac{\eta \nu}{\gamma}\right), \qquad (3.9)$$

$$h = 1.34 \frac{C}{\rho} * \frac{l}{\cos\theta_1 + \cos\theta_2 - \frac{l^2}{2\kappa^{-2}}} * Ca^{2/3}.$$
 (3.10)

The authors find good agreement in terms of scaling for their relations, however, there was some discrepancy in the prefactors (figure 8(c)). They attributed this inaccuracy to the presence of additional Marangoni flows. They also noted that in the case of incomplete wetting, deposition may not occur. The concept of the two printing regimes has attracted much attention in the field of solution printing. The same scaling for height versus printing speed for the Landau–Levich and evaporative regimes were found in theoretical work by Doumenc and Guerrier [134]. They created a macroscopic model using the lubrication approximation for hydrodynamic flows, vapor diffusion in the gas phase, and variation of physical parameters during drying with the shape of the free surface and evaporative flux profile determined by simulation (1.5D method).

Recently, Janneck et al [135] have proposed a predictive model for film morphology-coating speed relationship during meniscus-guided coating of OSC thin films. They proposed that the ideal printing speed for facilitating growth of aligned, large single-crystalline domains is in a window around the equilibrium front evaporation speed (v_{efe}), which represents the rate at which the edge of a pinned droplet recedes limited by the rate of solvent vapor diffusion above the meniscus. They identified the parameters of interest for controlling thin film deposition as solvent choice, coating speed, and substrate temperature. To determine the equilibrium front evaporation rate analytically, they began with an unsteady state mass balance on the edge-casting geometry (figure 9(a)) (3.11), assuming vapor diffusion limits evaporation rate. In this equation, m(t) and V(t) are the droplet mass and volume over time, ρ is the solvent density, D is the gas phase diffusion coefficient, c_s and c_∞ are the surface and bulk concentrations of the solvent vapor, and $h(\theta)$ is a geometric parameter depending on meniscus contact angle θ and length.

$$\frac{\mathrm{d}m(t)}{\mathrm{d}t} = \frac{\rho_{\rm s}\mathrm{d}V(t)}{\mathrm{d}t} = -D(c_{\rm s}-c_{\infty})h(\theta). \tag{3.11}$$



Figure 9. (a) Schematics of the edge- and zone-casting apparatus. (b) Linearization of equilibrium front evaporation speed measurements plotted for many solvents. (c) C_8 -BTBT films printed at a variety of speeds viewed by polarized optical microscopy (top row) and AFM (bottom row). Printing speeds are normalized against the equilibrium front evaporation speed, at which the best morphology was achieved. [135] John Wiley & Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Labeled image of solution shearing setup (inset) with simulated flows in the vapor and liquid. (e) Polarized optical microscope images of the printed C10-DNTT films. Reproduced from [136] with permission of The Royal Society of Chemistry.

Based on equation (3.11), the authors derived the equilibrium front evaporation speed (v_{efe}) shown in equation (3.12), after taking an assumption of large droplets whose length exceeds twice the capillary length, assuming bulk solvent concentration is negligible, applying the ideal gas law to relate surface concentration to the vapor pressure at the surface (and then substituting the Clausius–Clapeyron equation), and

making the temperature dependence of D explicit.

$$v_{\rm efe} = AV_M T^{0.7} \exp\left(-\frac{\Delta S_{\rm vap}}{R} * \frac{T_b}{T}\right).$$
(3.12)

Here A represents a lumped, temperature-invariant fitting parameter capturing the geometry of the system, diffusion coefficient, and entropic terms, V_M is the molar volume of the

solvent, T is the printing temperature, T_b is the boiling point of the solvent, ΔS_{vap} is the change in entropy during vaporization, and R is the gas constant. This relation compares favorably to data collected via edge-casting experiments using neat solvent, in absence of a moving blade (figure 9(b)). To demonstrate the utility of their prediction, the authors zone-cast films of C8-BTBT (figure 9(c)) and TIPS-Pentacene. They found that film morphology and effective mobility were optimized at the predicted $v = v_{efe}$. They proposed that for speeds lower than this rate, bulk nucleation/growth of crystals can occur within the meniscus, introducing misaligned crystals and defects. At speeds higher than v_{efe} , the printed ribbons narrow to form discontinuous islands, causing termination of the conducting channels and reducing effective channel width. This study approximated the OSC solution as neat solvent. This limits the generality somewhat, as solute interactions are known to substantially affect deposition patterns [53, 137].

Peng et al recently used finite-element simulation to model the solution shearing of C10-DNTT (figure 9(d)) [136]. The model assumes incompressible laminar flow (full Navier-Stokes), uses experimentally observed fluid profiles for the meniscus shape and a sliding wall substrate boundary to account for the shearing speed. Heat transfer within the liquid is solved for assuming negligible convection and radiation and accounting for the heat of vaporization (coupled to the evaporative flux). The concentration of vapor at the free interface is taken to be the saturated vapor pressure at a temperature calculated from the coupled heat transfer equation. The concentration profile in the air is calculated from the Laplace's equation and used to obtain the evaporative flux on the boundary. It is worth noting that the mass flux of solvent out of the liquid is not actually coupled to the fluid flow within the meniscus, and so predicted flow profiles did not correctly capture accelerating capillary flow. The shearing speed for optimal morphology was then calculated, assuming the optimal morphology is attained when the shearing speed matches with the evaporation rate as Janneck et al did [135]. The experimenters validated this approach via solution shearing of C10-DNTT in tetralin (figure 9(e)). They observed optimized morphology (aligned large domains) and mobility when printing at the calculated speed. They also observe that the direction of fastest charge transport occurred along the printing direction. At speeds lower than the optimum, they observed misoriented polycrystalline films, while for speeds faster than the optimum, discontinuities in the film inhibited effective charge transport.

3.2. Recent developments in meniscus-guided coating

Interest in the use of meniscus-guided coating techniques has spiked in recent years, with numerous researchers investigating the printing of small-molecules and polymers for both optoelectronic devices and thin-film transistors. Some recent work on understanding and engineering the fluid flow for controlling assembly has been summarized in an earlier account from our group by Qu *et al* [138]. Despite recent advancements, our quantitative understanding on the coupling of printing/coating flow with the assembly process and morphology outcome is still very limited. Here, we focus on describing the results of several recent investigations that developed innovative coating methods and achieved control over thin film morphology, in particular alignment.

Schott et al [37], recently investigated the in-plane alignment of donor-acceptor polymer DPP-BTz using a flexible blade-coating technique (figure 10(a)). The experimenters proposed that the crystallite size in as-deposited films depends heavily on the amount of pre-aggregation allowed by the solvent and thus they chose chlorobenzene as the solvent. They observed significant anisotropic alignment of the polymer chains (figure 10(b)) at a variety of coating speeds, which they attributed to shear forces applied by the blade. The optimal coating speed of $102 \,\mu m \, s^{-1}$ yielded dichroic ratios of 4.0, 14 ± 1 , and 159 ± 7 given by NEXAFS (surface layers), UV-vis (bulk), and GIWAXS (bulk). Past the optimal printing speed of $\sim 100 \,\mu m \, s^{-1}$, they observed a decreasing trend of anisotropy (dichroic ratio) (figure 10(c)). They attributed this to the movement of the film solidification front further away from the point of contact with the blade as speed increased. This, they reasoned, gave the polymer chains time to reorient and lose the alignment. Printing speeds less than $100 \,\mu m \, s^{-1}$ gave worse anisotropy, which they attributed to premature drying of the film which produced non-uniform deposition. Anisotropy of the saturation mobility parallel and perpendicular to printing directions was lower than the extent of domain alignment measured by UV-vis (figure 10(d)). For the $102 \,\mu m \, s^{-1}$ condition, the mobility anisotropy was 3.1 ± 1.6 . Printing at a slightly higher speed of $131 \,\mu m \, s^{-1}$ yielded a maximum mobility of $6.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by eliminating defects present at the lower printing speed.

Bucella et al [36] used a bar coating technique (figure 10(e)), in which a wire was wrapped around a bar brought to physical contact with the substrate and dragged across a pre-aggregated solution of the n-type polymeric semiconductor (O(NDI2OD-T2)). Via AFM they observed significant alignment of polymer nanofibrils in the direction of coating and proposed that alignment was due to shear flows. They noted that solvent evaporation had no influence because printing was performed by dragging out wet films. They found that film morphology depended on solution concentration: at low concentration, highly edge-on, submonolayer films were deposited (figure 10(f), left). At higher concentrations, they were able to cast 10 nm films (figure 10(f), right) that were face-on in the bulk, and edge-on at the free surface. Furthermore, polymer backbones aligned parallel to coating direction, with higher degree of alignment of backbones at top surface than in bulk and better alignment for the 10 nm film. Dichroic ratios of 4.8 and 7.7 were calculated for NEXAFS (surface) and GIWAXS (bulk) measurements. The authors reasoned that because the NEXAFS value averages in the contribution of likely isotropic amorphous regions of the film (which GIWAXS omits), the top surface was likely more aligned than the bulk. A large degree of charge transport anisotropy was also observed at different coating speeds (figure 10(g)), with worse performance at low speed, which they attributed to less shear. The maximum measured saturation mobility ratio (parallel: perpendicular) was 20.1 with the mobility in the parallel case reading $3.62 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. When investigating the impact of



Figure 10. (a) Schematic of flexible-blade solution shearing process with DPP-BTz polymer inset. (b) Polarized optical microscopy indicates highly aligned films. (c) and (d), Optical and charge transport anisotropy are maximized for intermediate shearing speeds. [37] John Wiley & Sons. CC BY 4.0. (e) Schematic of bar-coating process with O(NDI2OD-T2) polymer inset. (f) AFM reveals highly aligned films for both submonolayer (left) and thicker (right) films. (g) Mobility improves as shearing rate increases. (h) Mobility has a sensitive dependence on polymer molecular weight. Reprinted by permission from Macmillan Publishers Ltd: Nature Communication [36], Copyright 2015. CC BY 4.0.

polymer MW, intermediate MW led to the highest degree of alignment (figure 10(h)). They explained that if MW was too low, no aggregation or alignment occurred. At MW that were too high, excessive entanglement of the polymer chains precluded alignment.

Chang et al [139] also employed pre-aggregated solutions for solution shearing of P3HT and P3BT nanowires under a flat glass slide. Solutions were aggregated using UV irradiation and solution aging before being drop-cast onto pristine substrates and sheared across an electrode-patterned surface at various speeds. As the shearing speed was increased from 0.5 to 2.0 mm s^{-1} , the authors observed significant in-plane alignment of P3HT fibrils along the shearing direction, which they attributed to increasing shear forces.

Further beyond 2.0 mm s^{-1} , however, films lost alignment and became nearly isotropic, which they attributed to heating during the shearing process.

4. Interface-directed assembly

It has been widely reported that the morphology of thin films can be modified or controlled by the chemical and physical structure of the substrate-film interface. More recent investigations have also reported complex assembly at the free interface. In this section, we begin by reviewing the basics of heterogeneous nucleation and surface topology effects 4.1. Then, we describe recent studies into the role of changing surface chemistry/energy 4.2, surface morphology 4.3, and surface dynamics 4.4. Recent work has also demonstrated that interfacial effects commonly introduce morphology variation across the thickness of deposited films: from the free surface to the substrate 4.5.

4.1. Physics insights into the role of heterogeneous nucleation and surface topology effects

The presence of solid/liquid substrates, free surfaces, and other heterogeneities can affect the crystallization in multiple ways, such as by providing heterogeneous nucleation sites. In CNT, heterogeneous nucleation occurs via the same general process as homogeneous nucleation albeit with a reduced Gibbs free energy barrier (faster rate). For this reason, in systems where surfaces, defects and impurities are readily available, heterogeneous nucleation dominates. These represent the vast majority of practical cases [69]. As discussed before, the barrier to nucleation is composed of a volume term $(\Delta G_{\nu}, \text{ favorable})$ and a surface term (γ , unfavorable). For nucleation onto a surface, the penalty to forming a new surface is reduced and now depends on the substrate-liquid ($\gamma_{\rm SL}$), substrate-cluster (γ_{SC}), and liquid-cluster (γ_{LC}) interfacial free energies (4.1) [69, 140]. The interfacial free energy terms depend on the system geometry and wetting of solute cluster on substrate described by contact angle. These properties are largely determined by the chemistry of surface groups and the pairwise intermolecular interactions between the surface, the nucleating cluster and the solvent. For better wetting (stronger substrate-cluster interactions, lower contact angle), the barrier to nucleation is more suppressed [141].

$$\Delta G_{c,\text{heterogeneous}} = V \Delta G_{v} + A_{\text{LC}} \gamma_{\text{LC}} + A_{\text{SC}} \gamma_{\text{SC}} - A_{\text{SL}} \gamma_{\text{SL}}.$$
(4.1)

The morphology and topology of the underlying surface has also been shown to impact crystallization processes substantially [65, 140, 142, 143]. In particular, surface geometry (porosity) has been demonstrated to impact nucleation kinetics [65, 142, 144, 145]. Surface roughness likewise plays a role due to the presence of pits, cavities, wedges of various shapes, some of which serve as heterogeneous nucleation sites. As a result, an increase in roughness typically decreases the barrier to nucleation [146–148]. Surface curvature has also been noted to impact nucleation [143].

Compared to small molecules, heterogeneous nucleation of polymers is much less understood, particularly for conjugated polymers and crystallization from solution. Unlike small molecules, polymer chains undergo conformational change (extension) if they are to be incorporated into a perfect crystal, which often occurs slowly compared to the time available for crystallization. As a result, polymers often produce chain folded domains (lamellae) surrounded by amorphous regions [149]; the existence and extent of chain folding sensitively depends on polymer rigidity [150]. Over the past 50 years, modifications to Hoffman-Lauritzen theory have provided a framework for the crystal growth of flexible polymers [151]. Briefly, this model posits that growth rate is surface-nucleation controlled; polymers deposit onto the growth face chain by chain to form a new, atomically smooth, growth front which awaits further nucleation. Conjugated polymers exhibit several major structural differences from flexible polymers, which may affect their crystallization behavior. As discussed by Wang et al in their extensive review [17], conjugated polymer crystallization is driven by strong $\pi - \pi$ interactions and exhibits some key differences. Conjugated polymer segments are more rigid and extended (longer planar segments between folds) and tend to form 1D aggregates [17] rather than 2D lamellae. Molecular dynamics simulation support the importance of chain rigidity to crystallization behavior [152]. Liu et al demonstrated that changes to chain folding behavior in polythiophenes can lead to significantly varied morphology and crystallization behavior [150]; more rigid backbones characterized by higher interring σ bond rotation barriers did not exhibit chain fold. Investigation into interfacial assembly for polymer composites has been summarized by Ning et al in detail [153].

4.2. Surface chemistry and energy effects

The importance of the strength of substrate-semiconductor interactions (as reflected by the interfacial free energies) to nucleation of OSCs follows directly from CNT. Thus, the study and use of self-assembled monolayers (SAMs) and other interfacial 'buffer layers' to obtain favorable meso/ nanoscale ordering has become widespread [49, 154–159]. In this section, we review a small subset of works which demonstrate this principle.

Kim *et al* [160] investigated the role of SAM functionalization in the two-dimensional molecular ordering of regioregular poly(3-hexylthiophene) (P3HT). The authors spin-cast films of P3HT with thickness 70–80 nm onto a variety of SAMs surfaces terminated by groups with unshared electron pairs ($-NH_2$, -OH) and without unshared electron pairs ($-CH_3$). Using grazing incidence x-ray diffraction (GIXD), they determined that on SAMs with unshared electrons pairs, the P3HT molecules adopted an edge-on orientation minimizing the repulsive interactions with the conjugated π electrons of the thiophene backbone. In the case of methyl-terminated SAMs, P3HT molecules adopted a faceon orientation to maximize π -H interactions between the OSC and SAM layer. The use of surface treatment to control polymer stacking orientation is particularly important for optoelectronic devices in which charge transport normal to the substrate is critical.

Lee *et al* [161] have made use of lateral patterning of SAMs and surface energy differences to direct the solid-solid disordered-crystalline transition of triethylsilylethynyl anthradithiophene (TES-ADT) during solvent vapor annealing. Noting that the radial growth rate of TES-ADT spherulites depends on the surface energy of the substrate, the researchers pre-patterned the substrate with regions of fast growth (bare SiO₂) and regions of reduced growth rate on lower surface energy substrates (HDMS-SiO₂, various thioltreated Au) or higher surface energy substrates (UV-ozone treated SiO₂ and UV-ozone treated Au). They suggested that in the case of high surface energy substrates, the substratefilm interactions are strong enough to reduce molecular mobility and slow crystallization. For low surface energy substrates, they noticed that nanocrystals had already formed in the disordered spin-cast film, and that these misaligned crystals hindered directed growth. In the case of patterned SiO₂ channels growth sandwiched by pentafluorobenzenethiol- (PFBT) SAM coated Au patches on two sides, they observed a growth rate dissimilarity of 3:1. Crystals grew with the π - π stacking direction (fastest growth direction) aligned parallel to the channel with a tight orientation distribution. In further theoretical study by Fang et al [162], a model for the crystallization front growth speed based on CNT was proposed. They determined that the rate of guided crystal growth reduces with decreasing channel width down to a minimum feature size of $\sim 4 \,\mu m$.

Niazi et al [163] recently compared contact-induced nucleation and growth of two small molecule OSCs (diF-TES-ADT and TIPS-pentacene) prepared via spin-casting and blade coating onto gold electrodes. They found that in the case of spin coating, the use of highly interacting, fluorinated SAMs induced preferential crystallization on top of the contacts, as observed by Kline et al elsewhere [164]. In the case of blade coating at low speeds (ribbon-like domains) they found that the contacts had little impact for either OSC. When printing at high speeds (spherulitic domains), however, they noted that SAM treatment of the contacts led to disruption of spherulite formation and formation of small domains nucleating at the contact interface [163]. The different outcome between spin coating and blade coating may be related to the phenomenon that nucleation can either initiate from the top ink-air interface [165], or from the ink-substrate interface [25].

4.3. Surface morphology effects

In addition to surface chemistry, substrate surface morphology can have a multifaceted role in the assembly of OSCs. Factors such as surface roughness impact printing dynamics (solvent wetting and contact-line pinning [166]) as well as thermodynamic factors such as nucleation barrier in ways which can highly complicate deposition patterns. Recognizing this, research groups often use highly regular SAMs to present a smooth and uniform substrate for assembly [155, 167]. Conversely, purposely introducing substrate

20





Figure 11. (a) Schematic drawings of the growth of pentacene films onto OTS monolayers of different grain size prepared at -30 °C or 20 °C. (b) AFM images of 5 nm thick pentacene films grown on the various OTS monolayers. Substrates prepared at lower temperatures led to larger grain size in the semiconductor layer. Reprinted with permission from [167]. Copyright 2015 American Chemical Society.

morphology via roughness variation [168–173] and SAM domain size [167] have been used for tuning nucleation [147]. Notably, mechanically rubbed substrates featuring grooved patterns were shown to guide the alignment of subsequently grown polymer thin films [38, 39, 174, 175]. In this section, we feature examples of each of these techniques.

Separate from the chemical interactions, the texture of the underlying substrate can greatly impact the assembly of organic molecules such as pentacene [176, 177]. Stadlober et al [168] demonstrated that for vapor deposition of submonolayer pentacene thin films onto silicon dioxide, SiO₂; poly(vinyl phenol), PVP; poly(methylmethacrylate), PMMA; and poly(vinyl cinnamate), PVCi, grain area varied approximately inversely with surface roughness on the scale of 0.25 nm or less, with a concomitant increase in nucleation density. The authors attributed this latter phenomenon to an increased number of surface defects which served as highly active nucleation sites. Similar effects for vapor deposited pentacene thin films were reported by Fritz et al [169] (root mean square roughness up to 2 nm) for top contact devices. Recently, Kang et al [167] grew pentacene via vapor deposition onto specially prepared octadecyltrichlorosilane monolayers which had been grown at different temperatures: -30 °C, -5 °C, and 20 °C. The three films were measured to have similar surface energy and roughness but different crystalline grain sizes (figure 11(a)). It was found that larger grain size within the OTS film prepared at -30 °C led to an increase in the grain size of the pentacene film due to 'quasiepitaxial' heterogeneous nucleation at the interface and concomitant decrease in trap density and increase in FET mobility (figure 11(b)). To be clear, the examples cited in this paragraph involved vapor deposition of pentacene, which involves mechanistically distinct processes (adsorption, solidstate diffusion) than solution processing. While the quantitative scaling relations are non-transferable, the underlying



Figure 12. (a) Schematic of the 'sandwich' slow-evaporation tunnel. Reprinted with permission from [178]. Copyright 2014 American Chemical Society. (b) AFM images of substrate and deposited polymer films. Top row: unstructured substrate. Bottom row: 100 nm structured substrate. Reprinted with permission from [38]. Copyright 2012 American Chemical Society. (c) Mobility data for sandwich-cast films of conjugated polymer PCDTPT shows that charge transport is relatively insensitive to molecular weight. [39]John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

thermodynamic considerations may apply to the less-studied case of solution processing.

Investigation of roughness effects for solution-processed conjugated polymers have also been performed with various researchers observing a substantial decrease in mobility for films cast onto substrates exceeding a critical roughness [170, 171], sometimes attributed to a decrease in crystalline domain size [172]. In work by Jung *et al* [171], this threshold roughness was found to be 0.5-0.8 nm for solution casting of poly(2,5-bis(3-alkylthiophen-2-yl)thienol[3,2-b]thiophene) (pBTTT) onto low surface energy substrates. They speculate that above this critical roughness, pBTTT domains can no longer deposit conformally onto the substrate while maintaining favorable packing, leading to broken-up, smaller domains. Recently, Li et al [173] precisely controlled dielectric silica surface roughness at the scale of 0.15-0.39 nm in the dip-coating of a semi-crystalline 5,6-difluorobenzothiadiazole (FBT-TH₄(1,4)) based conjugated polymer. They determined that the performance of top-contact bottom-gate devices was highly sensitive to sub-nanometer dielectric roughness when the OSC was deposited as a monolayer, whereas the charge transport was nearly unaffected for thicker films. The authors attributed this to charge transport through layers further from the interface for multilayered films.

In a series of papers, Heeger, Bazan, and colleagues [38, 39, 174, 178] have used diamond scratched SiO₂ substrates to induce alignment in slow, macroscopically confined

solution casting (termed 'sandwich-casting'-figure 12(a)). Using this method, they found that the long axis of the polymer nanowires lined up along the 50-100 nm in width, few nm in depth scratched grooves (figure 12(b)), resulting in thin film anisotropy of 2-3 times measured by polarized UVvis spectroscopy. The hole transport was enhanced by more than an order of magnitude after alignment [38]. Interestingly, they later found that these results were insensitive to the MW of the conjugated polymer poly[4-(4,4-dihexadecyl-4Hcyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt-[1, 2, 5]thiadiazolo-[3,4-c]pyridine] (PCDTPT) that they used (30-300 kDa). They attributed this fact to the well-ordered long-range alignment they observed, which caused charge transport to occur dominantly along the conjugated backbone regardless of MW (figure 12(c)) [39]. In further work, the same group used surface-functionalized glass spacers to investigate the role of capillary forces in their 'sandwich-casting' setup. They also found that when the spacers were treated to promote wetting and the setup was tilted along the direction of the grooves, preferential solution flow aided unidirectional assembly [178]. Similar results were also observed for growth on nano-grooved flexible polymer substrates [174], offering a facile route towards high-performance flexible devices.

4.4. Surface dynamics

The surface dynamics of rubbery or liquid substrates have been shown to impact the morphology of vapor deposited small molecules (pentacene [179]) and solution coated donoracceptor polymers (DPP2T-TT, PII-2T [33]). Kim *et al* [179] investigated the role of polymer dielectric surface viscoelasticity on the assembly of vapor-deposited pentacene. They observed that below the polymer surface glass transition temperature ($T_{g,s}$), significantly lower than the bulk glass transition temperature measured from DSC), crystallization behavior was unchanged between rigid silicon and polymer substrates. Above $T_{g,s}$, however, the polymer films enter a rubbery state with substantial chain segmental motion. The researchers found increasing the deposition temperature past $T_{g,s}$ significantly suppressed nucleation and disrupted formation of large crystalline grains. As a result, the mobility dropped abruptly when the pentacene deposition temperature exceeded $T_{g,s}$.

In contrast, the opposite trend was observed for solution printed conjugated polymers. Mohammadi, et al of our group used a dynamically reconfigurable IL as substrate for printing donor-acceptor polymers DPP-2TT and PII-2T, which significantly improved film morphology across length scales and enhanced charge carrier mobilities along both π - π and polymer backbone direction [33]. The authors identify a key challenge in high throughput production of OSCs as the mismatch between timescales of polymer crystallization and evaporation rate during rapid solution casting processes. To address this challenge, they employed an IL substrate to enhance and direct conjugated polymer crystallization (figure 13(a)), mirroring how biopolymers template ion assembly during biomineralization. The IL chosen, [EMIM] [TFSI], has ultrafast surface dynamics [180, 181], and strong ion- π and electrostatic interactions with the polymer backbone (validated by NMR experiments and MD simulations). Through molecular dynamic simulations, the authors found that the cations and anions of the IL redistributed in the presence of polymers as to enrich the polymer concentration nearby up to an order of magnitude (figures 13(c), (d)). This effect diminished when IL molecules were artificially fixed in the simulation. Experimentally, they constructed dynamic templates by infiltrating IL into a nanoporous matrix to render it compatible with solution printing. Using the dynamic template as the coating substrate, highly aligned, highly crystalline polymer thin films were obtained over large area $(>1 \text{ cm}^2)$ (figure 13(b)), and charge transport was promoted several-fold along both the polymer backbone and the π - π stacking direction in the best-case scenarios. The highest dichroic ratio from IL-templated films reached 22.6 ± 0.1 (GIXD) and 10.1 ± 0.4 (UV-vis) (figure 13(e)), which were an order of magnitude greater than the reference cases (OTS treated silicon wafer), and are among the highest reported to date [37, 38, 46]. These IL-templated films yielded orientation order parameter of 0.82 for the DPP2T-TT polymer backbone; a value of 1 corresponds to 100% uniaxial alignment. Interestingly, only for the highly aligned thin films with dichroic ratio >10 (GIXD) and >5 (UV-vis) did the authors observed favorable hole transport along the direction parallel to the polymer backbone (figure 13(f)).

4.5. Vertical heterogeneity of morphology

Many researchers have noted that the morphology of solutionprocessed films may vary across the height of the film (an effect here termed vertical heterogeneity), and although the exact mechanism is still under investigation, it is widely agreed that interfacial phenomena are a cause [36, 37, 182, 183]. We note the recent excellent review by Jones *et al* on surface induced phases for small molecules [184]. In this section, we highlight several instances of vertical heterogeneity observed for conjugated polymer films.

Over a decade ago, Kline et al [185] demonstrated that for spin-cast P3HT onto OTS-treated substrates, there can be substantial variation in morphology from the top surface to the buried interface. Specifically, they determined that surface-induced nucleation led to the formation of a highly crystalline 'edge-on' layer of P3HT, with more poorly oriented crystals in the bulk (as determined by XRD rocking curves). More recently, an investigation by Duong et al [186] used GIXD to characterize spin-cast P3HT from various solvents. They also observed an ultrathin layer of ordered, edge-on aggregates buried under a disordered, 'face-on' bulk (figure 14(b)). Furthermore, they described film growth as composed of competing crystallization processes (figure 14(a)). As the film dries, there is initial, rapid edge-on growth of the interfacial layer. Then, slower growth of edge-on aggregates templated by the interfacial layer occurs concurrently with precipitation of metastable face-on aggregates from the bulk. They furthermore reported that by varying film thickness, they are able to vary the fraction of bulk-nucleated face-on to interface nucleated edge-on aggregates in the film (figure 14(c)). They observed that for their top-contact, bottom-gate devices, mobility is largely unaffected by the bulk morphology, which they attribute to the fact that charge transport occurs primarily through the highly ordered, edge-on aggregates at the interface only. Several recent studies have also reported that the predominance of heterogeneous (substrate-induced) versus bulk nucleation depends on kinetic factors such as drying speed [187–190].

Recent work by Qu, et al from our group has established a link between flow-driven assembly, interfacial effects and vertical heterogeneity of conjugated polymer domain alignment [165]. The authors have found that blade-coated poly(diketopyrrolopyrrole-co-thiophene-co-thiono[3,2-b]thiophene-co-thiophene) (DPP2T-TT) thin films comprise highly aligned fibrils at the free surface, with polymer backbones directed along the long axis of the fibril (along the printing direction). In the bulk, however, this alignment is partially or totally lost depending on film thickness, and fibrils are isotropic in-plane or aligned weakly transverse to coating direction (figure 15(a)). These conclusions are supported by characterization via GIWAXS, AFM, and polarized UV-vis. Films were printed in the evaporative regime at a fixed speed of 0.5 mm s^{-1} and temperature (25 °C). In order to vary the fraction of interfacial species to bulk, film thickness was modulated from 20.8 ± 0.8 nm to 168 ± 7 nm by changing solution concentration from 3 to 25 mg ml^{-1} . Charge transport measurements reveal that a much higher hole mobility anisotropy exists at the free interface than at the buried substrate-interface (figure 15(b)), with preferential transport along polymer backbones in either case. The mechanistic origin of the vertical heterogeneity is



Figure 13. (a) Schematic of the solution coating process over the ionic liquid infiltrated anodized aluminum oxide (AAO) substrate. (b) AFM images demonstrate that printing on the dynamic ionic liquid surface dramatically increases grain size and alignment transverse to the coating direction (white arrow). (c) Excess probability distribution for dimeric DPP2T-TT in the presence of dynamic versus static ionic liquid surfaces. (d) Radial distribution function, g(r), for ionic liquid cations and ions near the oxygen atoms in DPP2T-TT (left) and in the presence of chloroform solvent (right). (e) Ultraviolet–visible dichroic ratio and calculated order parameter, S, demonstrates that alignment is greater for thinner films. (f) Schematic of change in film morphology and charge transport pathways in thin (left, 20 nm) and thick (right, 200 nm) films. Reprinted by permission from Macmillan Publishers Ltd: Nature Communications [33], Copyright 2017. CC BY 4.0.

depicted in figure 15(c). The authors propose that crystallization begins at the free interface with the formation of a skin layer that delays crystallization within the bulk, supported via estimation of a high Peclet number (33). Change of in-plane alignment is attributed to differences in flow characteristics in the two regions. Near the free interface, shear approaches zero, but a strong extensional flow develops due to the evaporative flux gradient described in section 3. Extensional flow applies a net torque to

the anisotropic fibrils, causing them to align parallel to coating direction. The bulk, however, exhibits shear-dominant alignment which acts to orient fibrils in the direction of the vorticity, orthogonal to the coating direction.

Advanced characterization studies using near-edge x-ray absorption fine structure spectroscopy (NEXAFS) have also demonstrated vertical heterogeneity of morphology for films of conjugated polymers. Patel *et al* [191] used NEXAFS and



Figure 14. (a) Schematic of proposed solidification mechanism for P3HT. Initially, edge-on aggregates form rapidly at the substrate interface and begin to grow into the bulk. More slowly, face-on aggregates begin to form from the bulk and air interface to develop the final microstructure. (b) Sketch of edge-on and face-on crystallites with labeled stacking dimensions. (c) Fraction of face-on aggregates as a function of film thickness as determined by GIXD. As thickness decreases, edge-on stacking dominates. Reprinted figure with permission from [186]. Copyright 2012 by the American Physical Society.

GIXD to investigate molecular orientation of fibrillar regioregular cyclopentadithiophen-thiadiazolopyridine co-polymer (PCDTPT) films prepared via blade-coating (figure 16(a)). They determined that while the film retained an out-of-plane edge-on orientation under a variety of printing speeds and substrate treatments (nanogrooved or smooth), in-plane alignment of the bottom surface was significantly improved by the use of nanogrooves (figure 16(b), S is an order parameter reflecting out-ofplane alignment, while η reflects in-plane alignment). Studies by Schuettfort et al [182, 183] combined GIWAXS and NEXAFS to characterize the morphology of spin-cast thin films of conjugated polymer P(NDI2OD-T2). Interestingly, they found that polymer chains at the free surface were predominately edge-on, while those of the bulk where once again face-on. They noted that GIWAXS alone was not sufficient to elucidate morphology of the accumulation layer at the top surface. It is possible that a similar change in orientation at the free interface has been ignored by other researchers due to lack of precision in characterization.

5. Summary

In this review, we have sought to explain the critical role confinement, fluid flow, and interfacial phenomena during non-equilibrium assembly of organic semiconducting molecules. We began with a review of charge transport in OSCs its dependence on thin film morphology. In following sections, we focused on establishing a mechanistic understanding of how assembly outcomes couple closely to the solution processing environment, supported by salient examples from the recent literature. And it is evident that solution processing can modulate morphology at every length scale. For instance, we have seen that molecular packing and polymorphism are controlled by vertical confinement and substrate interactions. At a larger scale, crystallite nucleation, growth, and alignment can be controlled by lateral confinement via competitive evolution, fluid flows, and surface dynamics, chemistry, and morphology. In solution printing, it is thus not only desirable, but unavoidable that a combination of these phenomena guide assembly, morphology, and electronic performance. Thus, we hope that this review will help guide the rational design of solution printing techniques based on a fundamental understanding of directed assembly. As interest in organic electronics continues to grow, achieving a better understanding of the non-equilibrium assembly behavior of organic semiconducting polymers and small molecules will doubtless attract significant research and industrial attention. Ongoing challenges include better understanding phase transition and charge transport mechanisms in semiconducting polymers as



Figure 15. (a) Schematic of vertical heterogeneity of morphology at the top surface of the film versus the bulk. Insets are a combination of data obtained from AFM (green) and GIWAXS (yellow). (b) Hole mobility anisotropy as a ratio of mobilities parallel and perpendicular to coating. Anisotropy is significantly higher at the top surface. (c) Illustration of the proposed alignment mechanism. The extension-dominated flows near the free surface align parallel to coating, while the deeper shear gradients align polymer backbones transverse to coating. Reprinted with permission from [165]. Copyright 2017 American Chemical Society.



Figure 16. (a) Schematic of the blade-coating process, where the printing direction is parallel to the substrate nanogrooves. (b) Plots of the out-of-plane (*S*) and in-plane (η) order parameters versus coating speed for the top and bottom surfaces of the films as determined by NEXAFS and GIXD. Reprinted with permission from [191]. Copyright 2015 American Chemical Society.

well as establishing the processing-morphology-charge transport relationship to enable rational design approaches.

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