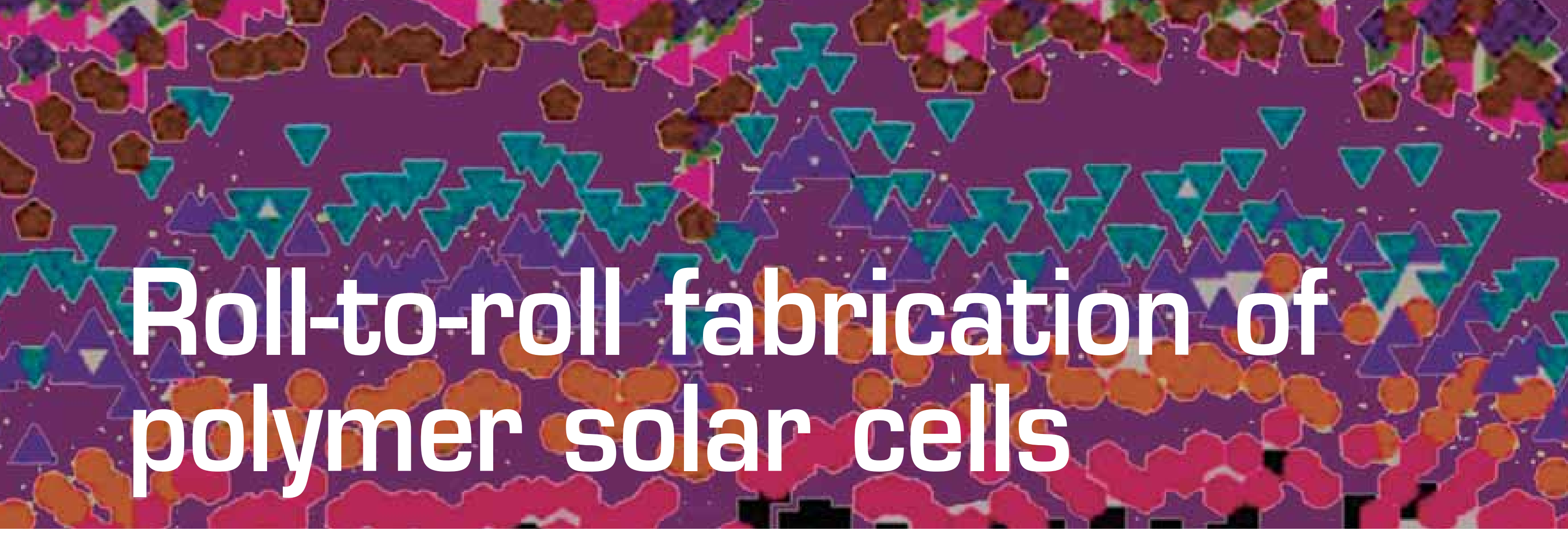

Roll-to-roll fabrication of polymer solar cells

As the performance in terms of power conversion efficiency and operational stability for polymer and organic solar cells is rapidly approaching the key 10-10 targets (10 % efficiency and 10 years of stability) the quest for efficient, scalable, and rational processing methods has begun. The 10-10 targets are being approached through consistent laboratory research efforts, which coupled with early commercial efforts have resulted in a fast moving research field and the dawning of a new industry. We review the roll-to-roll processing techniques required to bring the magnificent 10-10 targets into reality, using quick methods with low environmental impact and low cost. We also highlight some new targets related to processing speed, materials, and environmental impact.

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In order to reach its full potential, the imminent realization of the 10 %-10 yr target within the laboratory must transcend into a realistic industrial process. While this may seem trivial to many and even obvious to some, there are challenges that have perhaps been taken too lightly in laboratory reports. Often tiny spin coated devices prepared on rigid glass through toxic solvent processing and metal evaporation is said to be roll-to-roll and industry compatible. The view held here is that claiming to be roll-to-roll and industrially compatible without such instruments is similar to claiming that one can learn how to swim on a floor.

Solution processing, low cost, low energy budget, flexible solar cells, are keywords associated with organic solar cells, and through several decades the driving force for research within the field of polymer solar cells has been the huge potential of the technology to enable high throughput production of cheap solar cells. The evolution started with small area cells that used simple and relatively inexpensive techniques such as spin coating and thermal evaporation for the fabrication[1]. The unstable nature of conjugated polymers when illuminated in the presence of oxygen, and the reactive nature of low work function metals such as calcium towards water quickly led to the preparation of organic photovoltaic (OPV) devices in the protective atmosphere of a glove box. The main reason was the desire to raise power conversion efficiencies towards levels that are meaningful in the context of global energy supply. Claims of meeting these goals have now been made for small area solar cells (a few mm^2 to around 1 cm^2) with efficiencies reaching 8 – 9 %[2,3], (and reports above 10 % from Mitsubishi) but the field of organic solar

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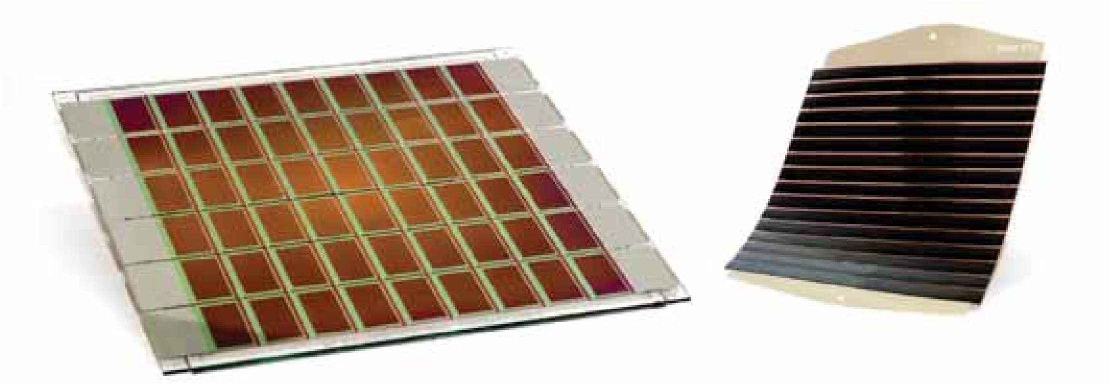

Fig. 1 An illustration of possibly the most refined example of an OPV module prepared using the laboratory route, comprising rigid glass substrate, spin coating, metal evaporation, getter materials, and a glass seal with a thick outline of several millimeters (left) and a flexible fully solution processed polymer solar cell module with a thickness of around one hundred microns (right).

cells is now facing the huge challenge of returning focus towards the original goal of large area production using a high throughput process. Such a shift in methodology does not automatically appear.

The general fabrication methods of spin coating and high vacuum thermal evaporation are not compatible with high throughput production which should preferably be performed in a continuous process such as roll-to-roll (R2R) processing. As a consequence of both the economical aspect of acquiring and running the necessary machinery and the focus on high efficiencies, the number of participants working with large area solar cells in true roll-to-roll coating processes has previously been limited. It should also be highlighted that the power conversion efficiency is considerably lower for larger area devices (currently < 3.5 %)[2]. In order for the organic solar cell to succeed as a technology, more effort must be directed towards large area fabrication combined with high throughput processing such as roll-to-roll methods. In this report we review some of the different printing and coating techniques that are fully compatible with R2R processing, and which could potentially be used in future mass production.

Film and device formation

An enormous palette of film forming techniques has been developed and many of them might be suitable for processing one or more of the layers in a polymer solar cell. In terms of development, an interesting distinction of the polymer and organic solar cell (when compared to most of the existing inorganic solar cell technologies) is that the development of processing methods for inorganic solar cells have been driven and defined by the solar cell technology. For polymer and organic solar cells, the possibility of solution processing has overturned this picture, and the wide selection of printing and coating techniques available may end up being what defines polymer solar cell technology.

When looking at OPVs as a technology it is important to consider our current position, which is in the doorway between the controlled and safe laboratory environment (behind us) and the outside world and field of application (in front of us). As our premise, we have the spin coating technique and the solution processed laboratory device. Our desire is to find the right combination of techniques that will yield the same result albeit on a larger scale, by a factor of > 1 000 000 in terms of both processed area and processing time (and several other parameters). In Fig. 1 we illustrate this by presenting a very refined version of a rigid solar cell module prepared using the laboratory method with good performance in terms of stability and efficiency[4]. In comparison we also illustrate a similarly sized flexible module prepared without a vacuum, produced entirely through roll-to-roll methods, using mainly water as the processing solvent. Both modules were prepared on laboratory scale equipment but while the total processing time for the rigid module is measured in days, the total processing time for the flexible roll-to-roll processed module is measured in seconds. The potential for increasing the throughput speed is present in both cases but the upper limit is inherently slower for the rigid module than for the roll-to-roll processed module.

In the most refined laboratory polymer cell, high performance is achieved through a delicate and highly empirical relationship between the processing method, the solvents, the additives, the drying, the materials, the substrate, and perhaps even the operator. When having to change virtually all these parameters in the effort to upscale, one may ask whether the laboratory performance should automatically be taken for granted in the large area roll-to-roll processed device? The answer is of course that it should not. A good argument in support of this view is that several high performing materials were reported years ago, but there have been no reported examples of high performing large area devices prepared by roll-to-roll methods using these materials (and it is not because it has not been attempted). The reason is that we have to re-invent or re-discover the processing conditions for the new setting which is not at all obvious, especially when considering that there are boundary conditions involved in fast roll-to-roll processing (speed, temperature, drying, multilayer processing, solvents, materials). In addition to this we do not know which printing or coating method will be the best choice for each layer in the polymer solar cell, which is typically comprised of five or more layers. There may thus be different film forming methods that are optimal for each layer in the stack. To approach the challenge constructively it is necessary to be confronted with these facts and use them as a guide. One should take the view that for a given materials selection there is a rational choice of both film forming methods and operating parameters.

In the following we will describe many of the available film forming methods with a view towards how they are particularly suited for processing polymer solar cells using roll-to-roll methods. We also stress that there are several important choices that should be made early on to avoid redoubling development efforts. As an example, an intimate part of a printing or coating technique is the solvent employed. We already know that the processing of OPVs on the gigawatt scale does not leave room for the use of any solvents other than water and perhaps some alcohols. Any effort spent using environmentally harmful chlorinated and/or aromatic organic solvents is thus likely to prove to be a wasted effort. A final point is that the OPV technology allows for very low processing temperatures and very thin outlines with low embodied energy. Life cycle analysis (LCA)[5-8] and financial analysis of roll-to-roll processed OPVs[9-12] are also tools that are used to direct research, and which have demonstrated that roll-to-roll processing of OPVs could yield very short energy pay-back times (EPBT) using simple approaches. By avoiding scarce elements such as indium, avoiding the use of vacuum processing, and using only solar heat and solar electricity, an energy payback time of the order of 1 day has been demonstrated to be possible[13]. This shows that researchers should be encouraged to go where it is difficult and try and address the difficult properties, rather than go where it is easy and then try and address the difficult properties. We should thus start out directly with roll-to-roll processing in the ambient atmosphere without a vacuum, using only environmentally benign solvents and processing methods. From here we should develop stable, low cost, and efficient solar cells. Any efforts reaching those latter properties in a manner that is not scalable at the 1-gigawatt-a-day level are likely to be in vain.

Printing techniques (wet films through contact)

Since the development of the printing press by Johannes Gutenberg (1440) 'the art of printing' has evolved to include a multitude of techniques; some of which are represented in Fig. 2. These techniques each have their own advantages and disadvantages, but they all rely on the same principle of transferring ink from a solid printing form to a substrate. Printing implies the transferring of a motif to a substrate through physical contact between the object carrying the motif and the substrate, and further implies that the pattern is two-dimensional. One exception to this rule is ink-jet printing where there is no direct contact.

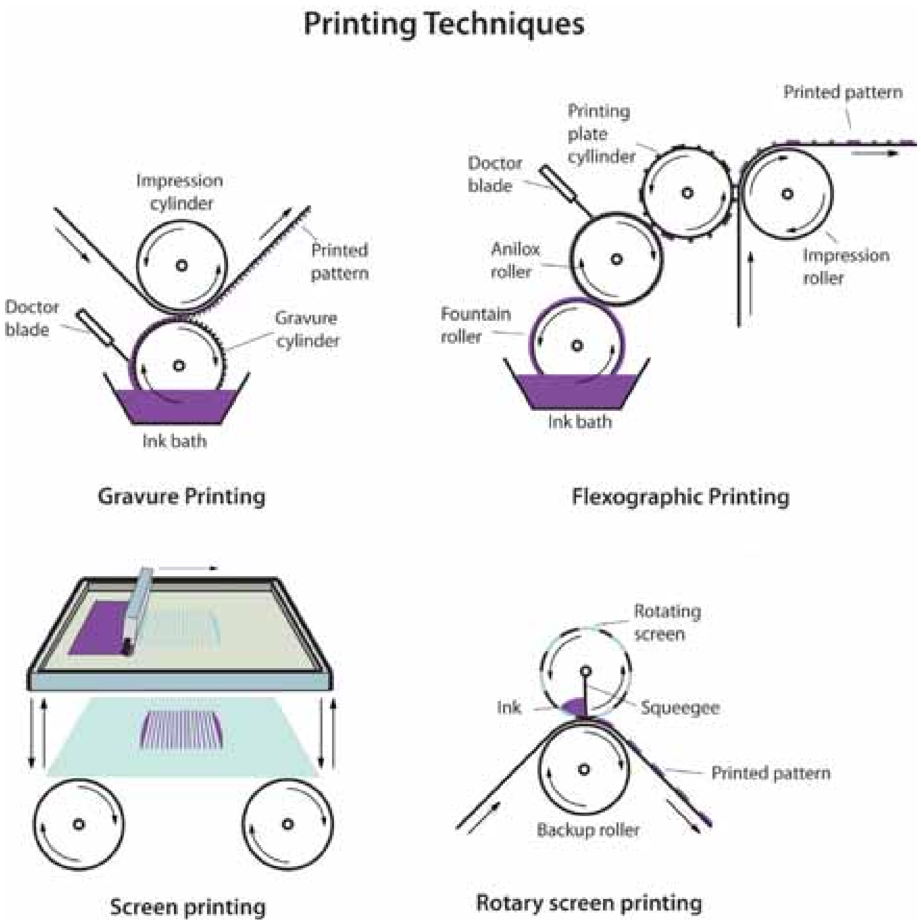

Fig. 2 Illustrations of the principles behind the four printing techniques; gravure printing, flexographic printing, screen printing, and rotary screen printing.

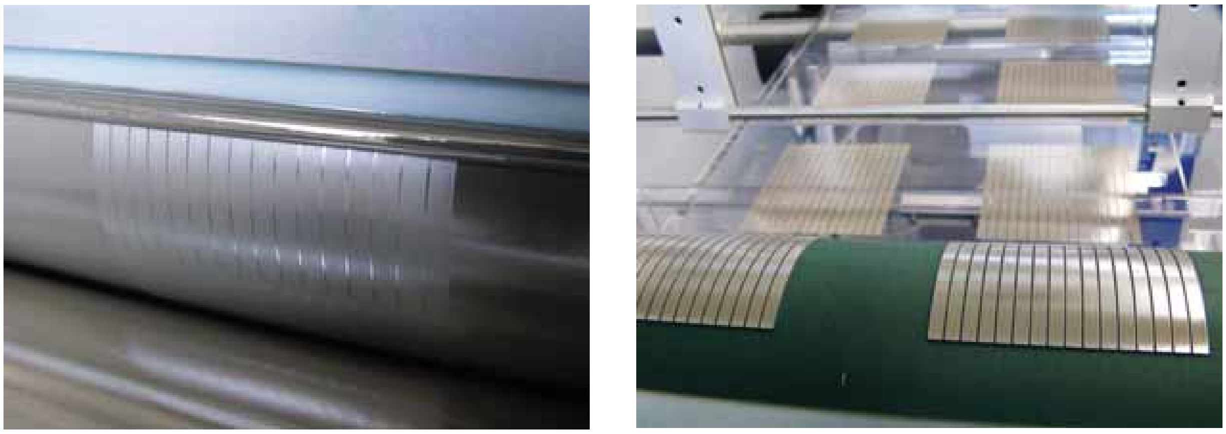

Fig. 3 The fountain roller disengaged from the anilox showing the negative print of the motif after ink pickout from the printing cylinder (left). The printing cylinder with the relief carrying the ink (in this case a silver paste) during printing. The final printed pattern on the web can be observed in the background (right).

Gravure printing

A commonly encountered printing technique in our everyday life is gravure printing which is widely used in the printing of magazines and high volume print runs like catalogues. As illustrated in Fig. 2, the technique relies on the transfer of ink, from tiny engraved cavities forming the pattern on the gravure cylinder, to the web by surface tension as the web is brought into contact with the gravure cylinder by pressure from the softer impression cylinder. The shape and thickness of the final imprint is defined by the pattern and depth of the cavities in the gravure cylinder. The engraved cells on the gravure cylinder are continuously filled from the ink bath and a doctor blade ensures removal of excess ink, ensuring that the ink is only present in the cavities. Gravure printing is suitable for the printing of low viscous inks at very high speeds, of up to 15 m/s, but careful optimization of the ink's surface tension is important, as the quality of the print is highly dependent on ink rheology, web speed, and the pressure of the impression cylinder. The use of gravure printing for the preparation of solar cells has only been reported in very few cases[14-17].

Flexographic printing

Flexographic printing is a R2R technology that differs from gravure printing mainly in the fact that the transfer of the ink is performed from a relief opposed to cavities (see Fig. 2). The final pattern stands out from the printing plate which is typically made from rubber or a photopolymer. The flexo system consists of fountain rollers that continuously transfer ink to the ceramic anilox roller which has engraved cells/micro cavities embedded into the exterior. This allows the collection of ink which is then transferred to the relief on the printing cylinder that performs the final transfer to the web. The ink pick out from the anilox corresponding to the negative pattern of the motif can be observed directly as shown in Fig. 3. Roll-to-roll flexographic printing is a relatively new technology for organic solar cells and has so far not been used for direct processing of the active layer, but examples of its use include the processing of modified PEDOT:PSS[18], processing of a wetting agent on the surface of the active layer[19], and the patterning of conductive grids (roll-to-roll) with a line width below 50 μm, which could potentially be used as electrode structures for ITO-free organic solar cells[20].

Screen printing

Screen printing is, in contrast to flexographic and gravure printing, a method that inherently allows for the formation of a very thick wet layer and thereby also very thick dry films, which can be useful for printed electrodes where high conductivity is needed. The typical wet layer thicknesses are in the range of 10 – 500 micron. There are two types of screen printing: flat-bed screen printing and rotary screen printing. The principle of the two methods is the same and outlined in Fig. 2. Photographs of the techniques in operation are shown in Fig. 4. The squeegee moves relative to the screen and forces the ink paste through the opening of the mesh, which define the desired motif. There are significant differences in the operation of the two techniques. The advantages of flat-bed screen printing (Fig. 4) are that the mask is low cost and it is possible to make one print at a time and make adjustments between each print if needed. For development and laboratory work this is a clear asset. In terms of production it is also possible to print on very large areas (on the scale of 10 square meters). Rotary screen printing differs in that the ink is contained inside the rotating cylinder with a fixed internal squeegee and the ink is less exposed to the surroundings. The mask is a lot more expensive than the flat-bed printing mask, but in terms of speed, edge definition/resolution, and achievable wet thickness, rotary screen printing is by far superior to flat-bed screen printing by at least an order of magnitude as it is a true roll-to-roll printing technique. It is the two-dimensional printing technique that allows for the largest wet thickness achievable (> 300 micron). Because of the cost of the mask, the more delicate operation, the more difficult adjustment, and the relatively time consuming cleaning procedures, rotary screen printing is not as well suited for laboratory work as the flat-bed technique. The printing techniques have proven particularly useful for the printing of the front and back electrodes for polymer solar cells[21-23] but also screen printing of active layers[24,25] have been reported.

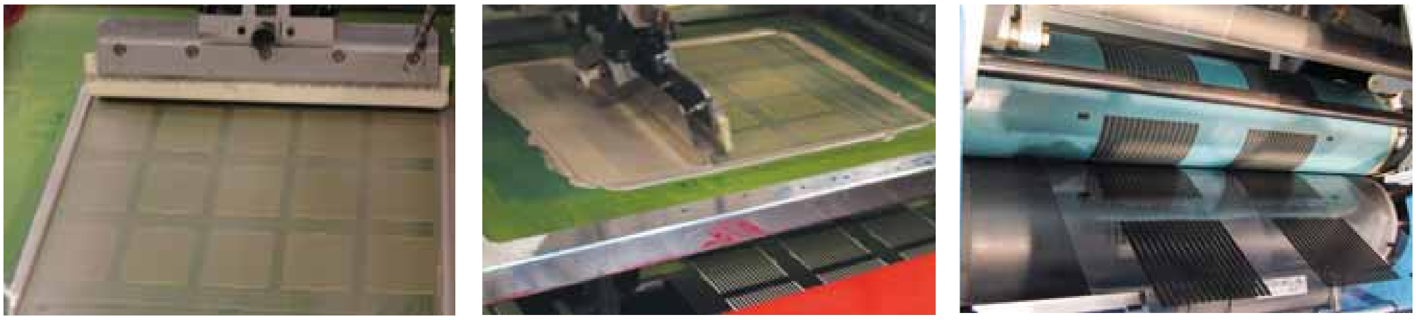

Fig. 4 Flat-bed screen printing of silver paste showing the squeegee after passage over the motif (left) and the squeegee during a printing cycle showing how the ink is forced through. The printed motif can be seen in the lower part of image (middle). A photograph of rotary screen printing of conducting graphite ink onto a clear polyester foil (right).

The coating techniques (wet films through a meniscus)

Whereas all of the printing techniques inherently allow for two-dimensional printing in the lateral plane through physical contact, the coating techniques lead to a continuous wet layer along the length of the web without contact between the *coating head* and the web. The coating itself is a result of continuous feeding of ink to a meniscus that is standing between the "coating head" and the web. Most of the coating techniques are thus zero-dimensional in the sense that no pattern is created as it is simply an even coat over the substrate. Most often, however, the control of the wet thickness is far superior to any of the printing techniques and very even layers can be prepared.

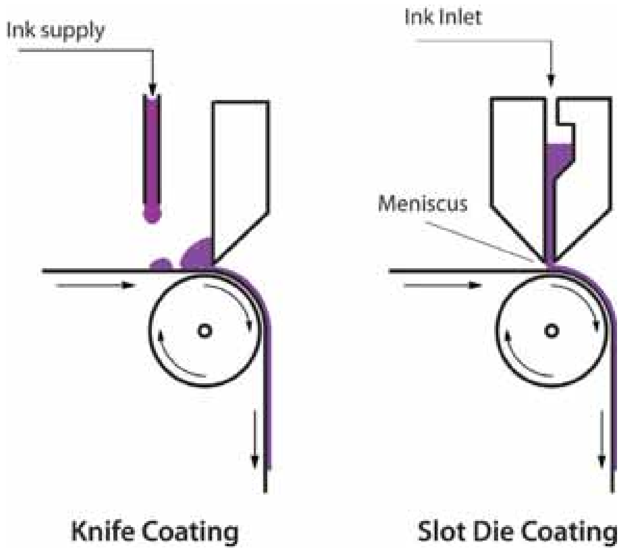

Fig. 5 A schematic illustration of knife coating where excess ink is kept ahead of the knife that is in close proximity to the web (left). Slot-die coating relies on the meniscus standing between a coating head with a slot from which ink is supplied to the standing meniscus thus forming a continuous (or striped) wet film (right).

The two coating techniques that have found most use this far for roll-to-roll processing of polymer solar cells are slot-die coating and knife coating[26,27]. These two techniques have been illustrated schematically in Fig. 5. Knife coating is very similar to doctor blading and laboratory results from laboratory doctor blading can be transferred quite readily to roll-to-roll knife coating. The knife coating process has an ink reservoir before the knife that serves to supply the meniscus with new ink as it is gradually deposited behind the knife as the web passes by. In the case of slot-die coating, it is possible to coat stripes of a well-defined width along the web direction and it is the only film forming technique which inherently allows for one-dimensional patterning. This aspect has enabled the very convincing demonstration of slot-die coating for the manufacture of polymer solar cells. In slot-die coating, the ink is supplied to the meniscus via a slot and a pump and it thus becomes possible to adjust the wet thickness by controlling either the speed of the web or the ink supply (or both). The natural limits to the achievable wet thicknesses depend on the coating window which is defined mostly by the ink properties and the web surface properties, but also by the coating geometry. Some examples of both slot die coating and knife coating are shown in Fig. 6 where the strength of slot die coating is evident. Many tightly spaced stripes can be coated at the same time at web speeds of a few meters per minute. This has been explored in several large demonstrations of polymer solar cell technology[22,28-31], of which the most elaborate example in terms of both miniaturization of the module, complexity of the product integration, and the number of units produced is that of the OE-A demonstrator in 2011[32].

Wet film formation without contact

Organization of the different film forming techniques according to the distinct categories of coating and printing is not straight forward and a few of the techniques that have been used for OPV have been named without taking the definitions above into account. In ink-jet printing, a two-dimensional pattern can be printed by specifically addressing each pixel in an area with (or without) an ink droplet. The third dimension (thickness) can in principle be achieved by printing multiple layers or by adding more ink to one spot. The method is entirely without contact between the printing head and the substrate as the ink droplet is ejected into the free space that exists between the nozzle and the substrate.

There are two types of droplet formation employed in inkjet printing as shown in Fig. 7. One where droplets are generated continuously and

Fig. 6 (a) Photograph of the standing meniscus during slot-die coating of the active layer of the OPV comprising many very tightly spaced stripes. (b) A total of 48 stripes (3 mm wide spaced by 1 mm) are coated simultaneously). (c) Knife coating with the open ink reservoir and the manual feed hose.

deflected onto the desired spot (pixel) on the substrate and one where droplets are only ejected on demand from a nozzle immediately in front of the pixel at the given time. In the former case speed can be very fast but since only one nozzle is used there are limits to the area that can be covered. On the other hand the drop on demand (DOD) system requires many nozzles. In early systems, the DOD systems were limited by the achievable web speeds and resolution, but today high resolution systems are commercially available that are capable of fast web speeds. From an industrial point of view, ink jet printing is a relatively new processing method with some speed limitations and restrictions on ink formulations. The latter point in particular has put restraints on the use of the technology for organic solar cells. Inkjet printing of organic solar cells has so far been limited to small scale devices (0.03 – 1 cm^2, up to 3.7 % PCE) to process either the PEDOT:PSS[33] layer, the P3HT:PCBM[34-36] layer, or both[37,38], and has in one case[39] been used for screening blend ratios, concentrations, solvent ratios, and film thicknesses. None of the reports on ink-jet printing in the context of OPV have been performed using R2R-processing and in all cases glass was used as the substrate. Although still largely untested in R2R processing, the possibility for complex pattern formation in high resolution from a digital master

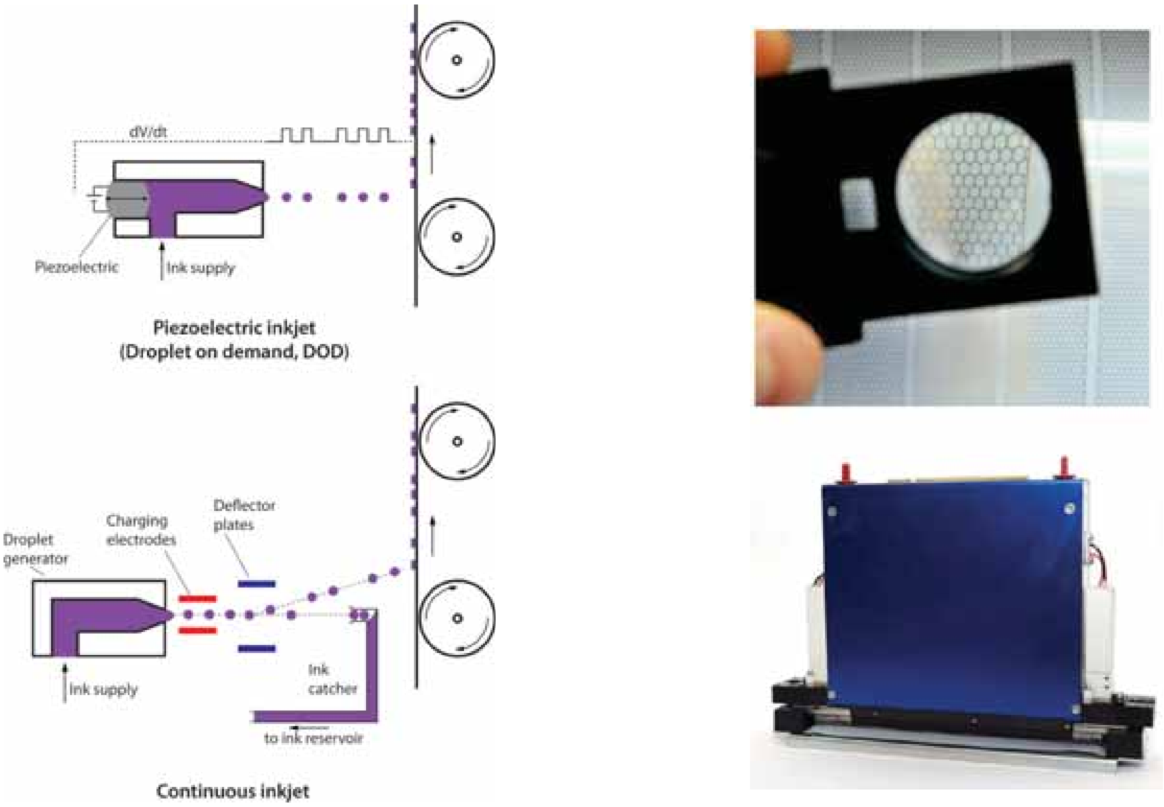

Fig. 7 (Left) Graphical illustrations of the principles behind drop-on-demand (DOD, here piezoelectric) inkjet printing and continuous inkjet printing. Photographs of (top right) a full roll-to-roll ink-jet printed pattern using a DOD system in a full width of 305 mm capable of printing with a resolution of 600 DPI and (bottom right) the 600 DPI printing head.

makes the ink-jet technique an extremely interesting future candidate for OPV processing.

Another film forming technique is spray coating, that like ink-jet printing achieves film formation through droplets and without physical contact between the coating head and the web. Similar to ink jet printing, the name is slightly misleading (no continuous wet film). Similar to ink-jet printing the ink is applied through droplets but where ink-jet printing achieves high graphical resolution through control of the droplets, spray coating does not allow for control of the pattern and is thus inherently a zero-dimensional coating technique. It is possible to pattern through a shadow mask but it is likely to prove impractical outside of the laboratory. Spray coating has been employed in several literature reports for the preparation of many of the layers in the OPV stack including the active area[40-43], silver back electrode[44,45], a combination of both hole transport layer and active layer[46,47], and in one case three layers (electron transport layer, active layer, and hole transport layer)[48]. Small laboratory sized roll-coaters has been developed where spray coating has been explored but so far there are no examples of roll-to-roll coated OPV prepared via spray coating[49]. A final technique that deserves mention is brush painting of the layers in the polymer solar cell stack. The use of a brush for film formation is possibly the oldest and most difficult one to model as it comprises a mixture of multiple parameters. It relies on ink that is withheld between the fibers of a brush through the surface tension of the ink. When brought into contact with the substrate, a meniscus forms between the fibers and the ink that is pulled out of the brush as it is moved across the surface of the substrate. The technique allows for some patterning depending on the brush size and it is thus a mixture of contact, meniscus, and two-dimensional patterning. It has not been employed in a roll-to-roll context until now but has been reported in the context of OPV in several instances and thus deserves mention[50-52]. It is conceivable that a roll-to-roll brush method could be developed for film formation in OPV.

Exotic coatings

In this section we will briefly review some of the techniques that certainly have the potential to become impactful when it comes to the formation of the polymer solar cell stack but that have been termed exotic since they are beyond what is presently possible or at the limit of it. This far we have viewed the film forming techniques according to the way the ink is dispensed and the way the different techniques can lead to a zero, one or three-dimensional pattern in the horizontal plane and we have viewed the formation of one wet layer comprised of one ink. Now imagine that we could apply several wet layers simultaneously on top of each other or process the layers dry without solvent. The former presenting a lot of challenges in terms of ink formulation and application and the latter elegantly avoiding problems with toxic solvents and while yielding control similar to vacuum processing achieves this without it through use of electrostatic forces or simply through dry nanoparticles that are merged in a separate process or through adhesive forces (Fig. 8).

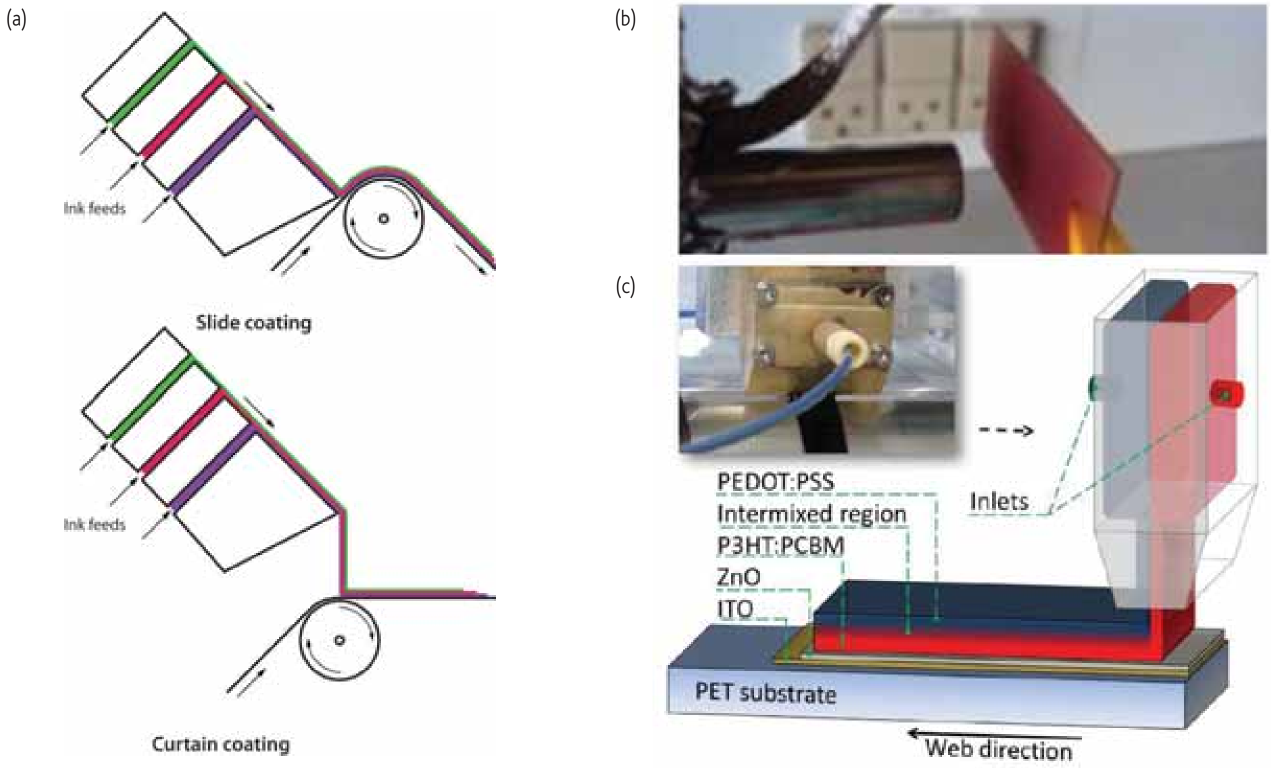

Fig. 8 (a) Graphical illustrations of slide and curtain coating, (b) dry coating of insoluble native polythiophene directly from the gas phase through nanoparticles, and (c) graphical illustration of double slot-die coating with a photograph showing double slot-die coating of a bilayer comprising P3HT:PCBM and PEDOT:PSS.

Curtain and slide coating techniques allow for the simultaneous formation of many layers (> 10), and ideally these techniques allow for the formation of the entire solar cell stack in one or two single coating steps. This would imply faster overall solar cell processing, less web handling, and less energy requirements (for machinery and drying) without having to increase the web speed. As our current understanding and capacity for ink formulation for the individual layers of the polymer solar cell stack is elaborate, it is currently inconceivable that we will be able to realize simultaneous formation of all the layers in the near future. A critical requirement of those two techniques is the web speed which has to be very high in order for the methods to work (typically 5 – 20 m s^{-1}).

There are some other film forming methods that qualify as exotic but have been used to form some of the layers in polymer solar cell stacks. One such method is double slot-die coating which is possible at much lower web speeds and on a much smaller scale than curtain and slide coating, and also allows for a much simpler control of the ink flow. The potential for double slot-die coating is large and it is the only multilayer coating technique that has been employed for organic solar cells in a full R2R process (and in general). Larsen-Olsen *et al.* proved that it was possible to simultaneously coat an aqueous nanoparticle dispersion of P3HT:PCBM and an aqueous dispersion of PEDOT:PSS on top of doped zinc oxide, preprocessed using single slot-die coating from water (See Fig. 8)[53]. The resulting cells showed relatively poor device performance, which was attributed to the far from perfect layer separation, due to the complex nature of the bilayer formation process. It did however demonstrate that it was possible to simultaneously form two layers of the solar cell stack.

The dry processing of the active layer has been described as worthy of investigation[1]. The use of dry ink systems is quite well known to most people from photocopiers and laser printers that rely on an electrostatic patterning of the dry ink in the form of micron sized particles. For OPVs there is a requirement for sub-micron film thickness which implies that the ink particles would have to be nanometer sized. It is a challenge to form dry nanometer sized particles that do not aggregate. In order to

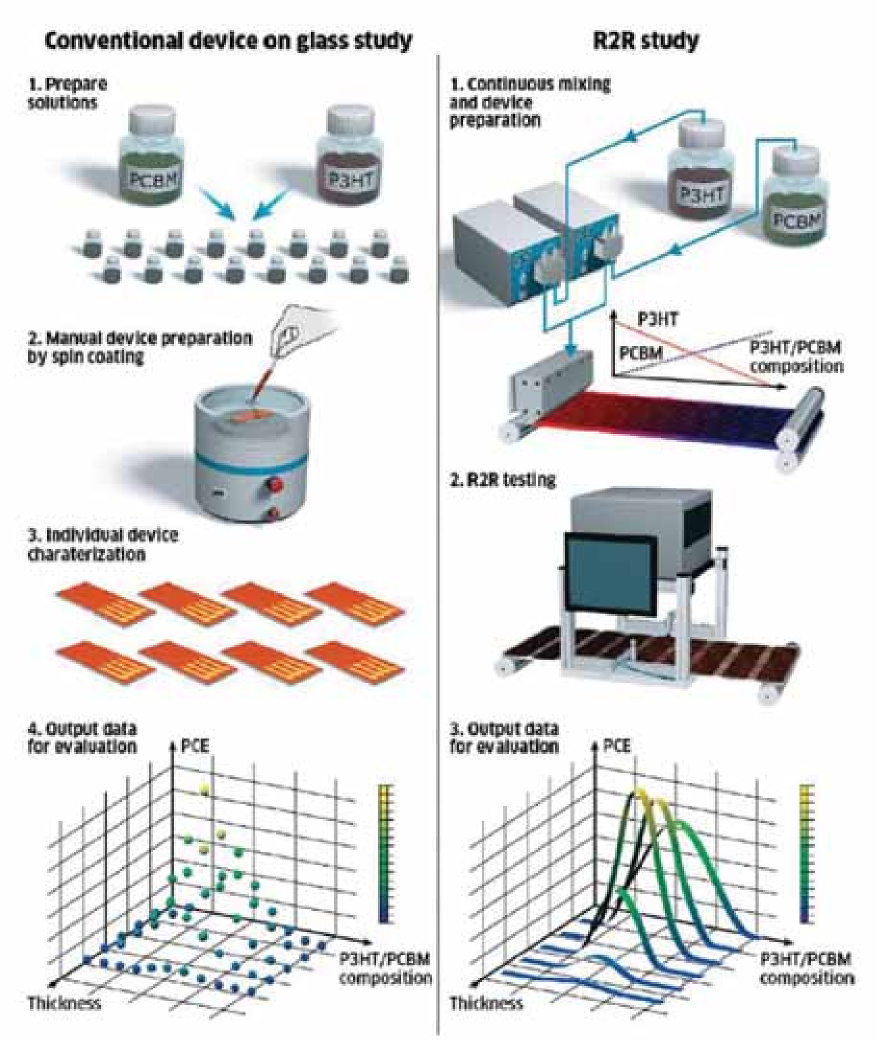

Fig. 9 Comparison between conventional spin-coating and differentially pumped roll-to-roll coating visualizing how a gradient of P3HT versus PCBM can be explored with great ease using slot-die coating. Reproduced with permission from[55] © 2010, American Chemical Society.

achieve dry coating of conjugated polymer systems, early experiments employed the gas phase formation of insoluble nanoparticles of native polythiophene mixed with PCBM[54]. The dry nanoparticles are formed in a gas stream and deposited directly from the gas phase onto the substrate (Fig. 8).

Advanced processing during coating and printing

One is often met with the argument that roll-to-roll processing is technical and not at the forefront of science. We would hold the opposite argument and claim that it both enable and provides considerably more control over and insight into complex phenomena. To give just two examples; think of the double slot-die coating technique described above, which gives access to complex segregated wet films with a complex topology both laterally and horizontally. A second example is the differentially pumped slot-die coating technique developed by Alstrup *et al*.[55], where two or more ink solutions are mixed and supplied to a modified slot-die coating head as illustrated in Fig. 9. With two ink solutions it is thus possible to set up a gradient mixing and coating two inks along a roll. This enables a whole new method to explore the very large parameter space of compositions and layer thicknesses for organic solar cells. In contrast to conventional spin-coating techniques it is for instance straightforward to analyze the composition diagram between the donor and acceptor with several hundred solar cells having different compositions in a single run using very little ink material in a matter of minutes. In a similar way the thickness of, e.g., the active layer can be explored using a gradient of the optimized donor/acceptor versus solvent to create a concentration gradient while keeping the wet thickness constant during the slot-die coating process[56].

Drying and advanced processing post film formation

The most common processing technique employed post film formation is drying of the wet film. Traditionally this has been achieved by heating the wet film, thus removing the solvents and leaving a dry film of the desired material. In recent years UV-curing has been developed for many adhesive systems as an approach to solvent free ink even though it is not a dry ink (at least not until it is fully cured). Drying and curing are complex processes that warrant a review of their own, but to give an example the very common process of hot air drying and UV curing have also been applied for screen printed silver back electrodes in inverted type OPVs[22]. Several different silver inks were compared with respect to power conversion efficiency and it was found that the only UV curable ink tested resulted in the highest PCE. A later study using light beam induced current (LBIC) measurements concluded that the solvent based silver inks degraded the current production in the adjoining active layer while this was not the case for the UV curable ink and nor was it for a specially developed water based thermally curing ink[57]. The use of an intense source of light to thermocleave polymer side chains in a R2R coating process of OPV is another example[58].

Using an oven set at 140 °C to thermocleave a polymer required four hours, making this an impractically slow process, while using a custom build lamp with narrow wavelength high intensity (Fig. 10) enabled much faster web speeds of 0.2 – 0.4 m/min.

With the introduction of lasers capable of delivering ultra short pulses (pico- to femtosecond), new possibilities of performing selective laser patterning have emerged with a potential use in R2R processed organic solar cells. Because of the short pulse duration very little heat is generated and it is thus possible to selectively remove a thin layer without destroying what is beneath. Initial reports related to solar cells have primarily been focused on the patterning of ITO on glass and PET[59-61]. So far the technology has yet to prove that functioning laser patterned solar cells can be produced, and cost wise the concept of removing applied material is generally not a preferred pathway in production if it can be avoided, but it has the potential to be a useful tool for niche productions.

One distinct advantage is that it can be used for scribing and this may prove useful in future OPV modules when very large geometric fill factors become important. Currently it is possible to reach geometric fill factors of 45 – 67 % using slot die coating and screen printing. With great accuracy this can possibly be increased to around 85 % but it is

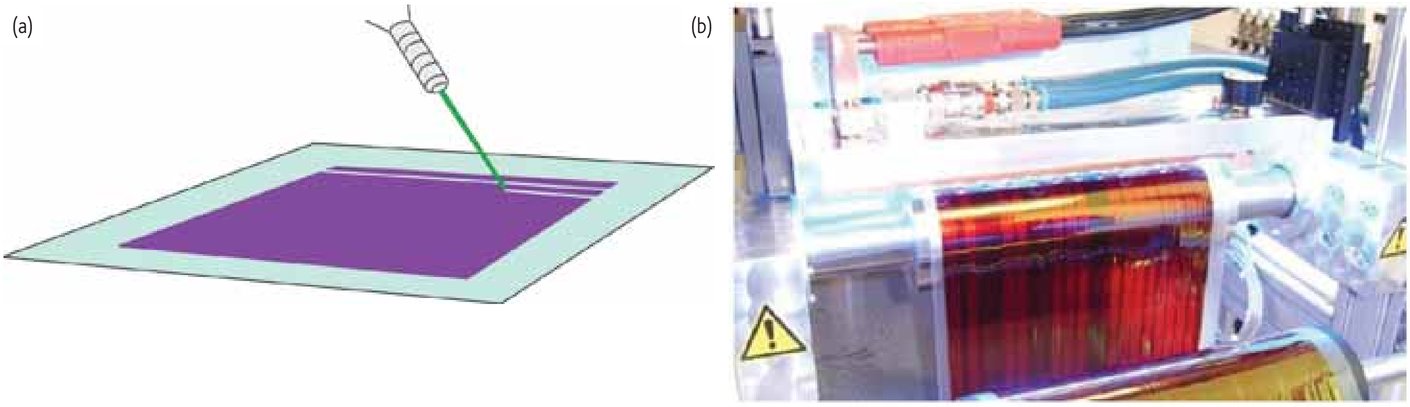

Fig. 10 (a) A Schematic drawing of patterning of the layers post processing and (b) the use of intense light with a specific wavelength or pulse length to selectively address, for instance, the active layer.

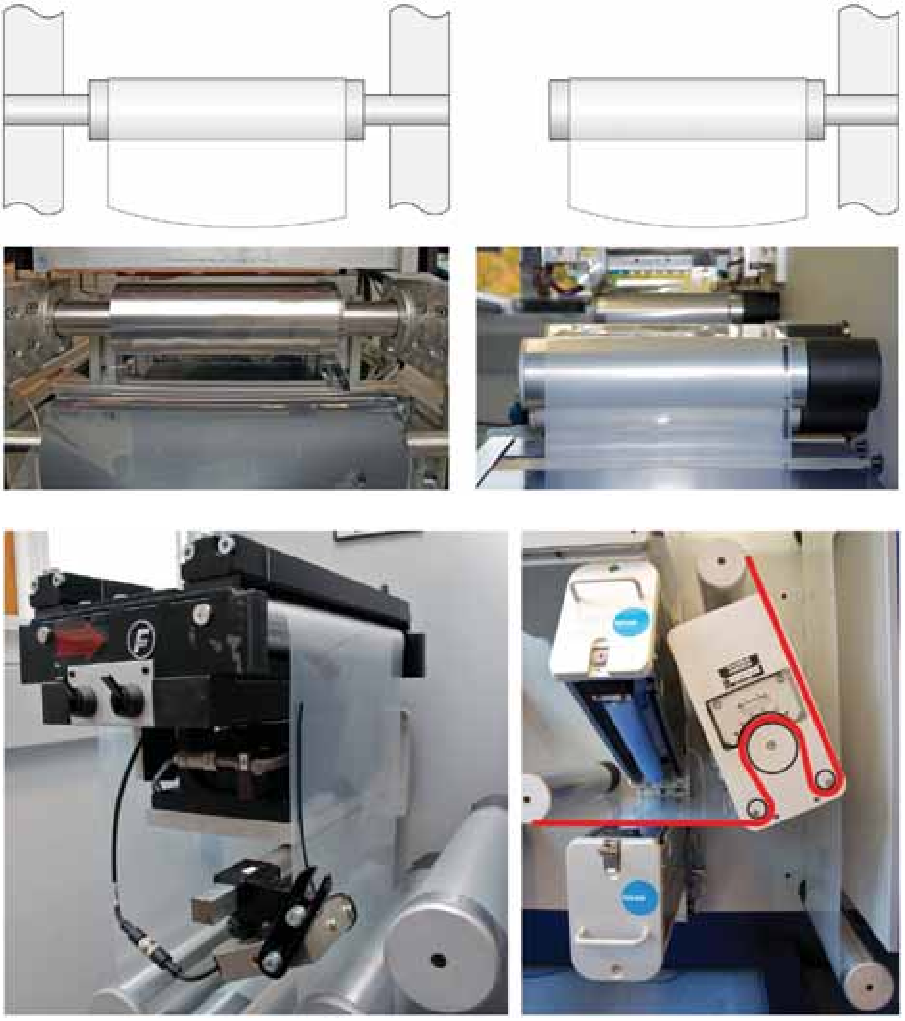

Fig. 11 Double sided roller mounting in schematic form with a photograph below (left) and cantilevered roller mounting with a schematic and a photograph (right). Below some web control and web processing tools are shown. A web guide used to correct the foil direction such that the edge of the foil is within ± 150 microns (lower left). A web cleaning and corona treating for higher surface energy is also shown. The red line shows how the web is guided through the corona treater (middle). A photograph of a nip which is used to separate different web tension zones between unwinder and rewinder on the machine (right).

unlikely to be taken further. Here laser scribing is likely to enable geometric fill factors in the 90 – 100 % range.

Machinery and web control

There are two basic ways that a roller carrying foil through a roll-to-roll machine can be constituted: double sided mounting and cantilevered, as illustrated in Fig. 11. Each system has its own advantages and disadvantages. The double sided roller mounting is particularly suited for large roller and web widths and heavy duty work yielding a stable machine, whereas a distinct disadvantage is the feeding of the machine with foil that has to be threaded like a sewing machine. The cantilevered machine on the other hand is well suited for narrow webs and does not allow for a web width much greater than 50 cm. For laboratory work and small production the cantilevered system is very well suited and allows for fast threading of the machine as everything can be accessed from one side.

Lamination

After the entire solar cell stack has been printed it needs to be encapsulated on the printed side for several reasons. The most important reason is operational stability. Another almost equally important factor during processing and handling is mechanical protection of the delicate printed layer stack. The process of lamination is in principle very simple and can be carried out in a number of ways using simple equipment, and the same basic principle of joining two lines of web by applying pressure as they are fed between two rollers. The use of cold lamination typically employs a pressure sensitive adhesive that is lined and applied to the laminate by a lamination process followed by removal of the liner and lamination onto the solar cell stack[22]. This is very simple and easy to control at the laboratory level at high speeds (> 20 m min^{-1} is easily accessible). Hot melt lamination uses the same principle, but here the laminate already has an adhesive material on it, which becomes adhesive

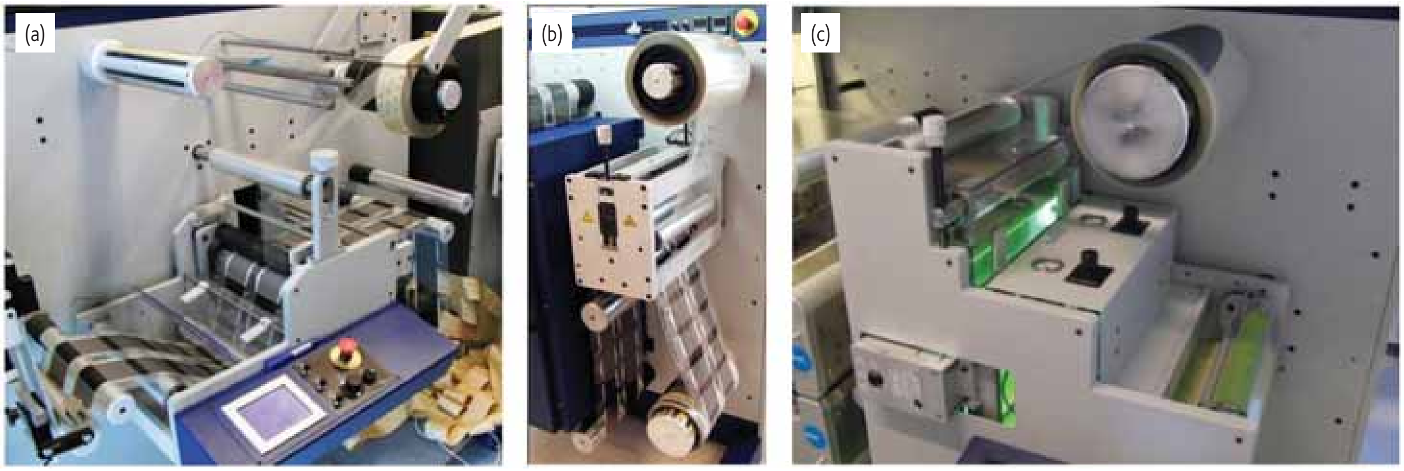

Fig. 12 Photographs of cold, hot-melt, and UV-lamination. (a) Cold lamination using lined pressure sensitive adhesives is shown for the lamination of solar cells. (b) A hot melt station is shown along with (c) a UV-lamination station.

when heated. The laminate and the substrate carrying the solar cells are then forced together between the heated rollers where the adhesive melts and forms a tight seal. UV lamination requires that an uncured adhesive or glue is applied by printing or coating immediately prior to bringing the two foils together. In the laminator the glue is cured by application of UV-light. In terms of operation, hot-melt is by far the easiest with cold lamination being slightly more complicated because one has to handle sticky adhesive and this implies that only one side of the foil can be handled (the non-sticky one). UV-lamination is by far the most complicated since it also involves a printing or coating step. Flexographic printing of the UV-curing adhesive is typically employed.

In terms of the adhesive thickness there are some limitations to the cold lamination where typically 50 microns of adhesive can be handled with ease. It is possible to employ pressure sensitive adhesives as thin as 20 microns, but it does present some challenges and the major drawback of cold lamination is the relatively thick adhesive layers that must be employed. Hot lamination on the other hand enables very thin adhesives to be employed and this may be an advantage in some cases but can present problems if the surface topography of the solar cells is rough (i.e., for a screen printed grid with a thickness of 5 – 20 microns). UV-lamination gives the widest accessible range of adhesive thickness and is in principle only limited by the printing method chosen and the curability of the adhesive (1 – 100 microns is achievable). Photographs of the different roll-to-roll lamination techniques in Fig. 12 show the relative similarity.

Inks and materials

As previously mentioned, one of the extremely important issues in high throughput production is finding suitable inks based on nontoxic/nonpolluting solvents, with water being both the cheapest and most environmentally friendly. The majority of materials used in solar cells today do not fulfill this demand, PEDOT:PSS being the only component

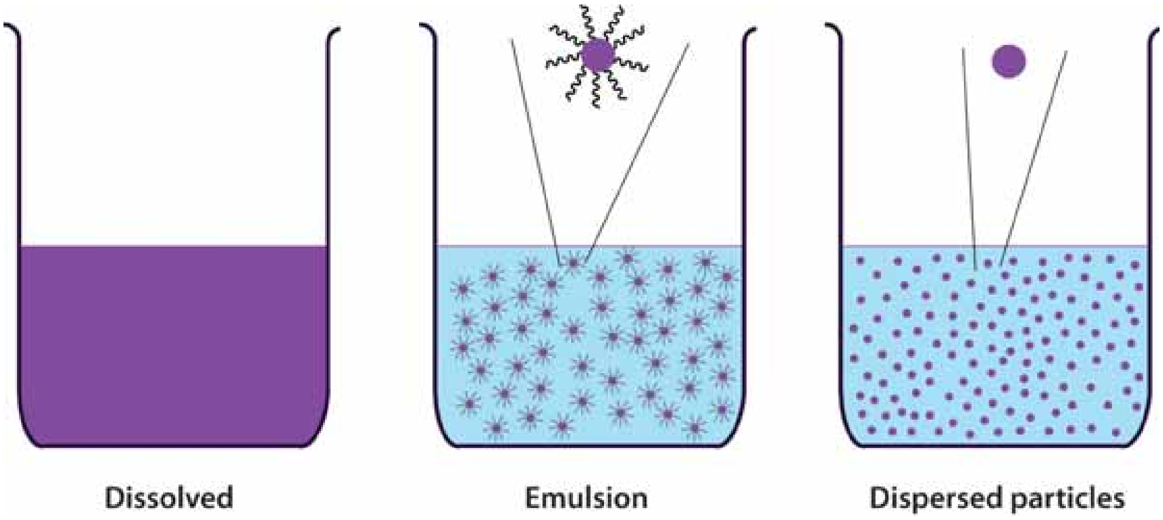

Fig. 13 Illustration of the basic types of ink formulations, which are fully dissolved, emulsions and dispersed particles.

that is generally processed from aqueous solution, so new approaches to processing (particularly the active layer) need to be developed. If we wish to process everything from water, careful consideration towards the potential of damaging layers that have already been processed need to be taken. Generally, ink formulations can be divided into three categories as indicated in Fig. 13: dissolved material (each separate molecule is fully solvated), emulsions (the material is kept in solution by additives which allows for micelle formation), and particulate solutions or pastes (solid particles are suspended in solution). The careful exploitation of different ink formulations might be the answer to how to replace the present use of orthogonal solvents (polar and non-polar) for every new layer, as each formulation type allows for the processing of different types of material.

With respect to non-transparent electrodes, silver is at present the only real candidate, and has been limited in R2R processing to the use of screen printing of highly viscous inks (paste) with relatively large silver particles, which ensures good conductivity. As previously mentioned, several types of silver paste are commercially available which can either be cured thermally or with UV light. None of these are water based, but screen printable water based silver pastes can be prepared quite easily using an aqueous binder, silver flakes, and water[62]. Low viscosity aqueous silver inks containing nanoscale particles are further commercially available, and could have potential use in solar cells processed by methods like gravure, flexographic, and inkjet printing. When using small particles sintering of the silver layer is required by either thermal or other treatment in order to achieve good connectivity[63,64].

As for the transparent electrodes ITO is still the leading material although extensive efforts are made towards replacing it because of the high cost of the material.

Regarding the processing of charge selective layers, the most widely used hole transport layer is PEDOT:PSS, which is commercially available in a large variety of inks that have been tailored with respect to conductivity, viscosity, and surface tension for different application purposes. As already shown in this review, a large variety of R2R techniques can be employed in the application of PEDOT:PSS. For electron selective layers, only the use of zinc oxide from acetone[65], methanol[55], or water solution[66] have been reported in R2R processes.

With respect to the processing of the active layers, chlorinated solvents have been used in the majority of R2R reports, but water based processing methods based on emulsified solutions have shown promising initial results as it is possible to process hydrophobic active components[53,62,66,67]. Because the micelle stage only exists in solution (the micelle collapses upon removal of the solvent) the active layer is insoluble in aqueous solutions after drying of the solvent and further processing from water can be carried out without damaging the layer. Using emulsified low-band-gap polymers in inverted structured R2R processed solar cells (4 cm^2) Andersen *et al.* thus achieved a PCE of 0.55 %[66], and Larsen-Olsen *et al.* used an emulsified aqueous solution to process one of the active layers in the first ever report of R2R processed organic tandem solar cells[67].

Testing the roll

At the end of processing polymer solar cells using roll-to-roll methods, one ends up with a roll of material. While some testing can be carried out during the processing of the individual layers, the functionality of the solar cell itself, i.e., the production of electrical energy upon being subject to illumination, has to be carried out at the very end, on the very roll that is the end product. One can thus view inline monitoring techniques as useful for guiding the process, but they can not guarantee the final performance. Therefore we also need roll-to-roll instrumentation to test functionality. The techniques that have proven useful for process control are the camera techniques, providing two-dimensional information using transmission, reflection, and dark field imaging of the printed or coated films, revealing detail on film thickness variations, registration, and particle detection. These techniques are non-contact techniques and apply to individual layers during manufacture. Once the solar cell modules have been prepared, the camera techniques still apply and new two-dimensional imaging techniques become possible that can complement the camera techniques. Methods such as light beam induced current (LBIC) mapping[57], dark lock-in thermographic imaging[68], electroluminescense imaging, and photoluminescence imaging[69,70]. Most of those techniques require electrical contact with the device module to enable extraction of information regarding solar cell function. Some techniques that also require electrical contact are zero-dimensional in the sense that they will tell you about the malfunction of the device but not the location of the problem. IV and IPCE measurements are of this type. A roll-to-roll characterizer is shown in Fig. 14. It enables the recording of IV-curves, LBIC images, IPCE data and the photographic imaging of modules. The speed of the instrument is on the order of 1 m min^{-1}.

Device integration and application

The final aspect of the manufacture of OPVs using roll-to-roll methods is of course what happens after production and testing. There have not been many well documented examples of OPV integration, application, and demonstration and clearly this represents an entire topic on its own that will develop in time once the OPV technology becomes widely available.

What will be required before one can take full advantage of the polymer solar cell technology is that the device or product integration is also achieved using a roll-to-roll technique, or at least a technique that allows for the OPV to enter the process on a roll. Otherwise the major strength that roll-to-roll technology has to offer is lost. The earliest demonstration example in a significant volume is possibly that of the solar hat, where a small solar cell module was used to charge a battery for a radio. A part of the process was roll-to-roll based, but during the manufacture of the solar cells the roll was broken up into sheets and the solar cells were finally processed in sheets. This early example was thus far from what has been specified above, but was an important part of the learning process[24]. A second example is that of a small lamp for the “lighting Africa” project, and here the solar cell was

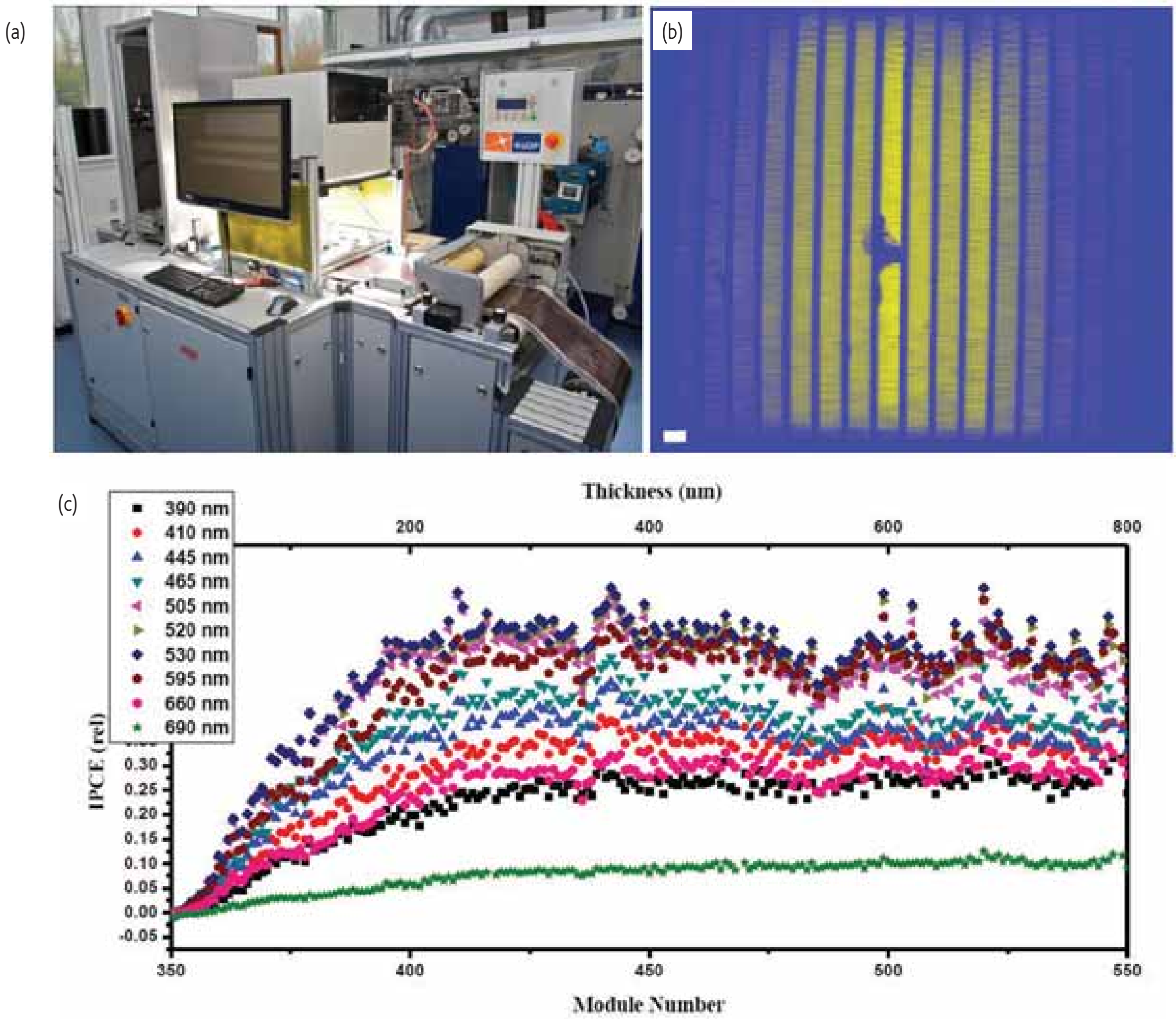

Fig. 14 (a) A photograph of a roll-to-roll testing machine allowing for solar simulation and two-dimensional imaging of devices (LBIC, photographic imaging, and IPCE). (b) An example of an LBIC image acquired roll-to-roll showing a defect (the resolution is 100 micron, the size of the imaged module is 305 x 250 mm, and data the acquisition time is around 1 second). (c) IPCE data for polymer solar cells along a roll recorded at different wavelengths using a powerful diode array.

entirely roll-to-roll processed, but the final confectioning of the lamp was made by handling the discrete unit. This example was a step forward in terms of processing and made use of the advantages that roll-to-roll processing has to offer[71]. The third example was the first instance of product integration in a fully automatic manner, even though the final confectioning was made by sheet processing where several units were handled simultaneously[19]. This final example was taken further in an experiment of miniaturization and product integration, where 10 000 units comprising > 30 discrete steps were produced through roll-to-roll processing and sheet based handling of 15 units at a time[32].

Summary and outlook

It is clear that roll-to-roll processing is at the heart of OPVs in the future and that the successful realization of low cost OPVs will be closely linked to this. There are however also other requirements and roll-to-roll processing and roll-to-roll methodologies are only one part of a large equation. In addition to efficient processing, efficient process control

Fig. 15 Illustration of the OE-A demonstrator for 2011 and an example of the laser cutting the processed sheets into the final product.

during manufacture is required, and new materials and processes are urgently needed. Some of the most important materials and processes are those that will enable the printing of semitransparent electrodes and complete processes that are built around enabling complete fabrication of efficient solar cells. The materials and processes should of course give access to OPVs that provide operational stability of > 10 years and they should be efficient (> 10 %). A particular requirement to the OPV is that it has as thin an outline as possible with low materials consumption, to achieve a low embodied energy. The processing should not be environmentally harmful and should, through use of the lowest possible temperatures, require a very low input energy for manufacture. This, taken together, will enable short energy payback times, and < 10 days should be possible. Manufacture of the entire solar cell stack at an overall speed of > 10 m min^{-1} will enable the manufacture of a daily energy production capacity of more than 1 GW$_{peak}$ and thus, in principle, fully address man-kinds future energy needs.

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REFERENCES

1. Krebs, F. C., *Sol Energy Mater Sol Cells* (2009) **93**, 394.
2. Green, M. A., *et al., Prog Photovolt* (2011) **19**, 565.
3. Service, R. F., *Science* (2011) **332**, 293.
4. Tipnis, R., *et al., Sol Energy Mater Sol Cells* (2009) **93**, 442.
5. Espinosa, N., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 1293.
6. Espinosa, N., *et al., Energy & Env Sci* (2011) **4**, 1547.
7. Espinosa, N., *et al., Sol Energy Mater Sol Cells* (2012) **97**, 3.
8. García-Valverde, R., *et al., Prog Photovolt: Res Appl* (2010) **18**, 535.
9. Nielsen, T. D., *et al., Sol Energy Mater Sol Cells* (2010) **94**, 1553.
10. Azzopardi, B., *et al., Energy & Env Sci* (2011) **4**, 3741.
11. Kalowekamo, J., and Baker, E., *Sol Energy* (2009) **83**, 1224.
12. Powell, C., *et al., Sol Energy* (2009) **83**, 1977.
13. Espinosa, N., *et al., Energy & Env Sci* (2012) **5**, 5117.
14. Ding, J. M., *et al., Sol Energy Mater Sol Cells* (2009) **93**, 459.
15. Kopola, P., *et al., Sol Energy Mater Sol Cells* (2010) **94**, 1673.
16. Kopola, P., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 1344.
17. Voigt, M. M., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 731.
18. Hübler, A., *et al., Adv Energy Mater* (2011) doi: 10.1002/aenm.201100394.
19. Krebs, F. C., *et al., J Mater Chem* (2010) **20**, 8994.
20. Deganello, D., *et al., Thin Solid Films* (2010) **518**, 6113.
21. Galagan, Y., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 1339.
22. Krebs, F. C., *et al., Nanoscale* (2010) **2**, 873.
23. Manceau, M., *et al., Org Electron* (2011) **12**, 566.
24. Krebs, F. C., *et al., Sol Energy Mater Sol Cells* (2009) **93**, 422.
25. Zhang, B., *et al., Jpn J Appl Phys* (2009) **48**, 020208.
26. Krebs, F. C. *Sol Energy Mater Sol Cells* (2009) **93**, 465.
27. Wengeler, L., *et al., Chem Eng Process* (2011) **50**, 478.
28. Blankenburg, L., *et al., Sol Energy Mater Sol Cells* (2009) **93**, 476.
29. Galagan, Y., *et al., Chem Eng Process* (2011) **50**, 454.
30. Krebs, F. C., *et al., J Mater Chem* (2009) **19**, 5442.
31. Zimmermann, B., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 1587.
32. Krebs, F. C., *et al., Energy & Env Sci* (2011) **4**, 4116.
33. Eom, S. H., *et al., Org Electron* (2009) **10**, 536.
34. Aernouts, T., *et al., Appl Phys Lett* (2008) **92**, 033306.
35. Hoth, C. N., *et al., Adv Mater* (2007) **19**, 3973.
36. Hoth, C. N., *et al., Nano Lett* (2008) **8**, 2806.
37. Eom, S. H., *et al., Org Electron* (2010) **11**, 1516.
38. Lange, A., *et al., Sol Energy Mater Sol Cells* (2010) **94**, 1816.
39. Teichler, A., *et al., Adv Energy Mater* (2011) **1**, 105.
40. Chen, L. M., *et al., ACS Nano* (2010) **4**, 4744.
41. Girotto, C., *et al., Sol Energy Mater Sol Cells* (2009) **93**, 454.
42. Park, S. Y., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 852.
43. Susanna, G., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 1775.
44. Girotto, C., *et al., Org Electron* (2009) **10**, 735.
45. Hau, S. K., *et al., Org Electron* (2009) **10**, 719.
46. Girotto, C., *et al., Adv Func Mater* (2011) **21**, 64.
47. Na, S. I., *et al., Sol Energy Mater Sol Cells* (2010) **94**, 1333.
48. Lewis, J. E., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 2816.
49. Dam, H. F., and Krebs, F. C., *Sol Energy Mater Sol Cells* (2012) **97**, 191.
50. Heo, S. W., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 3041.
51. Kim, S. S., *et al., Sol Energy Mater Sol Cells* (2010) **94**, 171.
52. Kim, S. S., *et al., Adv Mater* (2007) **19**, 4410.
53. Larsen-Olsen, T. T., *et al., Sol Energy Mater Sol Cells* (2012) **97**, 22.
54. Nan, Y.-X., *et al., Nanotechnology* (2011) **22**, 475301.
55. Alstrup, J., *et al., ACS Appl Mater Interfaces* (2010) **2**, 2819.
56. Bundgaard, E., *et al., Macromolecules* (2010) **43**, 8115.
57. Krebs, F. C., *et al., Sol Energy Mater Sol Cells* (2011) **95**, 1348.
58. Krebs, F. C., and Norrman, K., *ACS Appl Mater Interfaces* (2010) **2**, 877.
59. Haenel, J., *Proc SPIE* (2010) **7771**, 77710G.
60. Schoonderbeek, A., *et al., J Laser Micro/Nanoeng* (2010) **5**, 248.
61. Xiao, S., *Proc SPIE* (2011) **7921**, 79210I.
62. Søndergaard, R., *et al., Adv Energy Mater* (2011) **1**, 68.
63. Grouchko, M., *et al., ACS Nano* (2011) **5**, 3354.
64. Perelaer, J., *et al., J Mater Chem* (2010) **20**, 8446.
65. Espinosa, N., *et al., Materials* (2011) **4**, 169.
66. Andersen, T. R., *et al., ACS Nano* (2011) **5**, 4188.
67. Larsen-Olsen, T. T., *et al., Sol Energy Mater Sol Cells* (2012) **97**, 43.
68. Bachmann, J., *et al., Sol Energy Mater Sol Cells* (2010) **94**, 642.
69. Rösch, R., *et al., Sol Energy Mater Sol Cells* (2012) **97**, 176.
70. Seeland, M., *et al., J Appl Phys* (2011) **109**, 064513.
71. Krebs, F. C., *et al., Energy & Env Sci* (2010) **3**, 512.