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Dewetting Stability of ITO Surfaces in Organic Optoelectronic Devices

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1. Introduction

Heterojunctions are inherent in and essential to all molecular optoelectronic devices. In organic light emitting diodes (OLEDs), the interfacial region between the active organic layers and the inorganic contacts plays a primary role in device performance, through the control of effective carrier injection and long term device reliability. In organic solar cells (OPVs), heterojunctions play a defining role in all of the major processes: charge separation relies on effective organic/organic interfaces; charge transport is critically determined by the structure of the thin film, controlled by the organic/inorganic interfaces with substrates; and charge extraction can only occur at high quality inorganic/organic interfaces at the electrodes. Studies of various organic/inorganic interfaces have indicated that a wide range of interfacial types are possible in organic optoelectronic devices. To foster the next generation of devices, it is critical to understand the connections between heterojunction structure and morphology, and device performance. This connection is especially important with regard to the interfacial stability and lifetime in organic optoelectronic devices. Control of the complex interactions and the microstructure at the electrode-organic interfaces would allow the optimization of performance and lifetime.

In this chapter, we aim to review the current state of the art with regards to interfacial stability and control of the anode (indium tin oxide) electrode/active layer interfaces to understand the performance of organic optoelectronic devices. From examples of our own research and others relating to interfacial morphological changes, a comprehensive picture of the role of the interface in device stability can be formed. This chapter begins with a brief overview of degradation in organic devices, including definitions. Following that, the main focus of the chapter is on the morphological instability at the ITO surface as a main mechanisms of device degradation. Various approaches to overcoming device instability are given,

with special attention paid to the various interlayers that have been introduced into devices. This also includes examples where dewetting is used advantageously to produce novel device architectures and surprising solutions to device degradation.

2. Degradation

Unlike the field of inorganic electronics, organic electronics encompasses highly diverse technologies with devices that can be prepared with different architectures, using many different materials, processed by many different methods. Unlike their inorganic counterparts, all organic devices are to some extent unstable and their performance degrades over time [1]. After efficiency, lifetime is the second most important parameter for organic devices [2]. While inorganic semiconductors are for the most part intrinsically chemically stable, and insensitive to the ambient environment, for organic devices, the polymer or small molecule active layers themselves, the inorganic electrodes, and the interfaces between them are all potential locations for degradation. Degradation for organic devices is, therefore, highly complex and typically cannot be described by a single mechanism.

OLEDs [3] and OPVs [4-6] are known to degrade during both operation and storage (called shelf life or dark stability). From the moment the metal electrode is applied, the device is subject to degradation: in vacuum, in the dark and under operation [1]. The three physical mechanisms that degradation can take are the loss of conjugation and irreversible deterioration of the active organic layers; degradation of the interface conductive properties; and mechanical disintegration of device (dewetting, phase segregation, crystallization), all of which manifest themselves as a change in the electrical properties. The basic requirement of an emissive or absorptive technology with regards to lifetime is to provide adequate device performance over the intended time of use for the application. Stability for short term displays, such as cell phone monitors, requires different criteria than long term high performance solid state lighting. For solar cells, the requirements are different still with exposure to external environments that are not even a consideration for OLEDs, aggravated by the fact that many organic molecules undergo serious degradation in electrical properties upon exposure to light [7-11]. The desire for flexible substrates for both technologies brings yet another set of challenges. These requirements have stimulated much research in the thirty years since the first OLEDs and OPVs were produced at Kodak [12-13].

Though efforts are underway to establish standardized protocols for OLED and OPV characterization [14-16], official qualification procedures have not yet been established for lifetime testing. Stability testing protocols were proposed for OPVs by consensus among 21 international research groups in May 2011 to improve the reliability of reported values [17], and are still in the process of being adopted by other researchers. A comparison of reported lifetime values between different groups is difficult, as device lifetime is greatly affected by the driving voltage, number of duty cycles, length of rest cycles, initial luminance or power conversion efficiency, deposition conditions, and exposed environment. Though it is possible to estimate values for standardized test conditions using acceleration factors for both

OLEDs [18] and OPVs [19-20], in general it is more instructive to look at the relative improvement in the device lifetime, which is how it will be discussed in this chapter.

Known degradation mechanisms include diffusion of molecular oxygen and water into the device, crystallization or oxidation of organic layers, degradation of interfaces, inter-layer and electrode diffusion, electrode reaction with the organic materials, electrode oxidation, phase segregation or intermixing, dewetting from the substrate, delamination of any layer, and the formation of particles, bubbles, and cracks. There are four major decay mechanisms related to the bulk active layers: organic layer oxidation, crystallization, charge carrier/exciton damage, and photobleaching. There are also four decay mechanisms directly associated with degradation at the top contact: electrode oxidation, dark spot formation, electrode bubbling and delamination, and metal diffusion. As this chapter is focussed on the morphological stability on the anode surface, interested readers are directed to recent topical reviews specifically focussed on polymer photovoltaics [21-22], on OLEDs [23], and on interfaces [24], for a comprehensive look at degradation and degradation mechanisms. As many of the issues related to anodic degradation at interfaces are common for both OPV and OLEDs, and for polymer and small molecule active layers, all types will be discussed within this chapter.

3. Dewetting theory

It is the interplay between molecule-molecule self-interaction and substrate-molecule interactions that determines the stability on a given surface [25-26]. For thin films (<100nm) coated onto non-wetting substrates, van der Waals forces play the dominant role in determining film stability [27-28]. The Hamaker model [29] allows quantification of the instabilities that arise in thin films when VdW forces induce an attractive potential between two interfaces

$$E(h) = \frac{-A_H}{12\pi h^2} \quad (1)$$

where A_H is the effective Hamaker constant for the film and film-substrate interactions ($A_H = A_F - A_{FS}$) and h is the film thickness on an infinite substrate.

The thermodynamic instability is given by the “disjoining pressure” [26, 30], or the second derivative of the energy. For a single film, this is given by

$$\frac{d^2 E(h)}{dh^2} = \frac{-A_F + A_{FS}}{2\pi h^4} \quad (2)$$

As the disjoining pressure is inversely proportional to the film thickness to the fourth power, producing stable and defect free films is particularly difficult as the thickness decreases.

At the lowest limits, thermally or mechanically induced fluctuations (capillary waves) tend to cause film rupture [27, 31-32], a process known as spinodal dewetting. The surface undulations give rise to a pressure gradient which drives film instability if the effective Hamaker constant is negative (i.e. non-wetting) [31]. As the film thickness decreases, there is a trade-off between destabilizing vdW forces and stabilizing surface tension that leads to an amplification of capillary waves [33] and can therefore cause spontaneous rupture if the film is thin enough (typically <200nm, greatly enhanced at <10nm [32-33]). Additionally, the glass transition temperature (T_g) is lower for thin films due to confinement effects [34], further aggravating dewetting effects. Most OLED and OPV layers are less than 200nm thickness, making them highly susceptible to spinodal dewetting.

Aside from capillary wave destabilization, dewetting can be driven by nucleation and hole growth from defects (i.e. airborne particles) [27, 35], by the release of residual stress [36], by density variations [37] or by thermal expansion mismatch between substrate and organic film [27, 38], which can be highly anisotropic for organic molecules [39].

Dewetting effects are strongly related to the crystalline structure of organic thin films [40], and are thus quite different from the wetting – dewetting problems of an isotropic liquid. The situation is further complicated by the fact that many organic molecular crystals exhibit several distinct crystal structures, which are energetically very similar and may coexist [41-42]. For crystalline films, pseudo-epitaxy with the substrate can simultaneously drive both film stabilization and dewetting [42]. The predominance of physisorption, combined with the relatively large size of the molecule compared to the inorganic substrate allows organic films to accommodate much larger strains than those observed in inorganic epitaxy [42]. As having lateral organization in the thin film can stabilize against dewetting [40], the amorphous films often used in devices are even more susceptible to extreme morphological instabilities.

Regardless of the mechanism, dewetting begins with a nucleation event leading to the formation of a hollow which proceeds to grow by the transport of material away from the nucleation site to a retreating rim surrounding the hole. These holes eventually intersect, leading to the formation of ribbons of material along the contact line [27].

4. Anode/active layer contacts

The interface at the high work function electrode is especially influential in device stability as it often also forms the substrate upon which subsequent layers are deposited. The electrical, chemical, and morphological features of the electrode surface play a significant role for both OLEDs and OPVs as the quality of the interface and of the hole transporting (electron donating) (HTL) film deposited on it [38, 43] is often the limiting feature of the device, both for performance [38, 44-47] and stability [9, 38, 48-50].

For a high quality device, the HTL needs to fulfill a number of criteria including high hole mobility, good energy level matching with anodes and other active layers, good thermal

properties, high optical transparency to visible light, and a smooth, often amorphous morphology with good film forming properties [12, 51-59]. In small molecule OLEDs, excellent examples, and the first HTL materials [12], are triphenylamines such as TPD and NPB; in polymer OLEDs and OPVs, this function is often fulfilled by PEDOT:PSS (Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) [60].

An indium tin oxide (ITO) thin film on a glass substrate could be considered an archetypical anode for both OLEDs and OPVs due to its high transparency over the visible region, high electrical conductivity, and high work function [61-64]. Although ITO use is almost ubiquitous as the transparent conducting electrode in organic optoelectronic devices, it has a number of drawbacks, including variations in the surface properties depending on preparation method [47, 62, 64-67], poor energetic compatibility with active organics [68-69], and instability with a wide variety of hole transporting materials that directly impacts on the device stability. ITO has a bixbyite crystal structure [70-71] and the surface of polycrystalline thin films are dominated by the oxygen terminated (111) plane with many dangling O bonds [72] (see figure 1). Due to this rich oxygen landscape, the electrode surface has a highly variable electronic structure [73] that can be modified by a wide variety of surface treatments, and is very susceptible to moisture [74] and light irradiation [63, 75]. As the difference between the active layer highest occupied molecular orbital (HOMO) and the electrode surface work function plays a limiting role in device performance [76], ITO surface modification is typically focussed on increasing work function, by passivation with surface-active species [77] or by over 50 kinds of chemical and physical treatments [76, 78-79].

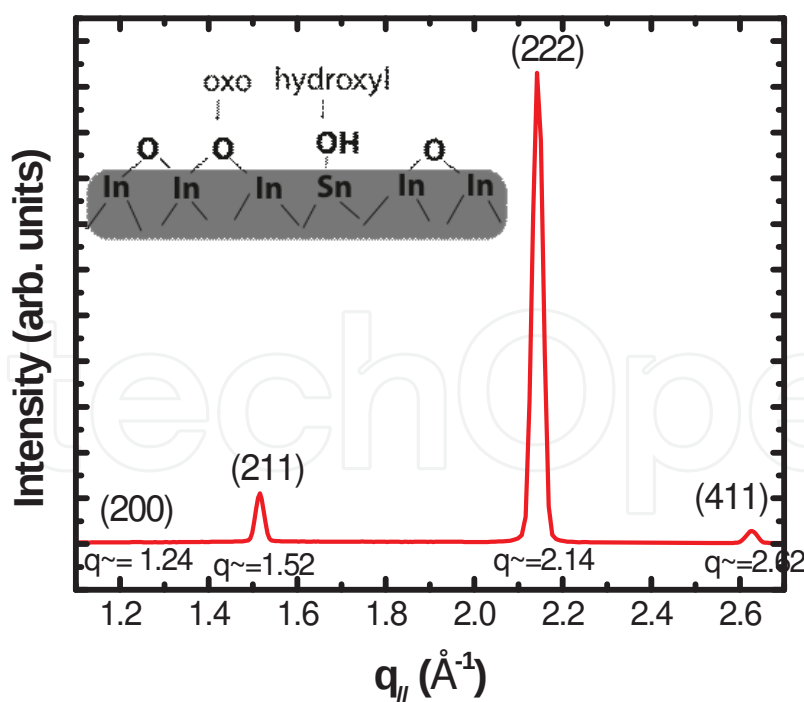


Figure 1. Grazing incidence x-ray diffraction of polycrystalline indium tin oxide surface with major planes identified showing the predominance of (111) planes, with a schematic of the ITO (111) surface with hydroxyl and oxo-terminations as an inset.

5. Morphological instabilities on ITO

In general, instability at the ITO/active layer interface can be related to morphological, chemical and electronic changes over the lifetime of the device. There are four major criteria which lead to an unstable interface: surface energy mismatch, low glass transition temperature (T_g) materials, surface reactivity with organics, and work function instability. The surface energy mismatch and low transition temperatures are the driving characteristics for the morphological instability discussed in this chapter.

As the ITO surface consists of many dangling O, surface treatments tend to saturate the surface with hydroxides, making it hydrophilic [80]. Advancing aqueous contact angles range from ~ 0 – 30° on treated surfaces [80–86]. By contrast, many electron donating organic materials are hydrophobic. Two widely used HTLs for small molecule OLEDs, TPD and NPB, have advancing contact angles of 80° , and 90° respectively [80]. This large mismatch in surface energy makes it difficult to grow continuous films necessary for devices. Thermally evaporated oligomers, such as NPB [87–88] and TPD [89] as well as many others, show a strong tendency to island (Volmer-Weber) growth (see figure 2a), with highly active surface diffusion to step edges and defects. Often, the initially formed islands can ripen laterally with continued deposition to form what appear to be continuous films [87], which are highly metastable. For molecules deposited from solution, the surface energy mismatch with ITO can also lead to inhomogeneous deposition, as seen in figure 2b for PEDOT:PSS.

Even when continuous films are able to form upon deposition, the relatively low T_g for many oligomer hole transporting materials (NPB 96°C , TPD 65°C [53]), can lead to dewetting under mild thermal treatments or even with storage over time at ambient temperatures [42, 90]. Diindenoperylene, a novel material of interest due to its well defined ordering [91], interesting growth behaviour [92–93], promising electron transport properties [94–95], favourable electronic structure [96], long exciton diffusion lengths [97], has recently been shown by us to have tuneable behaviour in solar cells based on its morphology [98]. As seen in figure 3, upon initial deposition, films of DIP form large flat islands on ITO with a high

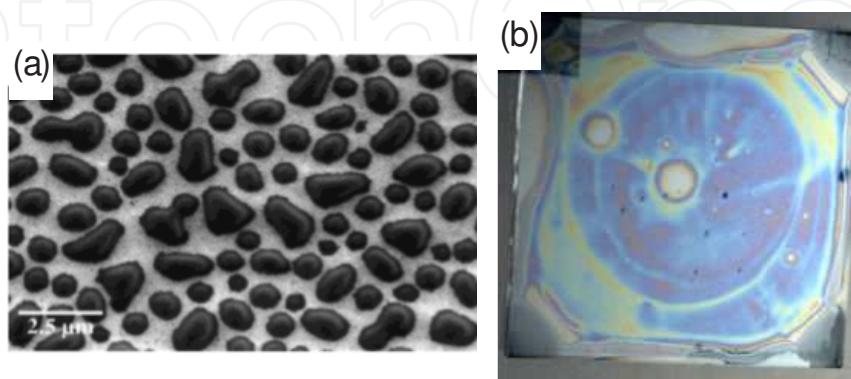


Figure 2. (a) SEM image of $(\text{EtCz})_2$ films deposited at $T_s = 90^\circ\text{C}$ on a bare-ITO substrate. Reprinted with permission from [68]. Copyright 2002 John Wiley and Sons (b) Incomplete coverage of ITO surface with PEDOT:PSS deposited from solution.

degree of order [98]; however, they are metastable at room temperature, showing very strong dewetting during storage at room temperature under vacuum for one month [99].

Though sometimes observed under high temperature treatments [3, 100], dewetting is not as significant a problem for polymer systems, due to the generally higher T_g of polymer materials [101]. However, device performance is heavily influenced by the morphology, especially in polymer-based bulk heterojunction solar cells [102]. The optimal morphologies require the spontaneous phase segregation of the donor and acceptor polymers during co-deposition. As such, the interpenetrating morphology required for high device performance, is also highly metastable, and driven by the substrate surface energy mismatch [103-105].

Beyond the limitations in the shelf life, metastability of the active layers can be a significant driving force for degradation during operation. The organic layers are subjected to thermal stress in a variety of ways at a number of points in the device lifetime. During fabrication, the metal cathode is vacuum deposited directly on the organic films, which can lead to localized heating of the organic film. During normal device operation, low mobility in the organic films can lead to high electric fields and local Joule heating [106-110]. Zhou et al. observed that the surface temperature for TPD based OLEDs can reach as high as 86°C, suggesting that the temperature inside the actual devices could be higher than 200°C [110]. Tessler et al. [111] saw temperature variation during operation as high as 60°C in the recombination zone. As semiconducting organic molecules tend to show poor natural heat dissipation [110, 112-113], such large temperature variations cannot be handled by the limited heat sink at the glass surface. Choi et al. [114] were able to find an inverse correlation between the OLED device lifetime and the internal device temperature, as measured by a scanning thermal microscope.

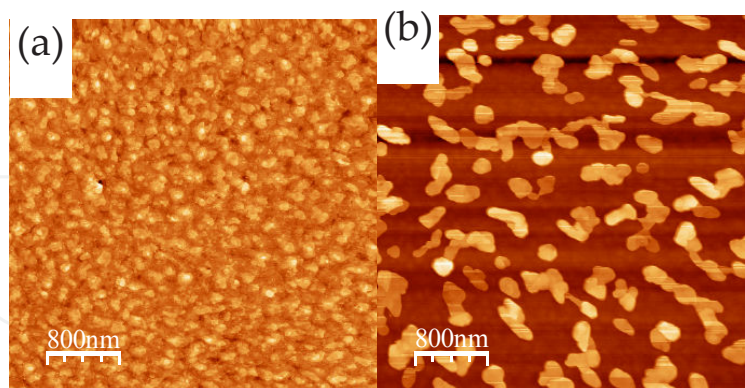


Figure 3. AFM micrograph of diindenoperylene (DIP) deposited on ITO surface at room temperature (a) immediately after deposition (b) after one month in a low vacuum, low humidity environment.

OPVs have the additional burden of illumination induced heating and cooling cycles, which can cause the internal temperatures to reach well beyond the T_g when coupled with Joule heating. Sullivan et al. [115] observed that UV induced heating (through UV absorption by the glass substrate) lead to a structural reorganization of pentacene, decoupling it from the ITO surface, causing kinks to form in the current density-voltage (J-V)

curves for PEN:C₆₀ solar cells. Paci et al. [116] observed that the metastable morphology of P3HT:PCBM solar cells was modified in a similar way under illumination as by deliberate thermal annealing.

Irreversible device failure has also been observed in operating OLEDs [38] and OPVs [117] heated above T_g of one of the molecular organic components. For many devices, the weakest link in the device lifetime is the low T_g of the HTL immediately adjacent to the ITO surface [117-121], as many electron accepting and transporting materials have relatively high T_g [53]. Fenter et al. proposed that device failure was a result of significant expansion of the least thermally stable material, TPD, leading to delamination from the ITO surface [38]. Do et al. for MEH-PPV [3] and Choi et al [114] for PFO, observed buckling behaviour, where the polymer layer completely detached from the ITO in a number of areas on the electrode surface. This inhomogenous delamination results in significant disruption of the multilayer structure, which can cause non-uniform contact between the electrode and organic layers. TPD undergoes significant structural changes even well below its glass transition temperature: at ~60°C, changes have been observed in its thickness and density by XRR [38] and serious dewetting has been observed by AFM [122]. Tokito et al. [123] observed a direct correlation between the glass transition temperature of the HTL and device degradation as a function of temperature; however, this was disputed by Adachi et al. [51], who saw no correlation specifically with the T_g, relating the stability more to the interfacial barrier to injection (and hence to Joule heating [124]). It is conceivable that dewetting, which compromises the integrity of the hole transport layer, would lead to inefficient hole injection by non-uniform coverage, and a modification of the other layers deposited atop the dewetted layer [125].

Any local failures due to morphological inhomogeneities on the ITO surface (In spikes, thinner organic regions, etc) [90], where the high local electric field would already encourage Joule heating, would also tend to both accelerate and be accelerated by dewetting. As many materials are also subject to annealing heat treatments for improved performance, film metastability can have catastrophic consequences for the device in operation. Do et al. observed complete separation of the active MEH-PPV layer during operation in a number of areas on the electrode surface, resulting in dead areas that eventually covered the whole surface [3]. Even without dewetting induced failures, over-annealing or elevated temperature storage over long time can lead to significant phase-segregation beyond the exciton diffusion length for bulk heterojunction devices [126-128], which ultimately decreases the performance over time [101, 127, 129-130].

Both dewetting and work function instability at ITO surfaces are accelerated by humidity [86, 90] or light irradiation [115-116]. The same mechanism is at work in both cases – the modification of the hydroxyl termination on the ITO surface [47], which leads to a change in the surface energy. This also helps to explain the strong correlation observed between the interfacial barrier to hole injection and OLED device degradation [51, 131-133], as both are related to this hydroxyl terminated surface.

6. Preventing interfacial morphological instability

There has been much research into methods of counter-acting dewetting from the ITO surface, as the integrity of the active layers is of paramount importance in the device performance and stability. Incorporation of the unstable film into a device, with a multi-layer film stack, already significantly suppresses the dewetting of single films [40, 125, 134]. Deliberate use of a stable inorganic capping layer, such as Al_2O_3 [135] or an electrode metal such as Ag [136] or Au [137], within the device can also greatly improve the stability of the underlying organic phases. Utilizing a rough substrate can also encourage wetting and stability [32, 46, 138-140], but that can lead to undesirable morphologies in the original deposition [99]. In order to further improve the stability at the ITO surface, two general approaches have been adopted: increasing the T_g of the active layer itself, or introducing stabilizing interlayers.

6.1. Increasing the glass transition temperature

There has been much work over the last 30 years focused on finding new hole transporting/electron donating molecules that have high morphological stability, as recently reviewed by Shirota [56]. General strategies for designing morphologically stable molecules were developed by Shirota [55-56], Wirth [141] and Naito and Muira [53] -- the underlying philosophy was to decrease the degrees of freedom and increase the rigidity of the molecules, through replacement/augmentation of the core; linear or branch linkages; or long substituents leading to starburst type molecules. The first and most widely used replacement of the original triphenyldiamine used in the Tang OLED (TPD) [12], was a benzedine derivative, NPB. It had excellent hole transporting and film forming properties in addition to a slightly higher T_g ($\sim 96^\circ\text{C}$) [133, 142-143]. Though NPB was widely adopted in OLEDs, unfortunately it too had a propensity to crystallization and dewetting albeit at higher temperatures [118, 144]. The original family of triphenyldiamines were successful in most other aspects as a hole transporting layer leading to the development of various derivatives, including triphenyl amines [120, 123], biphenyl amines [142], binaphthalene diamines [145], asymmetric triaryldiamines (TPD derivatives) [146], triphenylamine-based starburst molecules [147-149], and recently star-shaped oligotriarylamines [150]. Other approaches include using a fluorene core to increase the rigidity of biphenyl HTLs [121], carbazole derivatives [151], vinyl-type polynorbornenes with ethyl ester linked triarylamines [152], thermocleavable densified polymers [153-154], defect reduced polymers [130, 155-156], among many others. Though new materials are synthesized regularly with significantly higher glass transition temperatures than the classically utilized molecules, the correct combination of high hole mobility, good energetic compatibility with electron-accepting materials, and good optical absorbance has proven elusive, and many of these materials currently do not see widespread use in devices.

6.2. Interfacial structure stabilizing interlayers

Due to the difficulties in finding complete replacements to traditional hole transport/electron donating layers, much research has gone into introducing thin adhesion-promoting buffer layers between the active material and the ITO anode. The ideal interlayer should ex-

hibit strong adhesion to both the anode and the HTL, via physical adhesion or chemical bonds. Other desirable criteria for an effective buffer should include (1) high hole transport mobility; (2) easy deposition onto anode surfaces via straight-forward methods such as spin-coating, vapor-deposition, or self-assembly; (3) good conformal matching to substrate; (4) substantial thickness control; and (5) well-defined microstructure free of pinhole defects.

In addition to promoting adhesion and stabilizing against dewetting, buffer layers often have a number of added benefits for the device, including enhancing initial device performance [81, 86, 133, 157-167], encouraging better charge balance [45, 168-169] (often by preventing hole injection [131]), preventing chemical reactions between the active layer and ITO [9, 162, 170-172], blocking In and Sn diffusion [170, 173-176], increasing mechanical strength [177], and smoothing the ITO surface (preventing electric field inhomogeneities that are potentially responsible for dark spot formation) [64, 161-162, 171, 175-176, 178-180].

There are two broad classes of interlayers that have been used to suppress dewetting specifically, or device degradation more broadly: modifications of HTLs (covalently bound or polymerized versions of traditional hole transport layers; HTL materials doped with or into a stabilizing material); and any organic, metal or oxide buffer that is not also used as the HTL.

6.2.1. *Generic buffer layers*

The most widely explored class is that of generic buffer layers. These run the gamut from vapor or solution deposited organic layers, self-assembled monolayers, dielectrics, conducting oxides, insulating oxides, to metals. Virtually every element in the periodic table has been incorporated into the device with the aim of increasing the device lifetime. A wide variety of interlayers have also been introduced with no interest in their stabilizing properties, though film stability often also results as a side effect. These interlayers include metal doped ITO [181-183]; oxides including Y_2O_3 [184], Tb_4O_7 [184], TiO_2 [184-185], ZnO [184], Nb_2O_3 [184], Ga_2O_3 [184], SnO_2 [184], CuO_x [186], Fe_2O_3 [187], SiO_2 [188], VO_x [189-190], RuO_x [189], AZO [189], Al_2O_3 [191], NiO [192]; ultrathin metal layers such as Ni [184], Au [184], Sn [184], Pb [184]; F_{16}CuPc [193]; conducting polymers [194]; and a wide variety of self-assembled monolayers [44-45, 195]. While this is not an exhaustive list, it demonstrates that a wide variety of buffer layers have been attempted by researchers. The focus for the rest of this section will be on interlayers that are specifically shown to influence the device lifetime or stability of the organic layers deposited on the surface. The reported improvements in device lifetime for a variety of interlayers are summarized in table 1.

One of the first and still most widely used buffer layer for small molecule OLEDs is copper phthalocyanine (CuPc). Though an interesting semiconducting material in its own right [196-199] with current widespread use in solar cells as an electron donating material [200], it was first introduced as a stabilizing buffer layer for NPB [133]. It has been extensively employed as an anode HTL buffer layer, mostly due to its reported ability to enhance OLED performance [44, 132-133, 164, 201-202], energetic level matching [203-205], high thermal stability [204, 206], and low cost as a result of its use as a blue dye [207]. Other phthalocyanines have also been employed as buffer layers below the active layers [207]; the recent use of

ZnPc [63], for example, improved the stability of ZnPc:C₆₀ bulk heterojunction solar cells by ~3.5x (see table 1).

The use of CuPc prevents the ambient dewetting observed for NPB directly deposited on ITO [88], providing a metastable equilibrium structure for devices at room temperature. CuPc was also seen to increase the crystallization temperature of NPB significantly, to above 160°C [118, 144, 208]. This stabilization effect allows for longer lifetimes: Aziz et al. [169] observed more than a 5x increase in the luminance t_{50} using CuPc as a buffer (see table 1). Though the impact varies, many researchers have seen significant improvements in stability using CuPc under ambient conditions. However, poor device performance has been observed if the devices are used at even mildly elevated temperature [209-212]. It has been established that moderate heating as low as 60°C leads to CuPc crystallization [80, 88] (see figure 4), intermixing with NPB [118, 144, 213] and TPD [213], and dewetting. Ultimately, CuPc-buffered ITO does not prevent HTL crystallization and decohesion upon heating to temperatures near/above the HTL T_g. Additionally, CuPc is highly reactive with the ITO surface [118, 214], and its use leads to significant increases in the driving voltage for OLEDs [215]. To overcome some of these difficulties, researchers have used another buffer layer under the CuPc layer, such as Pr₂O₃ [158] or LiF [161], with some success.

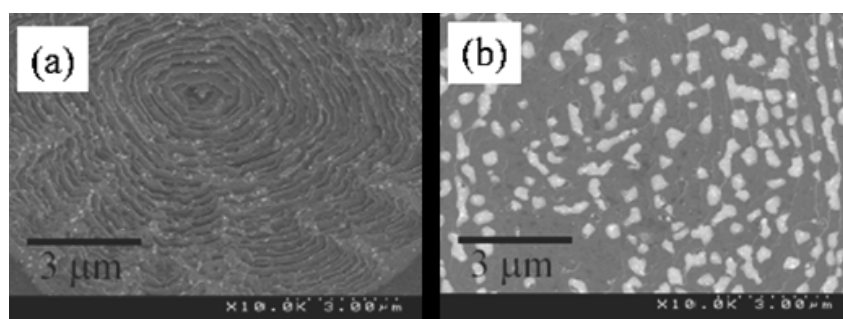


Figure 4. SEM micrographs for crystalline areas of: (a) CuPc type sample, and (b) NPB type sample. Reprinted with permission from [88]. Copyright 2007 American Institute of Physics.

The second commonly used interlayer material is PEDOT:PSS [234]. Due to its high hole mobility [217, 234], PEDOT:PSS is often actually classified as a conductor and referred to as a polymeric anode [50], rather than a buffer layer. Considered as an essential component of most polymer based devices, both PLEDs and OPVs, it is used in almost all polymer solar cells for its significant impact on the device performance rather than to improve stability. It was, however, initially introduced into PLEDs as a stabilizing layer [60, 166, 235] and many researchers saw substantial improvements in device lifetimes with its use [9, 60, 166, 235-237] (e.g. ~7x improvement in luminance t_{50} [217] table 1). The introduction of PEDOT:PSS into PLEDs allowed the device lifetime to go from a few days to hundreds [60, 166] or even thousands [235] of hours, effectively making early organic devices into a viable technology. Figure 5 shows DIP deposited on PEDOT after storage in vacuum for one month [99]. Unlike on bare ITO, where severe dewetting was observed (figure 3), the film is completely stabilized with a PEDOT buffer layer. X-ray

diffraction measurements (figure 5c) confirms that the crystal structure is also preserved during storage [238]. Although, PEDOT:PSS is widely used, much like CuPc, there are a number of drawbacks, most significantly its extremely high reactivity with ITO [59, 170, 239-241]. In some cases, this is a benefit, as the high solubility of In in PEDOT:PSS allows it to be used as a barrier against In migration into PPV [174, 242], or PCBM [242] improving the device stability. Again much like CuPc, one approach to overcoming these limitations is to introduce an underlying buffer layer, such as diamond-like carbon [170] or alkylsiloxane SAMs [173] to prevent In diffusion. PEDOT:PSS is also prone to oxidation [239], both from moisture in the ambient environment [243] and from the ITO surface, which decreases the device performance and stability [75, 230, 239, 244-245]. Unencapsulated P3HT:PCBM solar cell devices with PEDOT:PSS show rapid decay of the short circuit current, with t_{80} essentially equal with or without ITO [246]. Recently, the group of Karl Leo in Dresden introduced an ethylene glycol soaking treatment that improves solar cell lifetime by a factor of 1.3, by removing the insulating and hygroscopic PSS components in the layer [233]. As these PSS components can also react with other polymer layers [247], eliminating excess PSS leads to greatly increased lifetimes.

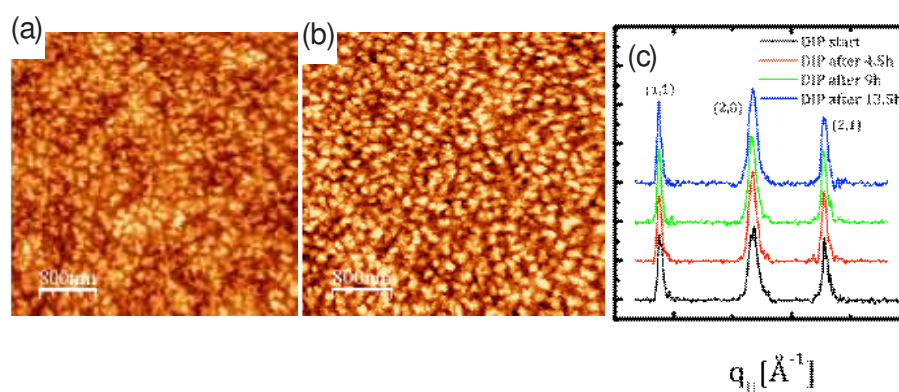


Figure 5. DIP on PEDOT:PSS (a) AFM micrographs of the bilayer structure as deposited (b) AFM micrograph of the same surface after one month in a low vacuum, low humidity environment. (c) grazing incidence x-ray diffraction scan of characteristic DIP crystal planes with accelerated aging at 90°C with 60% humidity (13.5hr equivalent of 1 month ambient exposure).

As a third approach, plasma or ozone treatment of the ITO surface is widely used to modify the work function and surface energy prior to deposition of the active layers. Though not technically an interlayer, the modifications are limited to a small region immediately adjacent to the active layer, resulting in effects similar to that of a buffer layer. The treatment of the ITO surface with plasma or UV ozone has a profound effect on the surface energy and hence the stability of the active layers deposited on the surface. The aqueous contact angle increases with plasma treatment [62, 85], correlated to the coverage of the surface with hydroxyl terminated O [85, 248]. As this saturation also controls the surface work function, and wetting behavior has been recently shown to correlate to the surface work function [248-249], the hydroxylated surface should encourage improved adhesion of the active layers and lead to better performance. Wu et al [78] saw almost two orders of magnitude im-

improvements in t_{50} with plasma treatments. Not all plasma treatments lead to the same response, however. The study by Huang et al [67] showed that the wettability of NPB is increased by H_2 , CF_4 and O_2 plasmas, but decreases with Ar plasma. They suggested that decontamination of the surface without hydroxylation leads to a dipole field on the surface that is stronger than the grain boundary and defect effects, promoting NPB nucleation. On the other hand, CF_4 and O_2 strongly encourage layer-by-layer growth, smoothing [219] and passivating the surface against defects that can lead to inhomogeneous electric fields. As an interesting aside, the results for UV-ozone treatment of the ITO surface by Fukushi et al [220] contradict the above. They saw ~5-6x improvement in t_{50} with a treatment that decreased the aqueous contact angle to 4° . They speculate that stronger adhesion of the HTL was possible, which contradicts thermodynamic wetting theory as the surface energy mismatch would be incredibly large. This underscores the likelihood that, as with many aspects of organic semiconductors, more than one mechanism is responsible for lifetime improvements in devices.

Silane based SAMs, such as tetraaryldiamine (TAA) [80, 213, 250], epoxysilane functionalized triphenylamine (TPA-silane) [81], dodecyltrichlorosilane (DDTS) [82], phenyltriethoxysilane (PTES) [82], 3-aminopropyl-methyl-diethoxysilane (APMDS) [82], alkylsiloxane [173], and alkyltrichlorosilanes (OTCS and FOTCS) [83] use a Si-O bond to anchor on the ITO surface, providing a robust interface with substantially higher surface energy. Chong et al [82] observed that the sticking and dewetting of NPB on various SAMs shows an inverse correlation with the measured aqueous contact angle, but Choi et al saw substantially longer lifetimes ($\times 11$ increase in t_{50} with 105° contact angle on FOTCS [83]). The improved adhesion of the active layer was attributed to interfacial reconstruction and interpenetration with the SAM [251]. Our recent study of quaterrylene molecules on SAM buffered surfaces showed a significant release of interfacial strain when the buffer was present [252]. As strain release is another mechanism that drives dewetting [36], better pseudo-epitaxial conformation with the surface for buffered films could be a mechanism for the observed improvement in performance.

A wide variety of other organic molecular interlayers have been used, with varying success in improving the lifetime, as summarized in table 1. These include oligomers such as 4,4',4''-(3-methylphenyl-phenylamino)triphenylamine (MTDATA) [147, 178, 253], parylene [162, 175, 254], cross-linked perylenediimide (PDMI) [255], N,N-bis(4-trifluoromethoxybenzyl)-1,4,5,8-naphthalene-tetracarboxylic diimide (NTCDI-OCF₃) [159], Alq₃, or fullerene (C₆₀). Most of these interlayers are thought to improve the active layer film formation on the surface, by smoothing [147, 162, 180, 255]. The high Tg of MTDATA [253] and NTCDI-OCF₃ [159] are also thought to contribute to preventing crystallization of the HTL overlayer. Polymer approaches include polyaniline (PAni) [172], fluoropolymer (FC-227) [179], plasma polymerized fluorocarbons [74, 160], tetrahedral amorphous carbon [171], polyimide [176] or radical ion salt doped amine polymer [221], which are thought to prevent oxidation [74, 160, 172] or block hole injection [221], in addition to stabilizing the surface against dewetting.

Metals such as Pt and Mg have also been used as interlayers, and though both show improvements, the mechanisms are almost completely opposed. High work function Pt enhan-

ces TPD wetting on ITO surfaces [46], while low work function materials such as Mg, Ca and Al give many orders of magnitude improvement in the luminance stability, correlated to the work function of the metal, by preventing the injection of holes into the Alq layer in OLEDs (intrinsic degradation) [169].

Most recently, MoO_x has been successfully employed to improve lifetimes in both OLEDs [157, 218] and OPVs [75, 230-232], especially as a replacement for PEDOT:PSS, and though the mechanism is still controversial, the energy barrier at the active layer/ITO interface is thought to play a significant role. Other oxides, such as SiO_xN_y [86] or ZnO [256], which can act as oxygen and moisture getters, have been successfully used to stabilize the ITO surface against contamination.

6.2.2. Modified HTLs

There are three modifications that have been made to the hole transporting/electron donating layer adjacent to the ITO surface to improve its wetting properties: doping, polymerization, and functionalization to allow for covalent bonding to the surface. Though many of the layers discussed in this section have also been tried as the HTL for a given device structure, they have found more success for high device performance coupled with stability when they are used as an ultra-thin buffer layer beneath the unmodified version of the molecule acting as the HTL.

Doping

The first approach to stabilization is through doping, either with nanoparticles or with other molecules. Doping with other molecules, often referred to as alloying or more recently as a bulk heterojunction, has been very successful in suppressing crystallization and dewetting in hole transporting molecules [131, 159, 169, 206, 225-227, 257-258]. Mori et al. used metal-free Pc to disrupt the crystallization of CuPc, showing ~2x improvement in lifetimes for operation above 85°C [206]. Chu et al. [159] and Lee et al. [227] used higher stability molecules NTCDI (diimide) and PFI (perfluorinatedionomer) to stabilize NPB and PEDOT:PSS, respectively. The incorporation of PCBM into various polymers, including P3HT [100, 259], PPV, MDMO:PPV [260], also stabilizes the morphology against heat treatment, and improves long-term stability [100, 259-260]. Addition of a diblock co-polymer of P3HT-C₆₀ to a P3HT:PCBM composite has led to even greater stabilization against phase desegregation [261-262]. In some cases, the hole transport molecule was doped into a more stable matrix, such as TPD into high T_g polymers [263] or MgF₂ [120], which significantly suppressed the crystallization. Rubrene:TPD [257], MADN:NPB [226], F4TCNQ:NPB [131, 169], DSA_Ph:NPB [225]) combinations have all been employed with various levels of doping, leading in most cases to ~2x improvement in the 80% luminance lifetime in small molecule OLEDs (see table 2). One very successful method of improving device stability has been doping of the Alq₃ layer in small molecule OLEDs with other molecules including TPD [258], NPB [210], NPD [218], quadricone [209], styrlamine [225], DMQA [264], rubrene [257, 265], DNP [266], Bphen [267], perylene [265-266], among many others [265]. This approach, however, is focused on combating the intrinsic degradation of Alq₃ by holes [168]. This mechanism, hole blocking, was also suggested as an additional mechanism for a few of the

doped hole transport layers (MADN:NPB [226], F4TCNQ:NPB [131, 169], DSA_Ph:NPB [225], Ir(piq)₃:NPD [268]). As the focus of this section is on the stabilization at the ITO surface, the summary in table 1 has been limited to doping in the HTL.

Doping with nanoparticles (LiF [88], C₆₀ [32, 88, 269-271], NaCl [215], Au [33]) has also been very successful in stabilizing hole transport layers, though there is sometimes a trade-off between stability and performance for such systems [88]. As particulates in the layer can act as nucleation centres for crystallization [272-273], care must be taken when selecting doping parameters. The concentration and layer thickness must be chosen such that the electrical performance is not adversely affected by the presence of the doped layer. Interparticle or surface forces strongly influence suspension behaviour of nanoparticles; therefore, not every nanofiller works with every organic. We observed that LiF greatly enhances the stability of NPB at 120°C, while having no impact on the crystallization of CuPc [88]. There is a long history of nanoparticle inclusions for stabilization in non-conducting polymers [32, 274-275]. Luo et al. [275] suggests that a combination of factors are responsible for the stabilization effects, such as the mobility of nanofillers, their size, interaction with the organic, and additional pinning effects at contact lines. Fillers work best if they are immobile; therefore, diffusion to and pinning at the substrate interface is one suggested mechanism for stabilization [32, 274]. Chu et al. [222] did in fact see similar improvement in stability with a C₆₀ layer deposited at the interface below NPB as Yuan et al. [270] saw with doping C₆₀ into NPB; Barnes et al. [32], however, saw greatly enhanced dewetting with C₆₀ at the Si surface for polystyrene thin films. Additionally, there are a number of cases where diffusion to the substrate is unlikely, as no phase separation was observed [88, 120, 215] even though stability was improved. Mukherjee et al. [33] recently observed a concentration dependence on the stabilization, where dewetting droplets form a core-shell structure, rather than leaving behind nanoparticles as the polymer layer retreats as would be expected for substrate segregation. In such cases, strong electrostatic or charge-transfer interactions between the particle and the organic layer leading to a cross-linked network are the most likely route to highly stable films [88, 274]. Other possible mechanisms for stabilization include changing the T_g with high volume-surface area ratio (effectively modifying the film rheology), preventing heterogeneous nucleation, and relief of residual stress in the film through de-segregation [33].

Functionalized HTL

Another approach to stabilization, spearheaded by Tobin Marks' at Northwestern University [45, 80, 163-164, 213, 250, 276-278], focuses on functionalizing traditional hole transport materials with siloxane groups. This allows the molecules to covalently bond to the ITO surface through the formation of Si-O bonds (see figure 6) in a manner similar to the SAMs discussed in section 5.2.1. Covalent bonds ensure strong adhesion and directly eliminate the surface energy mismatch [84, 163]. As the interlayer is the same molecule as the HTL, deposition continues in a self-epitaxial fashion, yielding uniform films as large as 25 μm² without cracks or pinholes [163]. Aqueous contact angles of 90° compared to 110° for the active layer ensures good wetting and physical cohesion in MDMO-PPV:PCBM bulk heterojunction solar cells [277-278] with dewetting prevention above 60°C. Typical examples include TPD-Si₂ [80, 163, 213, 276-277], NPB-Si₂ [80, 163, 279], PABT-Si₂ [278], penta(organo)fullerenes [84] (which use

phosphonic acid linkages [72] rather than silane), and fluorinated triphenyldiamine (FTPD) [280]. An additional step of thermal curing leads to a cross-linked siloxane network, resulting in thin layer with HTL characteristics covalently anchored on surface [163, 280].

Polymerized HTL

The final widely used method of increasing the stability of the active layer on the ITO surface requires a crosslinked polymer or highly crystallized version of a traditional HTL as an interlayer [55, 143, 146, 280-283]. This approach has been most commonly applied to TPD [55, 146, 280-282], where significant stabilization was observed above 80°C with polymerization. Bellman et al also observed that the voltage increase with time for small molecule OLEDs was slower compared to those without the crosslinked interlayer [280], suggesting increased stability. In-situ polymerization/crystallization, by heat treatment or high temperature deposition (NPB [143, 284]) or by UV irradiation (TPD [282]), lead to significant increases in the shelf life (>2 months for NPB), and operational stability at high temperatures. This approach has also been applied to polymers, where the most common approach is to use a heat-treatment [228-229, 285](already widely used in solar cells to improve efficiency [102]), with as much as two orders of magnitude improvement in lifetime [229]. Some success has also be observed for doping and irradiation induced polymerization, mainly with PEDOT:PSS [286].

Interlayer	t_{50}/t_{80}	HTL	
OLEDs			
CuPc	1.8x	NPB	[215]
CuPc	5.3x	NPB	[169]
PEDOT:PSS	6.7x	TDAPB	[217]
MoO ₃	5.9x (t_{90})	α -NPD	[218]
MoO _x	2.8x	NPB	[157]*
MoO _x	3x	NPB	[157]*
sc-MTDATA	4.7x	NPB	[178]**
MTDATA	1.75x	TPD	[147]
O ₂ plasma	20x	PVK:Alq ₃ :Nile red	[78]
O ₂ plasma	2x	PEDOT	[219]
UV ozone	4.7x	α -NPD	[220]
Mg	~60x (t_{90})	NPB:F ₄ TCNQ	[169]
CF ₃ /CF _x	2x	NPB	[74, 160]
OTCS	4x	MEHPPV	[83]
TMTPD+SbF ₆ :PC-TPB-DEGL	2700x	NPB	[221]
FOTCS	11x	MEH:PPV	[83]
C ₆₀	8x	NPB	[222]

NTCDI-OCF ₃	1.2x	NPB	[159]
Pr ₂ O ₃	~7x	CuPc/TPD	[158]
Alq ₃	4.2x (t ₈₀)	NPB	[223]
ta-C	orders of mag	PEDOT	[171]
Pani	~10x (t ₃₀)	MEH:PPV	[172]
NaCl:NPB	2.3x	NPB	[215]
metal free Pc:CuPc	3.4x	TPTE	[206]*
BHJ NPB:Alq	5.4x	NPB	[224]*
gradient HJ NPB:Alq	3.15x	NPB	[224]*
DSA_Ph:NPB	1.3x	NPB	[225]
F4TCNQ (5%-20%):NPB	40x	NPB	[169]
F4TCNQ (30%):NPB	14x	NPB	[169]
F4TCNQ (2%):NPB	2.5x	NPB	[169]
MADN:NPB	2.7x	NPB	[226]
PFI (3%):PEDOT:PSS	9.4x	PFO	[227]***
PFI (6%):PEDOT:PSS	8x	PFO	[227]***
heat treatment 35°C	3.5x	MEH-PPV LB	[228]
heat treatment 65°C	5.5x	MEH-PPV LB	[228]
heat treatment 110°C	9.4x	polyfluorene	[229]***
heat treatment 150°C	167.5x	polyfluorene	[229]***
OPVs			
ZnPc	~3.5x	ZnPc:C ₆₀	[63]
MoO ₃	~ 4x	H2TPP	[75]
MoO ₃	~24x	α-NPD	[75]
MoO ₃	~27x	P3HT:PCBM	[230]***
MoO _x	~80x	PCDTBT:PC ₇₀ BM	[231]***
sMoO _x	39x	P3HT:PCBM	[232]***
PEDOT	8.7x (t ₇₀)	FFTCNQ/ZnPc:C ₆₀	[233]

* modified using data from [215] ** modified using data from [147] *** modified using data from [217]

¹The most common description of lifetime for OLEDs is the illumination half-life (t₅₀) – the time it takes for the luminance to decrease to half of its initial value [216]. In OPVs, a similar standard has been used with t₅₀ defined as the time for the power conversion efficiency (PCE) to decrease to half of its initial value [21]. More recently, it has become more common to report the t₈₀, the time when the device has decayed to 80% of its initial performance [17]. In this chapter, t₅₀ and t₈₀ will be the commonly adopted lifetime values for OLEDs and OPVs respectively, unless otherwise stated.

Table 1. Relative improvement in t₅₀ (for OLEDs) & t₈₀ (for OPVs) compared to bare ITO for various interlayers used at the ITO surface¹

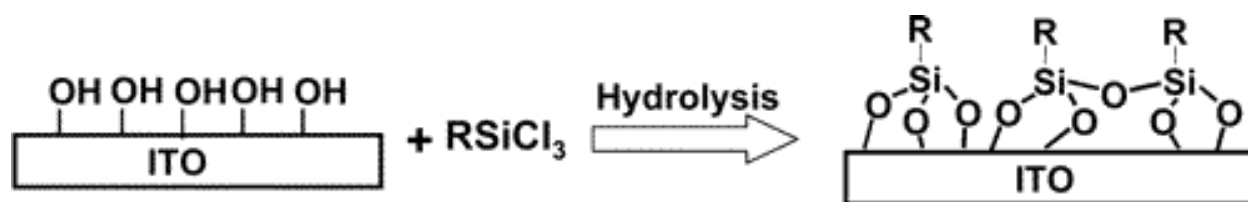


Figure 6. Scheme for ITO surface modified by covalently bound HTL materials. Reprinted with permission from [163]. Copyright 2005 American Chemical Society.

7. Using dewetting as an advantage

Though dewetting of the active layer is generally undesirable and implicated as a main mechanism in device failure, some groups have harnessed the effect to produce novel device architectures. As many of the films are metastable, they have a natural tendency to dewet into a stable equilibrium form, which can then be used as the starting point for device fabrication. Developing methods of tuning film morphology and rate of dewetting through total coverage, surface templating and temperature control are of significant interest in forming controlled organic nanostructures. Recently, we [98] used the strong island growth and dewetting tendency of DIP on ITO to produce columnar structures necessary for an interdigitated ideal bulk heterojunction solar cell, with four orders of magnitude improvement in the device efficiency. Ryu et al. [287] used the energy difference between PEDOT and PFO to form nanoscale dewetted islands of PEDOT at the internal interface in tandem polymer OLEDs. Wang et al. [288] produced sub-micrometer channel OFETs (field effect transistors) using SAM patterned SiO_2 to force PEDOT:PSS dewetting. With the PEDOT:PSS acting as the source and drain electrodes, a submicrometer channel of F8T2 polymer was formed. Benor et al. [289] was able to produce resist patterns of PMMA or PEDOT using selective wetting on hydrophobic and hydrophilic SAM patterns. Deposition on these patterned substrates lead to the formation of mesoscale patterns for radio frequency ID tags or thin film transistor electrodes. Chen et al. [104] used a similar patterning motif with SAMs that were selectively wet by the two components to encourage phase separation of P3HT:PCBM into an interdigitated columnar structure. Most recently, Harirchian-Saei et al. [290] used the phase separation of PS and PMMA on OTS striped patterns to deliver a periodic array of CdS nanoparticles. By dissolution of the nanoparticle into only one component; then taking advantage of the selective wetting, a templated nanoparticle array was produced.

8. Summary

This chapter represents a comprehensive summary of the state of the art with regards to interfacial wetting stability in organic light emitting diodes and organic photovoltaics. Though the challenges are slightly different, both types of optoelectronic devices are heavily influenced by the stability of the interfaces with the bottom side contact. As organic optoelectron-

ic technologies mature, the metastability of interfaces becomes more and more significant in the quest for greater performance.

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