

## Review

# Fabrication and processing of polymer solar cells: A review of printing and coating techniques

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## ABSTRACT

Polymer solar cells are reviewed in the context of the processing techniques leading to complete devices. A distinction is made between the film-forming techniques that are used currently such as spincoating, doctor blading and casting and the, from a processing point of view, more desirable film-forming techniques such as slot-die coating, gravure coating, knife-over-edge coating, off-set coating, spray coating and printing techniques such as ink jet printing, pad printing and screen printing. The former are used almost exclusively and are not suited for high-volume production whereas the latter are highly suited, but little explored in the context of polymer solar cells. A further distinction is made between printing and coating when a film is formed. The entire process leading to polymer solar cells is broken down into the individual steps and the available techniques and materials for each step are described with focus on the particular advantages and disadvantages associated with each case.

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## 1. Introduction

Why polymer solar cells? As a technology polymer solar cells are unrivalled in terms of processing cost, processing speed, processing simplicity and thermal budget. It is the only photovoltaic technology that potentially offers a convincing solution to the problem of a high cost commonly encountered for photovoltaic technologies. There are, however, unsolved problems of low power conversion efficiency, poor operational stability, materials cost and environmental impact.

### 1.1. A short history

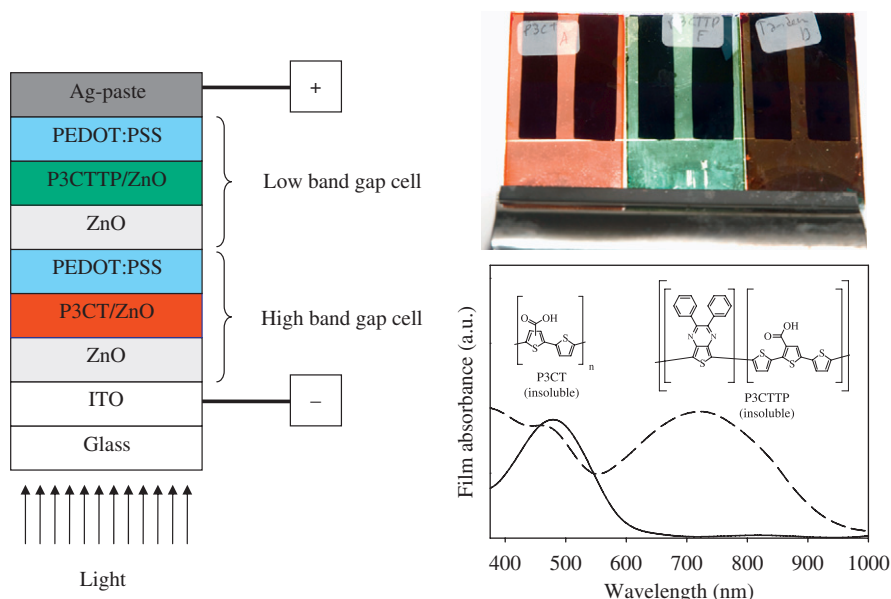
The field of polymer and organic solar cells has been the subject of reviews [1–20], special issues [21–27] and books [28–32] on several occasions during the past 5 years and the definitions of polymer solar cells are quite broad spanning all-polymer solar cells, polymer fullerene solar cells, small molecule and hybrid solar cells. By far the most successful of them are the polymer–fullerene solar cells that comprise a mixture of the polymer, which exclusively is the donor material and typically a soluble fullerene derivative as the acceptor material. While research on polymer and organic solar cells date back to the 1980s [2] the first example of a polymer solar cell with a convincing underlying understanding of the physics and chemistry is the bilayer heterojunction between the soluble polymer 2-methoxy-5-(2-ethylhexyloxy)-polyphenylenevinylene (MEHPPV) and the Buckminsterfullerene  $C_{60}$  [33,34] where a power conversion efficiency of 0.04% was obtained using monochromatic light. It is reasonable to define this report as the prototypical example of a polymer solar cell from which all modern polymer solar cells stem. The next convincing step was the application of a dispersed bulk heterojunction of MEHPPV and  $C_{60}$  [35] and later soluble derivatives of  $C_{60}$  [36–38], which increased the power conversion efficiency to 2.5%. The third step that represents the state of the art today is the exemplification of the interplay between the morphology reached by processing of the active layer and the function of the device which allowed efficiencies of up to around 5% to be reached for mixtures of poly-3-hexylthiophene (P3HT) and phenyl-C61-butyric acid methyl ester ([60]PCBM) [39,40]. A lot of original research has detailed methods for improving the function through physics and chemistry. The most important physical means for improving performance are the use of a thin layer of an insulator between the active layer and the low work function metal electrode [41] and more recently also in inverted devices [42], the use of optical spacers [43–45], the understanding of how the open circuit voltage is obtained [46] and by these means deriving an efficient method for predicting performance of materials combinations based on measurable materials properties [47] and finally the use of various mixing and annealing methods to control the morphology of the

active layer [48]. It should be mentioned that the latter methods are not generic and generally should be viewed as materials specific. Thermal annealing is a good example that will work well for some material combinations, but not others. Sometimes even the same material gives different results as in the case of P3HT where regioregularity and molecular weight plays a crucial role [17]. In terms of chemistry work has focussed on improving the properties of both donor and acceptor material. For the polymers (the donor materials), which in many of the reported devices are responsible for the light harvesting there has been special focus on obtaining a low band gap such that as much of the available energy from the Sun is harvested [5,11,18]. Many materials with low band gap have been prepared and while band gaps as low as 0.5 eV has been prepared it is remarkably few of the low band gap polymers that give devices that rival those obtained from materials with a larger band gap. The most successful fullerene (the acceptor material) is the derivative known as [60]PCBM [36]. In spite of intensive research for better fullerene derivatives (which would be a review topic of its own) there has been no derivatives being as performing as [60]PCBM except perhaps for the more difficultly accessible [70]PCBM [49] and the recent Bis[60]PCBM [50].

### 1.2. State of the art

Most improvements have been found through materials such as P3HT and the fullerenes [60]PCBM and [70]PCBM that represent the state-of-the-art well from a materials point of view. In terms of device structure efforts have been relatively limited for various reasons. Firstly, there is a considerable drive towards achieving high power conversion efficiency and this implies small devices and a high conductivity of the electrodes. Since the back electrode for “hero” cells is typically an evaporated metal electrode the limiting electrode in terms of conductivity is the necessarily transparent front electrode. The best performing transparent electrode material that combines high transparency over a broad range of wavelengths and high electrical conductivity is indium tin oxide (ITO). From the point of view of processing polymer solar cells on a large scale there are several impossibilities connected to the use of ITO but for the purpose of breaking power conversion efficiency records there are few. The reason that nearly all reported devices with any significant power conversion efficiency are prepared on ITO covered glass substrates is understandable. This has severely limited the evolution of both device geometry and processing techniques.

The most significant step is undoubtedly the stacking of both the high and the low band gap materials into a tandem solar cell with the highest reported power conversion efficiency of 6.5% [51]. In Fig. 1 an example of a tandem solar cell structure is shown along with examples of high and low band gap materials [52]. The tandem solar cell is a pleasing concept that itself has been subject to some

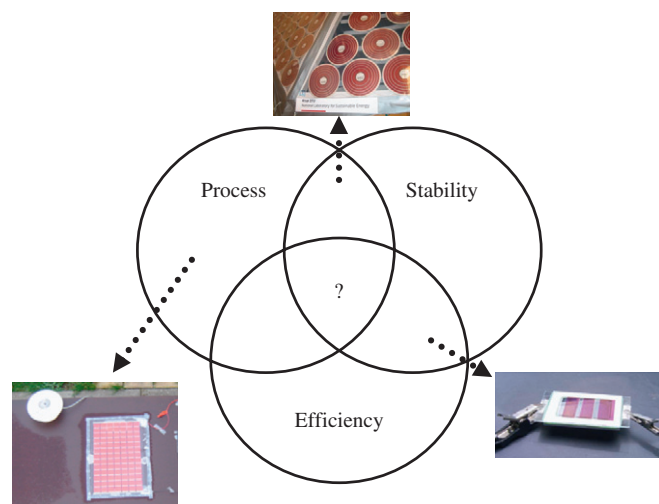


**Fig. 1.** A schematic of a tandem polymer solar cell comprising eight layers with electrical connections (left) and a photograph of the actual devices as seen from the front with backside illumination to emphasize the colour. The three devices shown are a single junction of P3CT/ZnO with a red colour, a single junction of P3CTTP/ZnO with a green colour and finally the tandem cell of P3CT/ZnO and P3CTTP/ZnO showing a brown colour (top right). The active layer film absorption spectra are also shown with P3CT/ZnO plotted with a solid line and P3CTTP/ZnO plotted with a broken line (bottom right).

evolution due to the complexity of its realisation. Since it is a multilayer structure where ideally all layers are processed without affecting underlying layers during processing this has taken some time and should by no means be considered completely evolved. Initially, the problems associated with multilayer solution processing was solved by processing small molecules entirely from vacuum [53,54] or by the use of solution processing for the first device in the stack followed by vacuum processing of the second device in the stack [55]. More recently, a careful choice of solvents allowed for solution processing of the entire stack when employing soluble polymer materials [56,57]. The most recent developments are the use of a folded reflective geometry, which offers simplicity in device processing but complexity in module assembly [58] and finally the use of thermocleavable materials that efficiently solves the problems associated with solubility of the underlying layers during processing. [52] While both of the latter examples have given rise to inferior performance they do prove the point that technical solutions are possible and that they should be sought. Another reason that has limited the evolution of device geometries is in part a result of the use of ITO in conjunction with the hole transporting layer poly(ethylenedioxythiophene):polystyrenesulphonic acid (PEDOT:PSS), which implies the use of a back electrode with a low work function such as aluminium or calcium. The use of these metals necessitates thermal evaporation (physical vapour deposition). It is thus reasonable to assume that this highly limited choice in device geometry have had some influence on both the choices made when engineering new materials and in the observed state-of-the-art. In essence all the new materials that have been prepared have been prepared for electrode combinations such as ITO-PEDOT:PSS and aluminium (or calcium) and it is interesting to speculate what the state-of-the-art would have looked like if research into the use of different electrode materials had been more popular.

### 1.3. The unification challenge

When the selective pressure on research is on one particular aspect such as the power conversion efficiency, other equally important areas of research may be neglected while they share



**Fig. 2.** A Venn diagram summarizing the unification challenge where the difficulty lies in finding the conditions that combines efficiency, process and stability into the same materials and device. The are good examples representing each of the areas and some examples that span two of the areas but there been no reports on the convincing solution such that all areas can be spanned. Examples that unify: stability and efficiency is P3HT-PCBM (shown here as a 10 cm<sup>2</sup> encapsulated module with three cells in series giving a PCE of 2.2%), process and stability is P3CT-ZnO (shown here are mass produced polymer solar cell modules with good stability in air) and process only as MEHPPV-PCBM (shown here is a 0.1 m<sup>2</sup> module processed by printing).

the same importance when it comes to realizing the objective of stable, efficient, low-cost polymer solar cells prepared by very fast processing techniques. This can be summarized in a Venn diagram as the unification challenge, which has been discussed earlier [16,31] (Fig. 2). A material that gives rise to highly efficient devices is thus of little consequence if its operation is not stable or if the process leading to the final device is difficult. There has been a recent interest in the operational stability of devices [16,59–64] and more importantly on the understanding of why devices and materials break down [16,65–74]. There is hope that new

materials can be derived that combines both efficiency and stability. The interest in processing of polymer solar cells has been limited to methodologies for improving power conversion efficiency and it is remarkable that there has been no interest in actually demonstrating the alleged significance of large-scale processing of polymer solar cells. After all, if large-scale processing proves to be problematic or impossible the concept of polymer solar cells would become a scientific curiosity with little consequence to mankind. The view held in this review is thus that the problems associated with industrial and large-scale processing must be addressed and taken into account alongside considerations of operational stability and power conversion efficiency before polymer solar cells can be attributed any importance (i.e. that they generate more power than is consumed during their preparation).

#### 1.4. Typical device structure

As highlighted above polymer solar cells typically comprise a multilayer structure where each layer in the stack may be formed by an individual film-forming technique. This should be viewed as a particular advantage of the technology for several reasons. Firstly, it is very versatile that one in principle can arrive at the same device geometry (i.e. layer sequence and materials combination) through many different routes. Secondly, it is of some importance from an intellectual property rights (IPR) point of view as this implies that it will be almost impossible to efficiently protect a polymer solar cell product unless it is materials specific. Since both the available device geometries and many materials are prior art there is little hope that one can protect ideas through a particular process sequence and even if possible it would be very easy to circumvent. A further complication lies in the fact that it is not always possible with a printed film at hand to establish how it was made. While some printing methods give rise to characteristics in the printed film that does allow for their identification it can be anticipated to be very difficult for multilayer films. This should be viewed as strengths of the technology as it increases competition and places focus of the competition on what matters, namely overall performance, and places the judgement in the hand of the consumer, where it should be, rather than Olympic records in scientific articles. Thirdly, this aspect makes it desirable to invent new device structures and electrodes as this would become valuable IPR in the event that a competitive device could be prepared.

#### 1.5. The myriad of film-forming techniques

It is noticeable that there are so many known, well developed and currently explored film-forming techniques, and yet so few of them have made their way into the world of polymer solar cells. There are at least three reasons that can account for this. Firstly, many of the techniques require large amounts of material, and secondly, reproducibility is sometimes difficult, and thirdly many techniques are unsuited for the small scale commonly employed in laboratory trials. The techniques that have been explored are generally well suited for individual processing of small substrates (i.e. spin coating, doctor blading and casting). There are, however, many more film-forming techniques available that have been developed for high volume processing of paper, plastic and textile materials where the substrate is in the form of a continuous roll of material. This is often called roll-to-roll coating or reel-to-reel coating (abbreviated R2R coating) and the processing equipment generally comprises: unwinding, coating and rewinding of the material. Many more processes may be involved such as cleaning, pre/post treatments of the fabric, heating, drying, etc. The importance of the coating techniques is that they are suited for

high-speed coating or printing and they have been developed with the aim of achieving a very low process cost. While this has not been shown repeatedly in the context of polymer solar cells it is generally accepted that R2R processing is cheap and fast. There has been one report [75] that details large-scale processing of polymer solar cells which in part was based on R2R processing and that study confirmed that processing by coating/printing is of low cost which is not surprising. The study also showed that while polymer solar cells have the potential to fulfil the expectations of low-cost processing this will not come easily and a dedicated effort will be required. One of the challenges currently is thus to identify the ideal coating techniques for polymer solar cells. Some techniques are suited only for coating an even layer over the entire substrate surface thus giving 0-dimensional control (i.e. no ability to create a pattern), other techniques allow for 1-dimensional control of the pattern and in the context of a substrate passing a coating head this implies that a striped pattern can be created. Further, some methods allow for full 2-dimensional control of the printed pattern where any shape can be reproduced on the substrates. Finally, some coating methods allow for the formation of multilayer films in the same coating step. Combinations of these techniques can in principle enable pseudo 3-dimensional control during printing (i.e. both pattern and multilayer structure). A second challenge is that with each of these coating techniques there are often a window of operation in terms of processing speed and achievable wet layer thickness that all hinges on the properties of the ink and the interplay between the surface that is to be coated. Viscosity, surface tension, surface energy, volatility are a few of the important ink properties that have to be taken into account when procuring the ink. It should be noted that it is customary in the coating industry to employ additives and adjuvants that are added to the ink to adjust the properties such that printability/coatability of the ink is achieved. This is all very well for traditional coating and printing where the transfer of a pattern is all that is required. In the case of polymer solar cells the coated pattern has to be functional after the film is formed. It should thus be anticipated that there is limited freedom when choosing additives to aid printing/coating.

#### 1.6. The ideal process

The ideal process should involve solution processing of all layers on flexible substrates by the combination of as few coating and printing steps as possible. The process should be free from costly indium, toxic solvents and chemicals and the final polymer solar cell product should have a low environmental impact and a high degree of recyclability.

#### 1.7. Aim of this review

The main purpose of this work is to guide the reader through some of the available coating techniques and allowing for a judgement as to the suitability of a given technique in the context of polymer solar cells. It is especially relevant for people involved in upscaling, preproduction and production of polymer solar cells and it is my hope that it will serve as a motivation for addressing the unification challenge and that it will bring attention to the hitherto little explored area of processing polymer solar cells on an industrial scale and enabling their production.

## 2. Coating and printing techniques

Before engaging into detailed descriptions and accounts of individual techniques that have been detailed in several books



and book chapters [76–81] it is important to distinguish coating from printing in this context. The distinction may seem somewhat rhetorical but it should become quite clear that it has physical meaning when considering the mechanism by which the film is prepared. Historically printing is used to describe a method by which a layer of ink is transferred from a stamp to a substrate by a reversing action. A good example is an office stamp that does just that. By contrast coating is used to describe a process by which a layer of ink is transferred to the substrate by essentially pouring, painting, spraying, casting or smearing it over the surface. The use of the word printing may also imply that a complex pattern is formed whereas coating generally does not infer this. Printing techniques thus include techniques such as screen printing, pad printing, gravure printing, flexographic printing and offset printing. Coating techniques include spincoating, doctor blading, casting, painting, spray coating, slot-die coating, curtain coating, slide coating and knife-over-edge coating. The only technique that could be placed in both categories is inkjet printing. Essentially it is a coating technique but the possibility to reproduce a complex pattern and its association with office printing on paper makes it equally suited for being termed as a printing technique which is also part of its name.

### 2.1. Printing and coating methods operating on a single substrate

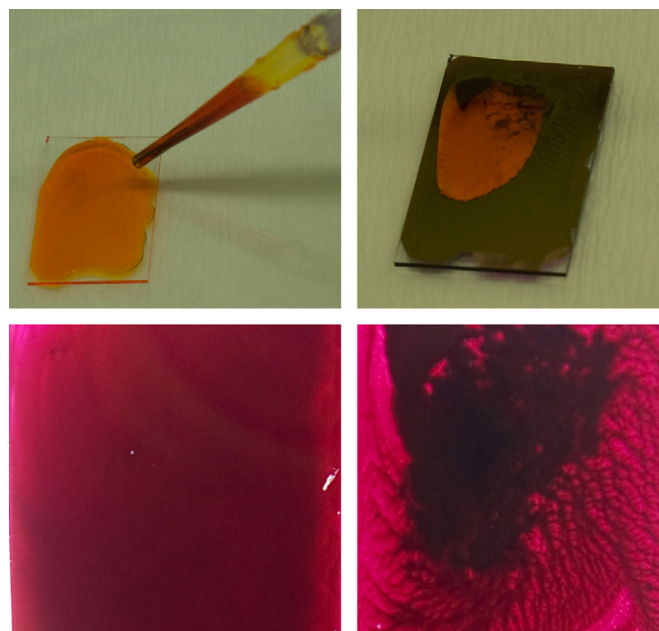
In the following some methods are described which allow for printing and coating in batch mode where typically a small substrate is printed or coated with (active) material. Some of the methods are R2R compatible and will be discussed in that form in Section 2.2 and some methods are not readily R2R compatible

#### 2.1.1. Casting

This is probably the simplest film-forming technique available (Fig. 3). The advantage is that no equipment is needed apart from a very horizontal work surface. The procedure is to simply cast a solution onto a substrate followed by drying. While it is possible to prepare films of good quality and also thick films the technique suffers from a lack of control over the film thickness and often picture framing effects are observed near the edges of the film or precipitation during drying. In cases where the surface tension of the liquid dominates the drying is inhomogeneous. Also there is a requirement that the material to be coated has a high solubility in the solvent used if crystallisation or precipitation is to be avoided.

#### 2.1.2. Spincoating

The film-forming technique that indisputably has been most important for the development of polymer solar cells to this day is spincoating. The technique has been subject to numerous fundamental studies and its use and scope has been reviewed recently [82]. In spite of the complexity of film formation it allows for the highly reproducible formation of films and has several advantages over other coating techniques during drying which allows for the formation of very homogenous films over a large area (the diameter of the substrate can be as high as 30 cm). The technique is used in the microelectronics industry during application of polymeric photoresists to silicon wafers and is involved in crucial steps during the production of digital versatile discs (DVDs) and compact discs (CDs). The typical spincoating operation involves application of a liquid to a substrate followed by acceleration of the substrate to a chosen rotational speed (as shown in Fig. 4). Alternatively the liquid solution may be applied while the substrate is spinning. The angular velocity of the substrate with the overlying solution results in the ejection of most of the applied liquid where only a thin film is left on the substrate. The thickness, morphology and surface topography of



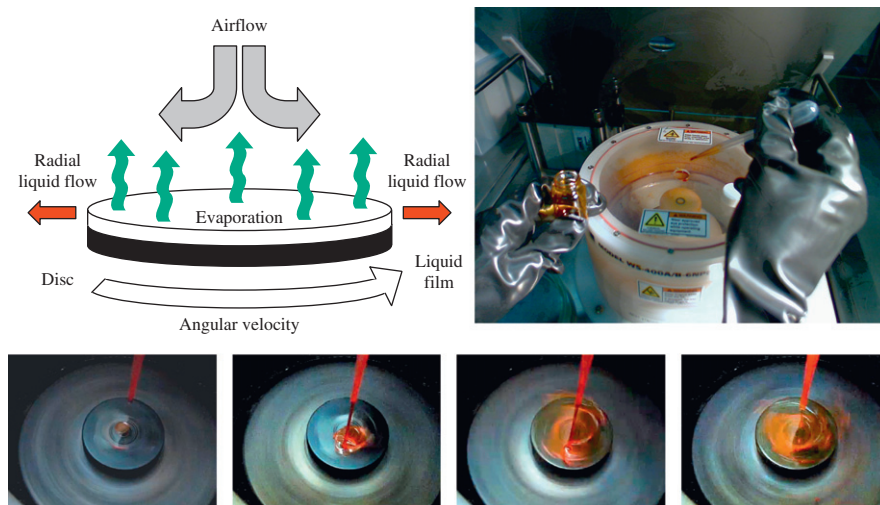
**Fig. 3.** Photographs showing casting (top left), inhomogeneous drying with crystallisation (top right), an example of a successfully cast film showing a very good homogeneity (bottom left) and a poor result showing picture framing, precipitation and drying defects (bottom right).

the final film obtained from a particular material in a given solvent at a given concentration is highly reproducible. It should be mentioned that one is sometimes limited to the observation of the resulting thickness, morphology and surface topography and that the preparation of a film according to different specifications may offer a considerable challenge and typically only a range is accessible (i.e. a only range of thicknesses can be obtained). These three properties are known to depend highly on rotational speed, viscosity, volatility, diffusivity, molecular weight and concentration of the solutes. They depend relatively little on the amount of solution deposited, the rate of deposition and the spinning time. The film thickness,  $d$ , obtained during a spincoating experiment can be expressed by the empirical relationship

$$d = k\omega^\alpha \quad (1)$$

where  $\omega$  is the angular velocity and,  $k$  and  $\alpha$  are empirical constants related to the physical properties of the solvent, solute and substrate. Typically,  $\alpha$  has a value of around  $-0.5$  and the constant  $k$  contains many parameters such as the initial viscosity of the solution. A careful review on this topic can be found in the literature [82].

The success of spincoating in the field of polymer photovoltaics is in spite of its wasteful nature understandable. Most of the applied solution is ejected during spincoating but since a very small volume is required to complete the operation this is not critical (experienced people can successfully spincoat using 0.1 mL). When a solution is deposited and most of the excess solution has been ejected during rotation the crude wet film is subject to several changes, which include evaporation of solvent, changes in viscosity, radial flow of the solution, shear thinning, molecular organisation at the solid–liquid and air–liquid interfaces, molecular orientation as a result of the shear field, formation of aggregates, phase separation of blends, diffusion of molecules in the film, etc. All these effects are influential when it comes to the operation of polymer solar cells and it is thus understandable that many scientific reports have dealt with various aspects of spincoating that correlate with device function.



**Fig. 4.** Schematic illustration of the spincoating (top left) along with a photograph of a typical spincoating operation in a glovebox environment (top right) and high-speed images showing application of a solution of MEHPPV to a rotating substrate and film formation. The images were recorded at  $300 \text{ images s}^{-1}$  (below). The timing of the images (from left to right) after impact of the first drop is:  $t = 17, 100, 137$  and  $180 \text{ ms}$ .

Most of the studies of film formation using spincoating have focussed on the film thickness and this is generally acknowledged to depend crudely on the rotational speed and the viscosity of the solution [76]. The latter is dependent on the concentration of the solute and the molecular weight of the solute if polymeric. In the context of polymer solar cells the thickness of the film is important but also the homogeneity and defect concentration is important (pinholes lead to short circuit). Further, the morphology of the film has been studied for blends of polymers and block copolymers and this is relevant in the context of polymer photovoltaics as the proper nanoscale morphology can significantly improve the device performance as can the surface topography. The fact that the interfacial properties are under some degree of control and that the technique allows for the reproducible formation of a film with a fixed thickness, morphology and surface topography is most probably the reason why it has been so successful. The best examples of this are possibly the spincoating of P3HT-PCBM mixtures from 1,2-dichlorobenzene [39,40] while allowing the wet film to dry slowly (either while spinning or by leaving the wet film in an environment saturated with solvent). While spincoating is extremely useful as an experimental technique on a laboratory scale during device optimisation and materials screening it is questionable if it will be competitive when it comes to production of polymer solar cells. Several facts raise doubt as to the applicability for the high volume production. Firstly, it is a serial technique that requires that substrates are handled individually and it is thus not directly R2R compatible. Secondly, the technique does not allow for patterning the formed film and this is expected to be crucial to the successful application of the technology (i.e. interconnecting devices in modules). Thirdly, the technique is not parsimonious with respect to usage of ink (recycling may be possible but it is not unproblematic). It is likely that these issues can be solved technically and it is thus too early to dismiss the technique in a production context while the issues raised are crucial and challenging.

### 2.1.3. Doctor blading

A little explored technique in the context of polymer solar cells [83,84] is doctor blading that allow for the formation of films with a well-defined thickness. In contrast to spincoating the technique is quite parsimonious and with some practice the loss of coating solution can be minimised such that less than  $\sim 5\%$  is lost. The

technique works by placing a sharp blade at a fixed distance from the substrate surface that is to be coated (typically  $10\text{--}500 \mu\text{m}$ ). The coating solution is then placed in front of the blade that is then moved linearly across the substrate leaving a thin wet film after the blade. The final wet thickness of the film is ideally half the gap width but may vary due to the surface energy of the substrate, the surface tension of the coating solution and the viscosity of the coating solution. It also depends on the meniscus formed between the blade and the wet film on the trailing edge of the blade, which is related to the shear field (proportional to the speed of the blade/knife). The final dry thickness of the coated film,  $d$ , can be calculated from the empirical relationship

$$d = \frac{1}{2} \left( g \frac{c}{\rho} \right) \quad (2)$$

where  $g$  is the gap distance between the blade and the substrate in,  $c$  is the concentration of the solid material in the ink in  $\text{g cm}^{-3}$  and,  $\rho$  is the density of the material in the final film in  $\text{g cm}^{-3}$ . The shear field is relatively small during doctor blading on a small machine as shown in Fig. 5 where linear speeds in the range  $1\text{--}100 \text{ mm s}^{-1}$  are common. Since there is essentially no loss of coating solution it should ideally be possible to arrive at functional films when very little material is available. In practical terms, however, and for prototyping work it takes some time finding the right conditions for coating and the initial loss of coating solution is large and thus gives no advantage over spincoating. Further, compared to spincoating where the wet film formation is fast, doctor blading is relatively slow and if the dissolved material has a propensity to aggregate or crystallise at high concentration this often happens during doctor blading.

It is likely that this is the reason for spincoating being the preferred technique over doctor blading as they are at about the same level in terms of instrumental cost and operational complexity. Whereas spincoating has no R2R compatible pendent, doctor blading is easily transferable to a R2R coating environment and is in this context known as knife-over-edge coating (*vide supra*). Of the few well documented studies where doctor blading is employed as a film-forming technique in the context of polymer solar cells one has focussed on the ratio between crystalline (crystallised) and amorphously (intermixed) [60]PCBM in bulk heterojunctions of MDMOPPV and [60]PCBM [83]. The study employed solid-state NMR techniques and highlighted that there is a higher degree of crystallised [60]PCBM in doctor-bladed films

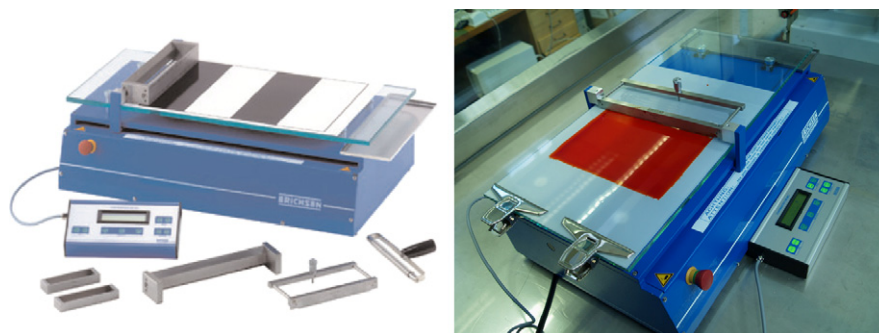


Fig. 5. A picture of the Erichsen Coatmaster 509 MC-I that can be used for doctor blading (left) and a photograph showing doctor blading of MEHPPV (right).

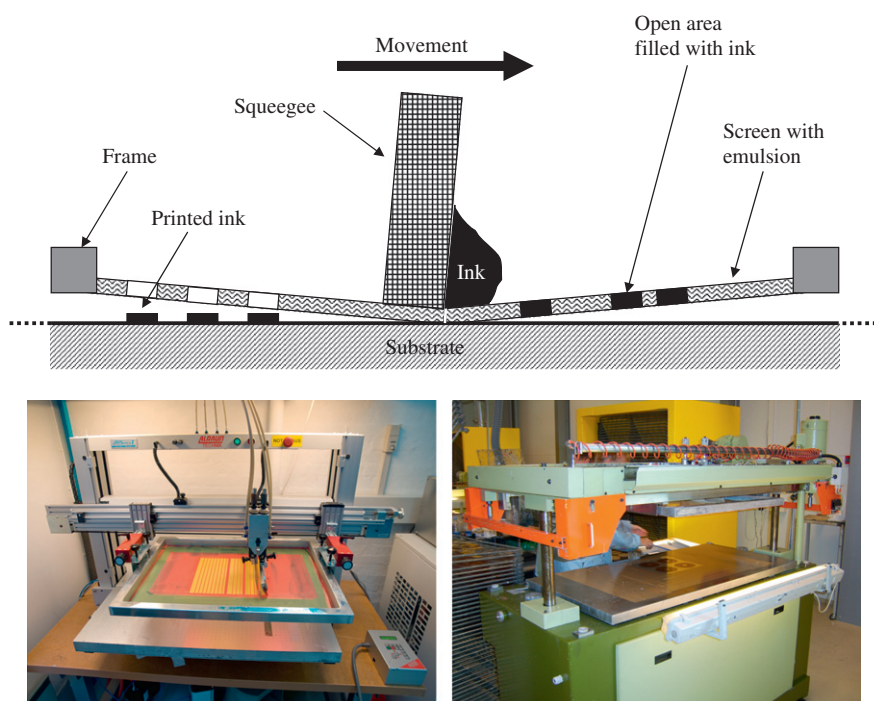


Fig. 6. Illustration of the screen-printing process (above) and examples of a laboratory screen printer (bottom left) and an industrial screen printer (bottom right).

as compared to spin-coated films using the same coating solutions and concentrations. This was ascribed to the slow speed of solvent evaporation during doctor blading as compared to spincoating. This also implies that spincoating give access to films that are perhaps further from thermodynamic equilibrium than doctor-bladed films.

#### 2.1.4. Screen printing

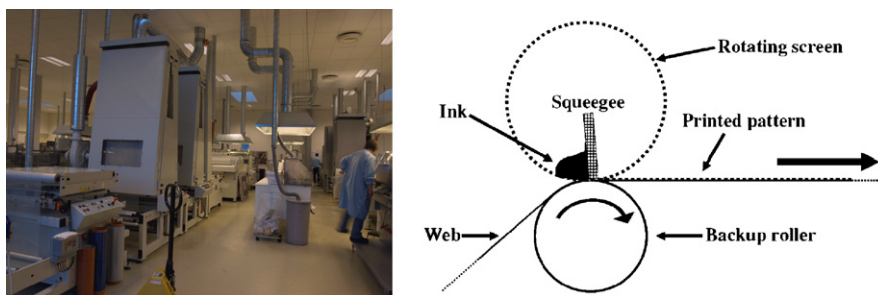
The first developments of screen printing date back to the beginning of the 20th century. It is a very versatile printing technique that allows for full 2-dimensional patterning of the printed layer. It is parsimonious and there is essentially no loss of coating solution during printing. Its main distinction from all other printing and coating techniques is a large wet film thickness and a requirement for a relatively high viscosity and a low volatility of the coating solution. The process is illustrated in Fig. 6 and involves a screen of woven material (i.e. synthetic fibre or steel mesh) that has been glued to a frame under tension. The pattern is obtained by filling the screen with an emulsion that is impervious to the coating solution in the areas where no print should appear. The area of the printed pattern is kept open (without emulsion). The screen is then filled with coating solution and brought into proximity of the substrate.

A so-called squeegee is forced into to screen bringing it into contact with the substrate and then drawn linearly across the screen thus forcing coating solution through the open areas onto the substrate and in that manner reproducing the pattern. The wet thickness of the coated film is in principle given by the theoretical paste volume of the screen,  $V_{\text{screen}}$ , i.e. the volume between the threads of the mask and the thickness of the emulsion.  $V_{\text{screen}}$  is measured in the volume of ink per area of open screen ( $\text{cm}^3 \text{m}^{-2}$ ). Some factors, however, are influential on this such that not all the material in the screen is deposited. This varies with the force with which the squeegee is pushed into the screen, the snap-off distance, the speed of the squeegee and the viscosity of the solution. The simple relationship in Eq. (3) describes the final dry film thickness,  $d$ , under the assumption that the material in  $V_{\text{screen}}$  is partially deposited and described by the pick-out ratio,  $k_p$ . The deviations can be derived empirically.

$$d = V_{\text{screen}} k_p \frac{c}{\rho} \quad (3)$$

where  $c$  is the concentration of the solid material in the ink in  $\text{g cm}^{-3}$  and  $\rho$  is the density of the material in the final film in  $\text{g cm}^{-3}$ . Screen printing is currently used extensively in industry for simple tasks such as printing text and etch resists and for





**Fig. 7.** A picture of a full R2R Klemm line extending into the photograph. The system comprise unwinder, edge guide, corona treatment, web cleaning, printing, UV-curing vertical drying ovens and rewinding (left). A schematic drawing of a rotary screen printer (right).

complex task such as printing conductors for flexible electronics and keypads. It has also been reported used in the context of polymer solar cells in a few instances [75,85–89]. The large wet thickness, the requirement for a high viscosity and low volatility has probably been a limiting factor and thus far, the most suited polymer for printing is MEHPPV that has a suitable rheology (high viscosity at low concentration) [31,90]. There are some patents on the screen printing of P3HT mixtures [91,92] and one example of large-scale industrial production of polymer solar cells where all the layers in the device are processed using screen printing [75]. In the latter case the challenges of large wet thickness, viscosity and volatility were efficiently solved [89,93]. The report showed the production of small serially connected modules with a module area of 132 cm<sup>2</sup> on flexible substrates. The modules were demonstrated in public by free distribution while powering small electronic gadgets [75]. Screen printing is inherently batch operated but highly R2R compatible as exemplified on a Klemm line where rectangular screens are used and the material is passed through the machine at constant speed. The screen and support follow the web at constant speed while printing is in progress. After each print the screen and support reverses back and the printing cycle is repeated.

It can also be fully adapted to a R2R process in rotary screen printing where the screen is shaped as a cylinder with a squeegee on the inside and the substrate fed past the outside of the rotary screen and supported by a roller as shown in Fig. 7. Screen printing is likely to become one of the important printing techniques for the large-scale processing of polymer solar cells. While the active layer may not be readily processed by screen printing transparent conductors such as PEDOT:PSS and metallic conducting pastes such as silver or silver–aluminium are available commercially as screen printable ink formulations. It is likely that these materials will enter in finally processed polymer solar cells through a screen-printing process. When considering the processing cost of polymer solar cells by screen printing a real example have shown that screen printing is viable [75].

### 2.1.5. Ink jet printing

Ink jet printing is a relatively novel process from the point of view of industrial printing and coating and the technology has been driven forward by the typical low-cost ink jet printer for the home office. Industrial ink jet printers where one has some choice in the type of solvents used have become commercially available recently (Fig. 8). The printing head is ceramic or especially resistant towards organic solvents and it is thus possible for the experimentalist to procure an ink formulation based on wide range of solvents. The ink jet printing process has the advantage of quite high resolution, which is easily 300 dpi and up to as much as 1200 dpi without too great difficulty. In contrast to most other printing techniques relevant to polymer solar cells there is no

need for a complex master as the source image to be printed is digital. A disadvantage is possibly a limitation in printing speed (i.e. coated area in m<sup>2</sup> s<sup>−1</sup>). The dry thickness of the ink jet printed film is given by the number of droplets delivered per area, the individual droplet volume and the concentration of material in the ink is as follows:

$$d = N_d V_d \frac{c}{\rho} \quad (4)$$

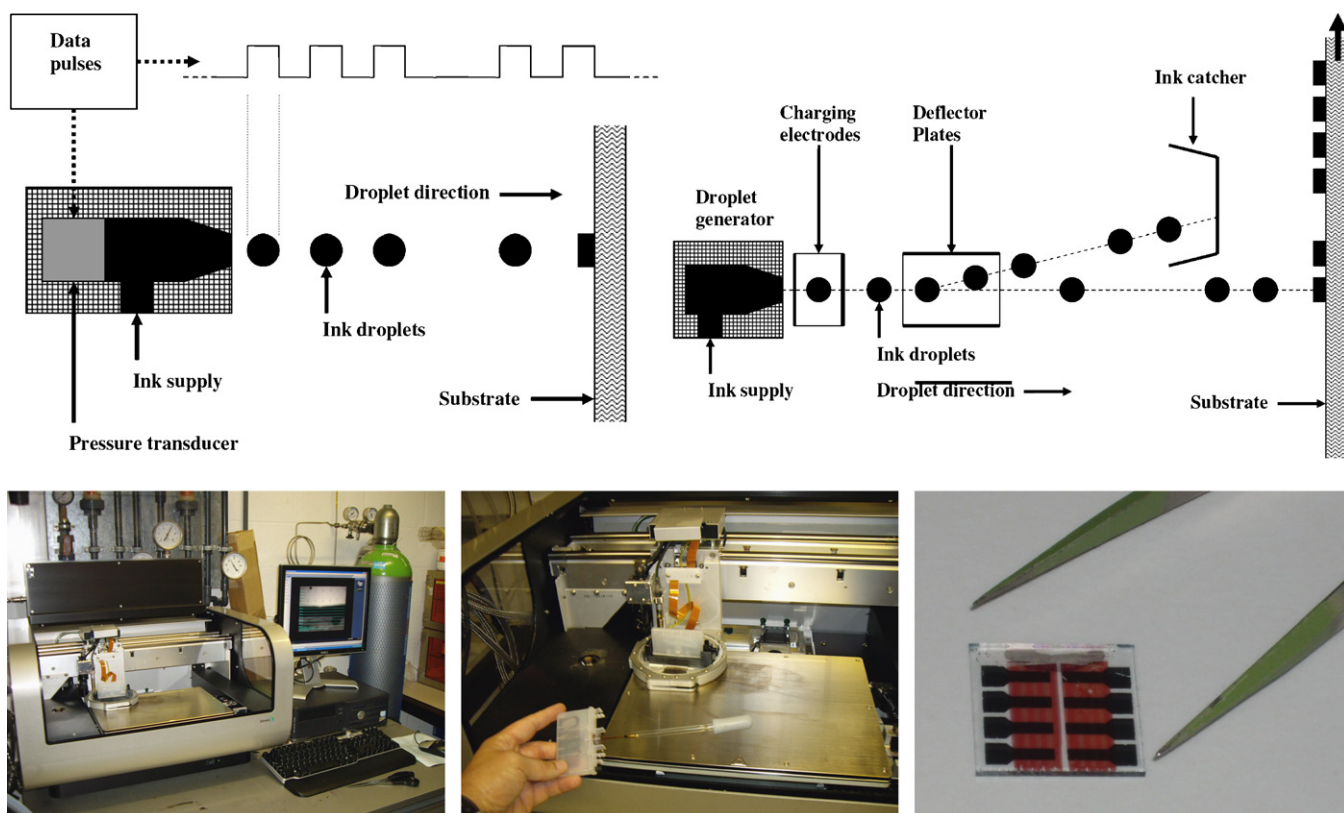
where  $N_d$  is the number of droplets delivered per area (cm<sup>−2</sup>) and  $V_d$  is the volume of the droplets (cm<sup>3</sup>). There have so far only been two scientific reports on the use of ink jet printing in polymer solar cells [94,95]. The printing technique is relatively complex and is based on the formation of a small droplet of ink that is then deposited on the substrate.

The formation of the droplet may be by mechanical compression of the ink through a nozzle (piezoelectric) or by heating the ink (and thus creating a pressure increase). The droplet is then electrostatically charged and accelerated towards the substrate by an electric field. This all puts some constraints on the ink formulation. Generally the inks are required to be of low viscosity (4–30 cP) and require to be electrostatically charged. Often the inks are a complex mixture of many solvents (sometimes 5–8 different solvents) where one or more of the solvent components are very volatile. There is some loss of ink droplets (especially for continuous ink jet printing systems) and while it is possible to recycle the ink it is complex to replenish the lost solvents in the ink that is recovered in the ink catcher. Further there is a requirement for having a high surface tension (typically >35 mN m<sup>−1</sup>) in order to easily generate a stream of droplets. Some additives are generally added and may make up as much as 1% of the wet ink. In the context of polymer photovoltaics this is a challenge as the polymer materials employed for printing the active layer generally are of a low concentration, which is also in the range of 1–5 wt/v. It is difficult at the current stage to determine whether ink jet printing will play an important role in the high volume fabrication of polymer solar cells. The advantages offered by the technique and the good literature examples of its use makes it likely that it will become of use for creating complex patterns and perhaps devices with a small outline of the active area.

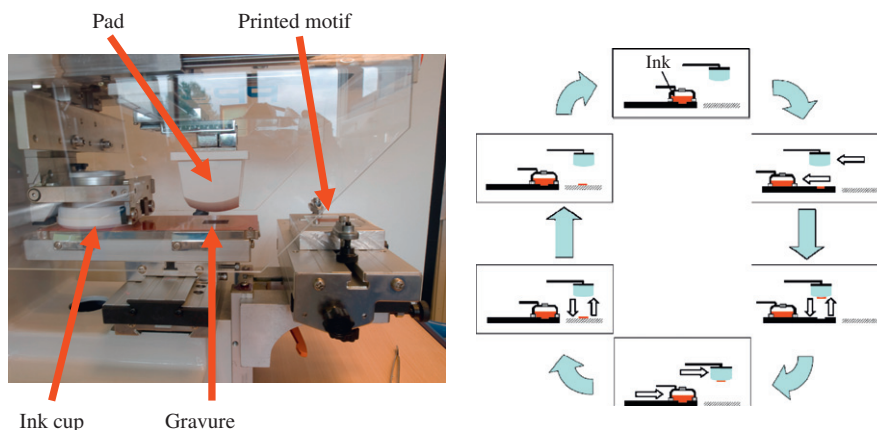
### 2.1.6. Pad printing

In cases where the surface of the substrate is corrugated or presents both concave and convex surface curvature there are few coating techniques that work well. Pad printing is one such printing technique that offers several other advantages. It should be mentioned that there are certainly also challenges before its widespread use can be generally expected. The technique is only suited for printing small areas but offer a full 2-dimensional printed pattern. The technique is an off-set technique that





**Fig. 8.** Schematic illustration of the ink jet printing process using a data pulse train to generate droplets on demand via a pressure transducer (top left) and a system where droplets are generated continuously and the pattern created by deflecting the unwanted droplets away from the substrate (top right). Photographs of the laboratory ink-jet printer used for printing the polymer solar cells reported in Ref. [95] (bottom left). Filling ink into the cartridge (bottom middle) The completed ink jet printed device (lower right). Photographs were taken and provided by Tom Aernouts, IMEC, Belgium.



**Fig. 9.** A photograph of a pad printer in the open position where the gravure is exposed (left) and the pad printing cycle (right).

employs a silicone rubber stamp to transfer the motif from a gravure to the substrate. The pad printing cycle is shown in Fig. 9 along with a photograph of a typical pad printer. Examples of the use of pad printing for printing the active layer in polymer photovoltaics [96] and printing of the silver electrode in silicon photovoltaics [97] are described in the literature. The advantages of pad printing include the use of an ink cup, which allows for the use of relatively volatile solvents. The wet motif is only exposed briefly to the atmosphere between pickup from the gravure and printing onto the substrate. The disadvantages are the relative difficulty with which the ink is procured and the relatively large ink volume required to operate the

printer. For a low viscosity ink around 20 mL is required whereas >100 mL is required for viscous ink materials. The method is parsimonious and only the ink printed is in principle used.

Similarly to screen printing, however, a certain volume of ink is required for operation. The thickness of the dry film is given by the volume of ink contained in the gravure per unit area ( $\text{cm}^3\text{m}^{-2}$ ),  $V_g$ , multiplied by the pick-out ratio,  $k_p$ , and the concentration of material in the printing ink as follows:

$$d = V_g k_p \frac{c}{\rho} \quad (5)$$

The pick-out is not always complete and in addition the force of the pad into the motif may cause the ink to flow thus locally producing a thinner printed film.

## 2.2. Roll-to-roll techniques

In contrast to the techniques described in Section 2.1 that all operated on a single device the methods described in this section all involve a substrate in the form of a very long sheet that is wound on a roll. The substrate material in this case is often referred to as the web and it is required to have some mechanical flexibility. During printing and coating the web material is unwound from the roll and passed through the printing or coating machine and once through the process the material is rewound on a roll. Aside from the printing or coating operation there may be other process steps involved such as heating, drying, UV-curing, etc. Ideally the raw substrate should enter the processing machine at one end and the completed flexible polymer solar cell should emerge in the other end. This is appealing and in the printing and coating industry one strives to process in such an integrated manner as the handling damage is significantly reduced and often throughput can be increased. For a polymer solar cell that comprises three printed or coated layers the distinction can be seen in Fig. 10. In practical terms this may not be straightforward as the integrated process requires that similar processing speeds can be achieved for each layer or step in the process and this can by no means be generally expected.

Thus until a full process is optimised it is advisable to use the discrete route where each layer is processed individually and once rewound the roll of material is moved on to the next machine. Alternatively it can be spooled backwards or moved back from the winder to the unwinder whereupon the next step can be processed. There have so far been only two detailed scientific reports of polymer solar cells where R2R processing have been involved [75,99] and only one of them where the active layers were coated by R2R methods [99].

R2R processing has been reported used for polymer solar cells but without scientific detail and it is thus difficult to judge what has been done by R2R processing and how it was done.

It is also very likely that as polymer solar cells evolve into products less and less information will be made available on the processes for proprietary reasons. It should be mentioned that most printing and coating methods only deal with the formation of the wet film and that the dry film that is employed in the solar cell is obtained by a secondary process to the printing and coating operation such as drying or curing. Drying is as complicated as coating and will not be detailed specifically in this review. It

should, however, be mentioned that the physical size of the coating unit does not scale with the web speed whereas the drying unit does. Thus, the drying unit for a system operating at  $1\text{--}10\text{ m s}^{-1}$  is much larger than a system operating at  $1\text{--}10\text{ min}^{-1}$ . A R2R coating system may be small and compact in the case of discrete steps, narrow web widths and low speed or it may be very large in the case of large web widths, integrated and high-speed processing. A small system suitable for lab-scale experiments is illustrated in Fig. 11 and comprises unwinder, coating unit, dryer and winder. There are a lot of practicalities associated with a coating or printing machine such as tension and speed control of the web, cleaning of the web, removal of static electricity (especially for plastic substrates), surface treatments, IR-heating, hot-air drying, UV-treatment and web cooling. An example of a commercially available coating system [98] has been described in the literature [99] and is illustrated in Fig. 11. The printing or coating may take place over unsupported web but is most often carried out over a roller of some sort that guides the web past the coating or printing unit and acts as a solid support. The coating roller may be driven by a motor or may simply rotate freely and follow the web. The simplest systems comprise at least one roller (i.e. knife-over-edge, slot-die and curtain coating) but more rollers may be involved as in 2-roller gravure systems where one roller with the pattern to be printed is brought into contact with web supported by the coating roller. More rolls may also be involved where a feed, metering or fountain roller is employed that feeds the roller carrying the motif with ink. In flexo- and offset-printing multiple feed roller systems supplies ink to the coating roller and in lithography many inking and damping rollers are employed. In Fig. 12, the simplest coating systems are shown schematically. The coating and printing of inks have been detailed in several textbooks and specialised texts [76–81]. Common to all of them, however, are that the printed or coated ink material is rarely functional except perhaps when it is a metallic conductor [79,100–102]. It is thus uncommon in the coating business to think of the coating or printing process to give a final film with a complex function that relies on the nanoscale morphology, molecular organisation and interfaces between layers in multi-layer composite films. In the following, simple details of the techniques are given that should aid the experimental scientist involved with polymer photovoltaics to get started in R2R coating of active layers for devices and modules.

### 2.2.1. Knife-over-edge coating and meniscus coating

This technique is similar to doctor blading except that the knife in this case is stationary and the web is moving. The knife is suitably used in conjunction with an ink bath positioned in front

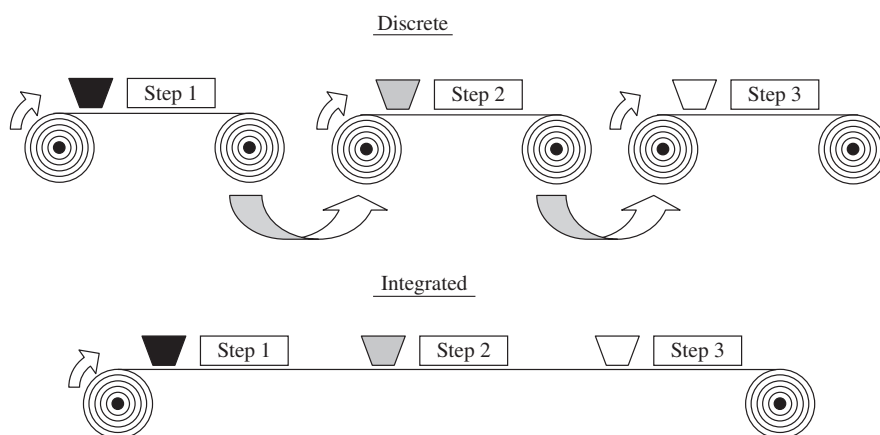
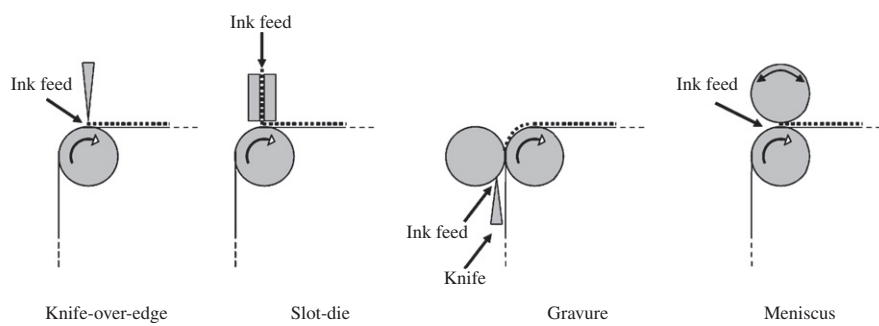


Fig. 10. Illustration of R2R processing of a 3-layer polymer solar cell in discrete steps (above) or in an integrated process (below).



**Fig. 11.** A discrete laboratory-scale coating system from Solar Coating Machinery GmbH, Germany [98]. The system is built on versatile metal alloy profile allowing the user to modify the system with ease. The system shown on the photograph is also described in detail in Ref. [99].



**Fig. 12.** Schematic drawings of roll coating and printing systems. The coating roller and coating unit are shown in grey shading. The web is shown as a thin line and the coated material is shown as dotted line.

of the knife (with respect to the direction of movement of the web). The knife may also be positioned over unsupported web. In Fig. 13, a typical knife-over-edge coating system is shown.

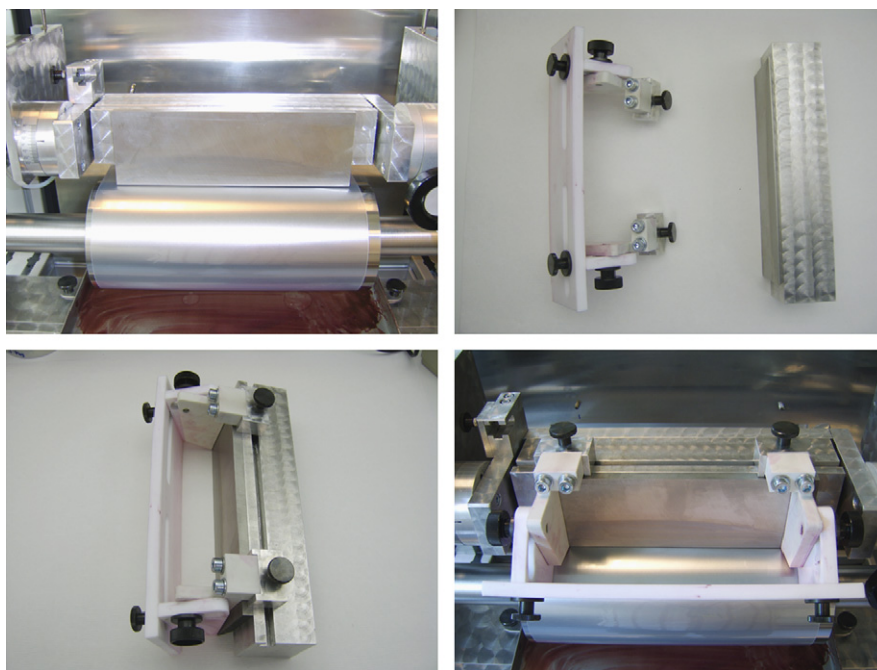
Knife-over-edge coating is a 0-dimensional coating technique and the coating is applied evenly over the surface of the substrate. While it is not suited for patterning, the barriers of the coating bath may be adjusted so as to limit the coating to a part of the knife width. The edge definition is, however, not sharp and depends on the gap between the knife and the substrate and the web speed. At slow speeds and a short knife-to-web distance the meniscus of the liquid will draw out along the knife and will extend over the entire length of the knife. The thickness of the coated film is given by Eq. (2) provided that the knife edge is flat and parallel with the surface of the substrate. If this is not the case the thickness is subject to some variation. The ink bath shown in Fig. 13 is not suited for liquids with a viscosity  $< 50$  cP and liquid will leak and run back over the coating roller along the web. In the setup shown in Fig. 13 this is not a problem if the ink does not dry out (but it is impractical due to loss of ink). The technique works well for liquids of low viscosity without the ink bath as shown in the top left of Fig. 13. The feed of the ink can be done manually thus ensuring that only a small amount of ink is in front of the

knife and avoiding that it runs down over the roller. Alternatively a small piston pump (Fig. 14) may be employed to maintain a sufficient flow of liquid in the front of the knife. There is no waste of ink solution during coating and depending on operation knife-over-edge coating is a premetered coating technique as all the material supplied to the knife will be coated onto the substrate. In addition, knife-over-edge coating fills out an uneven surface and if the ink has good levelling properties very smooth films are obtained (even on rough surfaces). Meniscus coating offer the possibility to coat an even layer over the surface just like knife-over-edge coating but the metering of the ink is done by a roller separated by some distance from the coating roller carrying the web. The direction of rotation of the roller may be in the same direction as the web or opposite. The meniscus formed in the gap between the two rollers can be controlled and a variation in the thickness may be obtained by controlling the gap distance and the speed/direction of the roller [103].

#### 2.2.2. Slot die coating

Being a 1-dimensional coating technique slot-die coating allows for the coating of stripes of material which is well suited for making a multilayer solar cell with stripes of different





**Fig. 13.** Knife-over-edge coating system. The direction of rotation for the roller is clockwise when viewed from the right. The knife is shown over the coating roller without ink bath (to left). The knife with an ink bath that gives the possibility to adjust the coating width is shown disassembled (top right) and assembled (bottom left) and finally installed on the coater (bottom right).



**Fig. 14.** Examples of feed systems. A small piston pump (left) or a pressure tank (right).

materials layered on top of each other. The alignment of the pattern is easy as the coating head is simply translated along the direction perpendicular to the direction of the web movement. The technique belongs to the premetered coating techniques where all the ink supplied to the coating head is coated with no loss. The ink is feed to the coating head with a pump or by a pressure system as shown in Fig. 14.

The slot-die technique is robust and simple in operation while the coating head is quite complex as compared to knife-over-edge coating. A disassembled slot-die coating head is shown in Fig. 15 and comprise several pieces that are assembled with gaskets such that it supports pressurisation of the ink during coating. The most important part is the mask that defines the slots and the void in the coating head that disperse the ink through the individual slots. In Fig. 15, the mask can be seen for a pattern that comprise 1, 2, 3 and 8 stripes with a width of 9 mm spaced by 3 mm. The coating head and the mask are stainless steel and the mask thickness may typically range from 10 to 100  $\mu\text{m}$ . It is difficult to handle masks thinner than 20  $\mu\text{m}$  and masks thicker than 50  $\mu\text{m}$  require very viscous inks to be useful.

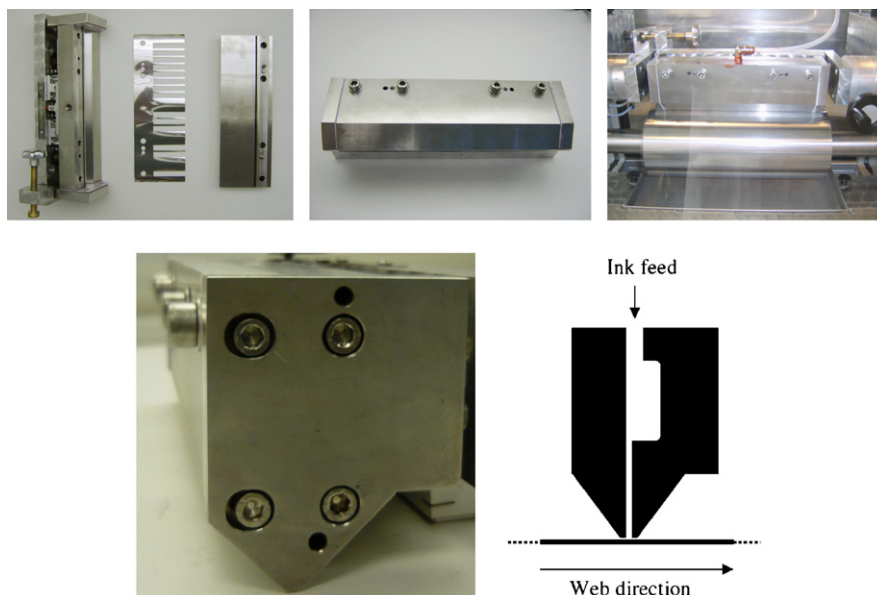
In the case of ink solutions for polymer solar cells that typically have a low viscosity in the range 1–20 cP the range of mask

thicknesses of 20–50  $\mu\text{m}$  are suitable. Some extra measures may be needed to control the meniscus when wishing to coat a fine pattern accurately with low viscosity solutions at low coating speeds of  $<2 \text{ m min}^{-1}$  [100]. It is easy to change the coated pattern as only the mask needs to be exchanged. Slot-die coating has been studied intensely and works very well for relatively viscous solutions ( $> 100 \text{ cP}$ ) at high coating speeds ( $> 10 \text{ m min}^{-1}$ ) [76,77]. Ideally the wet thickness is controlled by the speed of the web and the rate of feeding the liquid to the coating head. For a given web, ink flow rate, coating width and solid concentration the dry thickness can be estimated as follows:

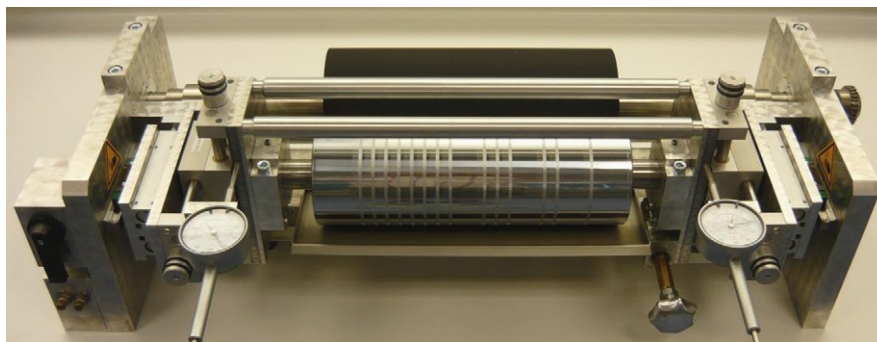
$$d = \frac{f}{S \cdot w} \cdot \frac{c}{\rho} \quad (6)$$

where  $d$  is the thickness in cm,  $f$  is the flow rate in  $\text{cm}^3 \text{ min}^{-1}$ ,  $S$  is the web speed in  $\text{cm min}^{-1}$ ,  $w$  is the coated width in cm,  $c$  is the solid content in the ink in  $\text{g cm}^{-3}$  and,  $\rho$  is the density of the dried ink material in  $\text{g cm}^{-3}$ . It should be noted that there is a range of web speeds in which slot-die coating is operational for a given ink composition and when passing beyond those limits (either towards low speeds or high speeds) coating is no longer possible.





**Fig. 15.** Slot-die coating head. Partially disassembled showing back assembly, mask and front piece (top left). Assembled coating head viewed from the lip side with the slots (top middle). The slot-die coating head mounted over the coating roller (top right). A close-up side view of the coating head (bottom left) and a schematic (bottom right).



**Fig. 16.** A 2-roller gravure system is shown. The black roller is the driven rubber coated backing roller. The printing roller is the blank roller. The gravure is visible as stripes running around the roller. The ink is placed in the bath beneath the printing roller. The dials and knobs are for adjusting the printing roller with respect to the backing roller. The web enters from beneath between the two rollers. Excess ink is doctored off the printing roller by a knife (not visible).

### 2.2.3. Gravure coating

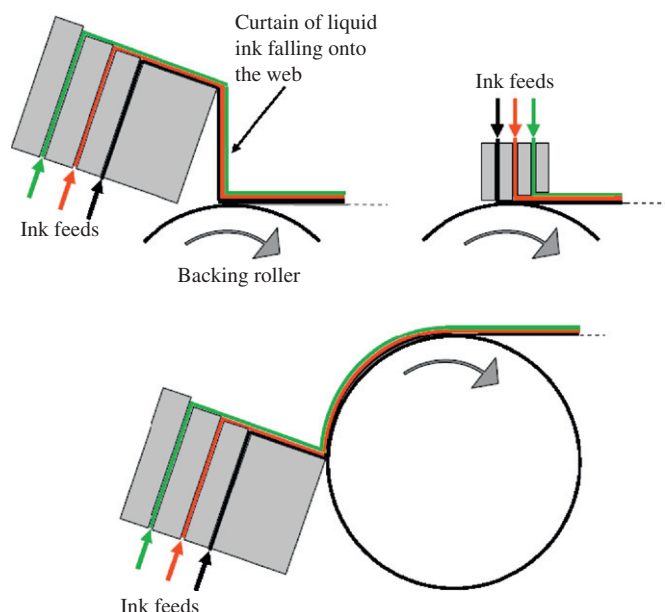
The achievement of a 2-dimensional pattern by R2R methods introduces a new challenge of aligning the pattern transversely and along the web. This is by no means simple and we deal here with the coating of 1-dimensional stripes using gravure coating. The gravure technique is increasingly complex as compared to knife-over-edge coating but is equally parsimonious when it comes to usage of ink. In its simplest form it comprises a 2-roller system (often referred to as direct gravure) where the coating roller has an engraved pattern (Fig. 16). The coating roller is partially inserted into a bath of the ink such that it is continuously refilled. The excess ink is doctored off the roller just before the roller is brought into contact with the web. The coating roller is forced into the support roller that guides the web. The support roller is most often made with a hard rubber coating such that it gives way for the gravure roller. Upon contact the ink in the gravure is transferred to the substrate in the desired pattern. The gravure technique suffers from the fact that the change of pattern requires that a new roller is engraved and this is a costly process.

The shape of the gravure on the roller is quite important for the printing process. There have been many studies of the effect of the microscopic pattern of the gravure in the printed areas and the efficiency of printing that to a large extent also depends on the

nature of the ink [104–107]. The advantage of gravure is that low viscosity inks work very well and very high web speeds are possible  $1\text{--}10\text{ m s}^{-1}$ . There has been only one example of gravure printing of the active layer in polymer photovoltaics [108] and one example of use for coating  $\text{TiO}_2$ -based inks [109].

### 2.2.4. Curtain, multilayer slot and slide coating

These printing techniques have the potential to become the most important coating techniques in the context of polymer photovoltaics. It is possibly also the most costly and complex coating techniques to develop. Slide and curtain coating allows for the simultaneous coating of a multilayer film (up to 18 layers may be deposited simultaneously). These techniques were developed for the photographic film industry where many layers were coated simultaneously on top of each other. This means that for the right combination of ink solutions all the layers in the solar cell may in principle be printed in a single coating step. The large number of layers that can be coated implies that it would in principle be possible to process tandem and multijunction cells in one coating step. The challenge with these coating techniques is that a very rapid ink flow is required and this implies that a large web speed is needed for the coating to work properly when thin films are prepared. Typical web speeds exceed  $4\text{ m s}^{-1}$  and the



**Fig. 17.** An illustration of curtain (top left), multiple slot (top right) and slide coating (bottom) for the simultaneous coating of three layers.

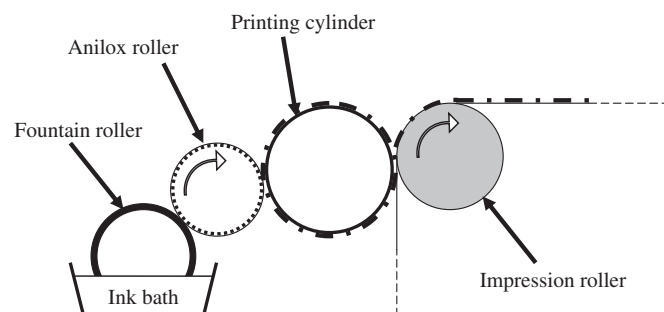
development of the technique will thus require large amounts of material and substrate. In addition to this there is naturally the morphology control and annealing requirements of each of the layers in the film. The potential saving in cost is, however, so large that it is very likely that some or all of the layers in future low-cost polymer solar cells will be coated using slide or curtain coating techniques as shown schematically in Fig. 17.

### 2.3. Other film-forming techniques that may become relevant

Printing and coating is an integrated part of human communication and there are many techniques that have not been explored and perhaps not even contemplated for use in polymer photovoltaics simply because the complexity of the technique puts so many constraints on the ink that it is an entirely new research field to simply procure the ink for the process. So far efforts within polymer photovoltaics have been placed more humbly on making polymer materials that work in solar cells and the procurement of inks has been limited to dissolving the polymer material in a few solvents and using this solution as the ink. Additives have been explored little while there are a few successful examples of using thermocleavable solvent materials [48,75,89,93].

#### 2.3.1. Spray coating

This technique involves forcing the printing ink through a nozzle whereby a fine aerosol is formed. A carrier gas and electrostatic charging may be involved to aid in directing the aerosol at the surface that is to be coated. The formation of the aerosol and evaporation of some of the solvent is complex and while spray coating in principle is R2R compatible, allows for patterning of the coated film with a reasonable detail (millimetre scale) it can be difficult to prepare films with a smooth surface. The aerosol droplets have to level once they have reached the substrate and this is not necessarily granted. The ease with which inks are prepared ranges from simple to complex and the range of viscosities that will work is wide. There is no simple relationship describing the wet film thickness while it is possible to prepare both thin and thick films. There has so far been a few examples of the use of spray coating in organic photovoltaics [110].



**Fig. 18.** An illustration of the flexo offset printing technique in a 4-roller configuration with a fountain roller that fills the anilox roller, the anilox roller metering ink to the raised pattern on the printing cylinder and finally the web passing between over the printing cylinder and the impression roller with transfer of the ink pattern.

#### 2.3.2. Flexographic printing

Flexography is similar to gravure printing except that the printed image stands up on the printing roller the surface of which is typically made from rubber. It is in many ways similar to pad printing and can be viewed as continuous pad printing where the image information is shaped into the pad. The typical flexo system is a four roller system comprising a fountain roller that fills an Anilox roller (a roller that has an engraved pattern all over) the flexo roller with the pattern is then filled with ink from the Anilox roller and applies the print to the web, which is guided by a back-up roller (also called an impression cylinder or roller). The process is simple and should be highly applicable to polymer photovoltaics with some requirements of a low volatility of the ink. It may be an advantage with a closed ink chamber whereby exposure of the ink to the atmosphere is limited to the surface of the Anilox roller and printing roller only (Fig. 18).

#### 2.3.3. Offset lithography

An interesting technique that may hold promise for the future printing of polymer solar cells is lithography. Lithography is a 2-dimensional printing technique that unlike most other techniques is planographic (i.e. both printed and non-printed areas are in the same plane). Originally the offset lithography process has been based on water chemistry (but water-free processes do exist) and works by having hydrophobic areas that is wetted by the ink and hydrophilic areas that does not wet by the ink. When an inked roller is passed over such an image plate or roll only the areas that should be printed accept ink. The inked image is then typically offset to a roller that transfers the print to the web. Offset lithography is a fast process and the preparation of the master is relatively low cost compared with gravure. It is an appealing technique but is will require some development of ink systems before it can be envisaged used in polymer photovoltaics.

#### 2.3.4. Electrophotographic, electrographic and magnetographic

Some techniques that should be viewed as far removed from possible at the moment are the techniques that essentially rest on the principle of photocopying where an image is formed by selectively discharging a statically charged drum using light. Such a process is the electrophotographic process that has the advantage that the image is easily transferred to the roll and there are thus no special requirements for making masks or masters. The clear disadvantage is the ink, which is commonly in the form of a solid powder or toner that attaches electrostatically to the charged areas of the roller. Subsequent transfer to the web and curing secures the image on the surface of the web. There is a requirement that the substrate can also be charged statically such that the image is held in place until cured. The development of

solid ink systems for polymer photovoltaics is currently unheard of but perhaps not so far fetched. The largest challenge is to find methods that give very thin films. Electrographic methods employ an electrically conductive master plate where the image information is in the conductivity of the surface of the master. Liquid inks can be used and the process of transferring the image to the web is otherwise similar the electrophotographic process. Electrostatic printing charges the substrate directly followed by applying the toner directly onto the charged areas. Finally magnetographic is similar except that the image information is stored on a roller with a magnetic surface. The ink or toner must also be magnetic which has a severe limitation in the context of polymers but may be useful for the printing and coating of metallic electrode materials which may possibly be prepared in magnetic forms either based on inherently magnetic materials or by having particles with a magnetic core. Common to all of the techniques in this section is that the image must be rewritten for every print (magnetographic images have some latency and may be used several times).

#### 2.4. Comparison of the film-forming techniques

It is important to compare the techniques and while many techniques have been mentioned only the few that are readily adaptable (or that might be very relevant) to polymer photovoltaic film processing have been discussed in detail. A requirement is still that the ink systems are developed. In Table 1 some of the techniques are compared by taking parameters such as parsimony of the use of ink, the ease with which a pattern is formed and controlled, the possible printing speeds, the difficulty of preparing the ink, the wet thickness that can be obtained and the compatibility with R2R processing.

#### 2.5. Commercially available inks

There are currently very few commercially available printing inks for polymer solar cell development and only one company offer application ready polymer solutions optimised for preparation of the active layer [111]. There are, however, many available inks that are relevant for processing of the auxiliary layers such as semitransparent PEDOT:PSS formulations optimised for screen printing, gravure printing or slot-die coating [112,113] or screen printable pastes for silver electrodes [114]. The limited availability

of inks signify where there technology is at the moment and it should be emphasized that both PEDOT:PSS and silver pastes have been developed for different purposes and the current area of application lies elsewhere (antistatics and flexible electronics).

### 3. Patterning and juxtaposition of multilayer films

A polymer solar cell is inherently a multilayered thin film structure comprising an active material in contact with two different electrodes. While it is possible to envisage a device geometry with coplanar electrodes all convincing examples of polymer solar cells to this date have involved the active layer as being sandwiched between the two electrodes (sometimes including additional layers). The properties of the materials available for use put some constraints on the device geometry that is possible if the electrical power is to be extracted efficiently. In turn this has influence on the requirements for the pattern of the individual layers and their juxtaposition.

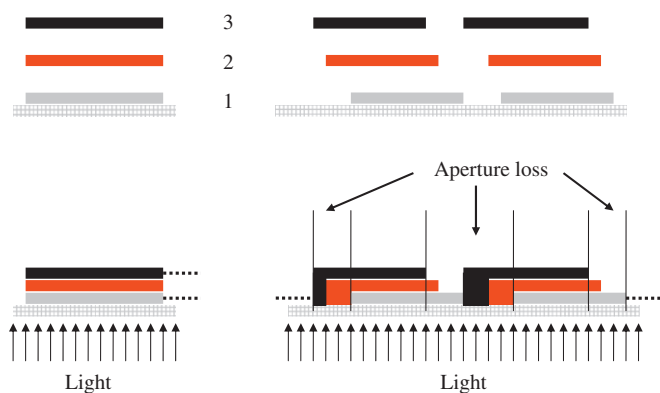
#### 3.1. Zero-dimensional coating

Techniques such as spincoating, casting, doctor blading, meniscus coating and knife-over-edge coating gives rise to a coating with no pattern i.e. the entire surface of the substrate is coated evenly. If possible to use for preparing all layers this would be the simplest manner to prepare polymer solar cells since one would ideally coat each layer in the stack, one after the other. There is in this case no need for aligning the individual layers with respect to each other. However, there is a strict requirement for a very high conductivity of the electrodes. This is not a problem to solve for one of the electrodes since it may simply be a thick metal sheet. However, the requirement in a solar cell with a sandwich structure is that one of the electrodes is transparent or semitransparent and this is problematic as there are no available transparent electrodes with a sheet resistivity even approaching that of metals where values in the range of  $\text{m}\Omega\text{square}^{-1}$  are easily achieved. In practical terms this means that methods employing 0-dimensional coating only works for very small active areas where one is not limited by sheet resistive losses. Also the method of applying the electrical contacts must not lead to penetration of the active layers thus creating a short circuit. One advantage in the ideal case is that there is no aperture loss and all of the exposed area is ideally active.

**Table 1**  
Comparison of film-forming techniques by printing and coating

Technique	Ink waste	Pattern	Speed	Ink preparation	Ink viscosity (cP)	Wet thickness ( $\mu\text{m}$ )	R2R compatible
Spincoating	5	0	–	1	1	0–100	No
Doctor blade	2	0	–	1	1	0–100	Yes
Casting	1	0	–	2	1	5–500	No
Spraying	3	0	1–4	2	2–3	1–500	Yes
Knife-over-edge	1	0	2–4	2	3–5	20–700	Yes
Meniscus	1	0	3–4	1	1–3	5–500	Yes
Curtain	1	3	4–5	5	1–4	5–500	Yes
Slide	1	3	3–5	5	1–3	25–250	Yes
Slot-die	1	1	3–5	2	2–5	10–250	Yes
Screen	1	2	1–4	3	3–5	10–500	Yes
Ink jet	1	4	1–3	2	1	1–500	Yes
Gravure	1	2	3–5	4	1–3	5–80	Yes
Flexo	1	2	3–5	3	1–3	5–200	Yes
Pad	1	2	1–2	5	1	5–250	Yes

Ink waste: 1 (none), 2 (little), 3 (some), 4 (considerable), 5 (significant). Pattern: 0 (0-dimensional), 1 (1-dimensional), 2 (2-dimensional), 3 (pseudo/quasi 2/3-dimensional), 4 (digital master). Speed: 1 (very slow), 2 (slow  $< 1\text{ m min}^{-1}$ ), 3 (medium  $1\text{--}10\text{ m min}^{-1}$ ), 4 (fast  $10\text{--}100\text{ m min}^{-1}$ ), 5 (very fast  $100\text{--}1000\text{ m min}^{-1}$ ). Ink preparation: 1 (simple), 2 (moderate), 3 (demanding), 4 (difficult), 5 (critical). Ink viscosity: 1 (very low  $< 10\text{ cP}$ ), 2 (low  $10\text{--}100\text{ cP}$ ), 3 (medium  $100\text{--}1000\text{ cP}$ ), 4 (high  $1000\text{--}10,000\text{ cP}$ ), 5 (very high  $10,000\text{--}100,000\text{ cP}$ ).



**Fig. 19.** An illustration of a 3-layer solar cell prepared by 0-dimensional (left) and 1-dimensional (right) coating techniques. The transparent electrode is shown in grey, the active layer in red and the metallic electrode in black. The coating sequence of the layers and their positions are shown (top) and the associated introduction of an aperture loss when connecting 2 cells in series. Electrical connections are shown as dotted lines.

### 3.2. One-dimensional coating

A single dimensionality of the pattern allows for creating a striped pattern. The stripes themselves may be wide or narrow but otherwise there are not many possibilities in terms of a pattern (any modulation of the stripe structure is assumed to require a higher dimensionality of the film-forming technique).

A 1-dimensional pattern allows for creating an electrical connection between layers thus enabling serially connecting devices. This efficiently solves the problem of a high sheet resistivity for the transparent conductor but also introduces an aperture loss since the area required for interconnection does not contribute towards harvesting the sunlight. In Fig. 19, the aperture loss is illustrated in the simple case of a three-layer cell prepared by 1-dimensional coating (in the 0-dimensional case there is no aperture loss). In practical terms the aperture loss is significant and while exaggerated in Fig. 19 it easily accounts for 20–60% of the available area

### 3.3. Two-dimensional coating and methods for juxtaposing separately printed layers

With two dimensions available for the pattern in the plane of the substrate it becomes possible to create a complex pattern such as text or a comb-like pattern. The ranges of techniques available are many and the most important aspect is how the pattern is indexed or juxtaposed with respect to the pattern already on the substrate. In the 1-dimensional case this is easy as exemplified by stripes that run along the length of the web. In the case of two dimensions there has to be some method of positioning the print with respect to the surface of the substrate, both along the direction of the web and in a direction perpendicular to it. This is especially important if the final device structure comprise many layers where overlap of layers is essential for control of interconnectivity and for the avoidance of short circuit. The difficulty with which the printed or coated pattern is juxtaposed with a pattern already on the substrate may range from simple to complex. In the simplest cases as for example slot-die coating a striped pattern on top of a striped pattern already on the substrate it suffices to simply translate the slot-die coating head in a direction orthogonal (or perpendicular) to the web direction (provided that the stripes run along the direction of the web). In the intermediate case such as screen printing it is customary to co-print markers that allow for the adjustment of the screen in

directions along the web direction and orthogonal to it. The most difficult case is when the printed pattern is on a roll as the only reasonable way to view the adjustment is through printing and observing the misalignment followed by correction. This may be very difficult during operation for simple coating systems whereas this has been solved efficiently for offset colour printing where many printing stations are placed serially along the web.

### 4. Ink requirements, surface energy and surface tension

The likely reason that these topics have been explored little in the context of polymer solar cells (or at least reported to a very limited extent) is that there has been little need for it until now and possibly since spincoating has been used almost exclusively for film formation and it allows for the formation of high-quality films for inks that will not wet the same surface during static conditions (i.e. aqueous PEDOT:PSS does wet an ITO surface well without a rotational shear field). In most reports experimenters have simply gotten away with not knowing about these parameters and since their work have allowed other experimenters to reproduce their report one could argue that there was no compelling need for including the information in the report. The property that ink must have in the context of coating a given surface has, however, been subject to numerous studies in the context of the traditional coating industry. There is a lot of knowledge on this these important aspects that have been detailed in many excellent accounts [76–78,81]. It should perhaps be mentioned briefly that some ink properties relate to the coating technique itself such as the viscosity and volatility of the ink and some of the properties relate to the interaction of the ink with the surface of the substrate. The most important aspects here are the ability of the ink to wet the surface well, to level giving a smooth film and for the wet film to stay stationary where it is printed (i.e. it must not run and smear the pattern). The surface tension of the ink must generally be lower than (or equal to) the surface tension of the surface (also known as the surface energy when dealing with a surface) in order for the ink to wet the surface well. The manner in which this is generally solved is by employing additives (i.e. by addition of detergents to lower the surface tension of the ink solution) or by treating the surface of the substrate (i.e. by corona treatment to increase the surface energy).

### 5. Processing post-film formation

Once the film has been formed it is in the traditional view of coating technology still wet and will need treatments (i.e. drying) before it is finally rewound on a roll. In the context of polymer solar cells there are some additional treatments that are customary to reach the required functionality of the film in a solar cell sense. The classical treatments are thermal and solvent annealing of the freshly prepared film. Those two are in principle easily realised during coating as the wet film can be allowed to dry slowly (at slow web speeds) and the drying may serve as a thermal annealing step. There are other processing techniques that are customary in traditional coating industry that may prove useful in the context of polymer solar cells such as chemical processing, light processing (using infrared, visible, UV or microwave radiation). At this point it is difficult to judge which techniques that may enjoy prevalence in the future.

### 6. Substrates and transparent electrodes

The requirements for the substrates that are useful for R2R processing is that they are flexible and this includes plastic



substrates and thin metal foils. Most often the substrate is viewed as a carrier of the solar cell only but a judicious choice of a metal foil may in principle be used as the substrate and one of the electrodes. Until now the most successful flexible transparent substrate material comprise a polyethyleneterephthalate (PET) carrier with a sputtered layer of transparent conducting ITO on top. As discussed in the introduction ITO is problematic since it contains the element indium and PET has many desirable properties while being limited in the maximum temperature it will endure during processing ( $\sim 140^\circ\text{C}$ ). There is an urgent need for the development of flexible indium-free transparent substrate/electrode composites and while some novel examples exist in the literature much more work is needed in this area as there in essence is very few alternatives to indium and PET. Ideally the development should include a transparent conductor solution that enables the experimental scientist to prepare the polymer solar cell structure on any R2R-based substrate by starting with a coating procedure leading to the transparent conductor (or finishing with it).

## 7. Solution versus vacuum processing

The only preparative technique that will give polymer solar cells at very low cost is a method that grants full R2R processing (a solid ink would also be possible). This implies that vacuum steps should be avoided. Often reports detail all solution processing starting from typically an ITO substrate that was arrived at by a vacuum process. Since there is no commercially available transparent conducting substrate without ITO or simple methods to prepare it, work in this area is urgently needed. While no solution can be given in this review some suggestions would be to explore inverted device geometries starting from metal foils or the development of conducting grids embossed in the transparent carrier substrate.

## 8. Conclusions

In this review the coating and printing techniques that are most relevant to the field of polymer solar cells have been given along with an overview of the extent to which they have been applied in the field. A large and dedicated amount of work is needed before the existing knowledge can be transferred to a large-scale coating process. The main reason for this has been identified as due to the near exclusive use of the spincoating technique for materials development and laboratory work. The advantage of spincoating is that parameters related to the ink and the interaction between the ink and the surface that is to be coated are not critical. In the context of most other coating and printing technologies these parameters are highly critical. The development of inks in the context of polymer solar cells is a whole new research area that also will require extensive work as the inks will need to be optimised for the particular coating or printing technique that is chosen. It has been difficult to clearly identify coating and printing techniques that are likely to be successful in future production and eliminate those that are not. It is, however, quite clear that techniques such as spincoating is of little relevance for potential fast high-volume production whereas knife-over-edge, slot-die and gravure coating are likely to gain prevalence. In addition the perspectives of being able to coat many layers in a single coating step using curtain or slide coating techniques and the preparation of dry ink systems hold great potential for, respectively increasing processing speed and enabling new coating and printing methods.

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