

Chapter 2

Solution-Processed Organic Photovoltaics

Claudia N. Hoth, Pavel Schilinsky, Stelios A. Choulis,
Srinivasan Balasubramanian and Christoph J. Brabec

Abstract The technology of organic solar cells has matured to an extent that commercialization of first products has already started. However, with the first products pushing into the market, the research community realizes that a qualified product requires more than only high efficiency and good stability. Cost is of course as important as efficiency and lifetime, but to achieve high productivity, multiple technologic challenges have still to be solved. To reduce production costs, printing of functional layers from solution has evolved to a promising manufacturing technology for flexible organic electronics. Current processing of organic photovoltaic devices is mainly based on traditional methods like spin coating or doctor blading. However, these techniques have several disadvantages such as the incompatibility with a roll-to-roll setup and the processing of only small areas at laboratory scale. Enormous benefits in the manufacturing of organic photovoltaics are achieved by using low-cost roll-to-roll capable technologies including screen printing, spray coating, inkjet printing, gravure/flexographic printing and curtain/slot die coating. This review will shed some light on the role and importance of production technologies for organic photovoltaics and give an update on the most recent achievements in the field.

C. N. Hoth (✉) · P. Schilinsky
Konarka Technologies GmbH, Landgrabenstrasse 94, 90443 Nürnberg, Germany
e-mail: choth@konarka.com

S. A. Choulis
Department of Mechanical Engineering and Materials Science and Engineering, Cyprus
University of Technology, 3603 Limassol, Cyprus

S. Balasubramanian
Konarka Technologies Inc., 116 John Street, Lowell, MA 01852, USA

C. J. Brabec
Institute Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-
University Erlangen-Nürnberg, Martensstr. 7, 91058 Erlangen, Germany

Keywords Organic solar cells • OPV • Printing • Coating • Polymer • Fullerene • Bulk heterojunction • Device fabrication • Lifetime

2.1 Introduction

Amorphous semiconducting polymeric materials have attracted significant interest in the field of organic electronics due to their processing advantages [1–3]. The possibility of applying these materials at low temperatures using solution coating techniques has resulted in intense research activity in recent years. The developments in the fields of organic field effect transistors (OFET or OTFT), organic light emitting diodes (OLED), organic photodetectors and organic photovoltaics (OPV) have now made organic electronics commercially viable. The low-temperature solution processability allows for roll-to-roll printing or coating on flexible plastic substrates which is expected to lead to light-weight, low-cost electronic devices including among others displays, photovoltaic devices and thin film batteries.

For photovoltaics in particular, roll-to-roll production is attractive due to the requirements of low cost, light weight and large area coverage that characterize these products.

Other technologies such as thin film inorganic semiconductor devices that require, for instance, chemical vapour deposition or lithography do not realize the vision of low-cost products due to higher manufacturing cost when compared to printing and coating.

Inorganic bulk semiconductors do not, or only in a very limited way, offer a processing window adequate for solution processing. Inorganic solar cells based on colloidal semiconductor nanocrystals (CdTe and CdSe) spin coated from solution have been presented by the Alivisatos group. These air-stable devices performed well with 2.9 % power conversion efficiencies (PCE) [4]. Inorganic solution-fabricated CIGS ($\text{Cu}(\text{In,Ga})\text{Se}_2$) cells are being commercialized with over 10 % PCE [5, 6], but these materials suffer from complex processing, e.g. high temperature conditions, which do not enable the use of low-cost flexible plastic substrates and roll-to-roll processing. Roll-to-roll vacuum processing of thin film inorganic photovoltaic based on materials like amorphous silicon has also been demonstrated. However, this approach is characterized by much lower throughput and significant higher costs than printing technologies.

In addition to production costs, the competitive position of a photovoltaic technology must be assessed comparing how much efficiency can be gained per spent dollar with the different approaches.

In this chapter we analyze the potential of low-cost printed organic photovoltaics. The challenges associated with large-scale printing or coating procedures are addressed together with an overview of OPV performance in terms of efficiency and operational stability.

At present bulk heterojunction (BHJ) composites based on blends of a polymer donor and a fullerene acceptor for ultrafast charge transfer at the donor/acceptor

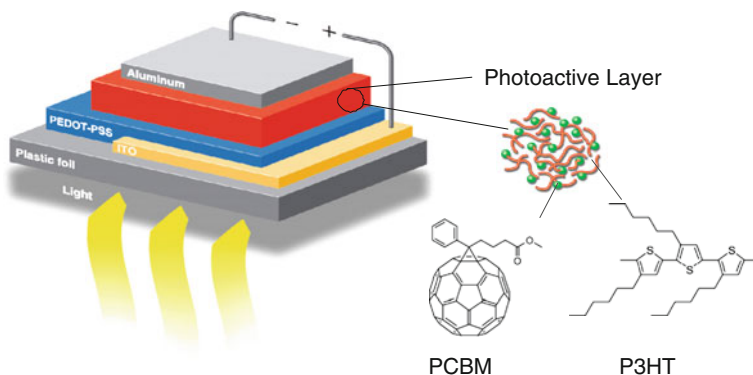


Fig. 2.1 Organic solar cell device structure. The photoactive layer consists of a blend based on poly(3-hexylthiophene) (P3HT) and the C60 derivative PCBM ([6,6]-phenyl-C61-butyrac acid methyl ester)

interface are the organic material system with the highest reported efficiencies. The working horses for electron donating and accepting materials in the BHJ structure are the well-known poly(3-hexylthiophene) (P3HT) and the C60 derivative PCBM ([6,6]-phenyl-C61-butyrac acid methyl ester). The chemical structures of the materials as well as a typical device configuration are shown in Fig. 2.1.

For a solar cell at least one transparent electrode is required, which is typically a conductive oxide (TCO). The transparent electrode is often defined by indium tin oxide (ITO) coated on glass or flexible plastic carriers. Together with a thin layer of the intrinsically conductive poly(3,4-ethylene dioxythiophene) doped with the polyanion polystyrene sulfonate (PEDOT:PSS), a high work function hole-collecting electrode is built. The photoactive layer is formed by the donor–acceptor blend film, which forms morphologies with phase separation in the nm-scale characterized by good percolation pathways for efficient charge collection and decreased charge recombination. The use of two materials emphasizing different electronic levels is one of the most important design concepts for organic bulk heterojunction solar cells. With this donor–acceptor material combination several groups have reported laboratory device efficiencies in the range of 4 % [7–9]. Low-bandgap benzothiadiazole-fused thiophene copolymers such as poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta [2,1-b;3,4-b']-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) used as donor materials represent a promising route to improved device efficiency, due to the better overlap between the PCPDTBT absorption spectrum and the solar emission spectrum [10–14]. A new class of polymer materials which are viable for OPV manufacturing currently give certified performance beyond 8 % [15]. In this chapter, however, we focus our analysis on the well known and widely used P3HT:PCBM blends.

The origin of the open circuit voltage (V_{OC}) is a matter of controversial discussions. V_{OC} is the voltage at the terminals of a solar cell when no current flows and is basically determined by the distance between the highest occupied molecular orbital

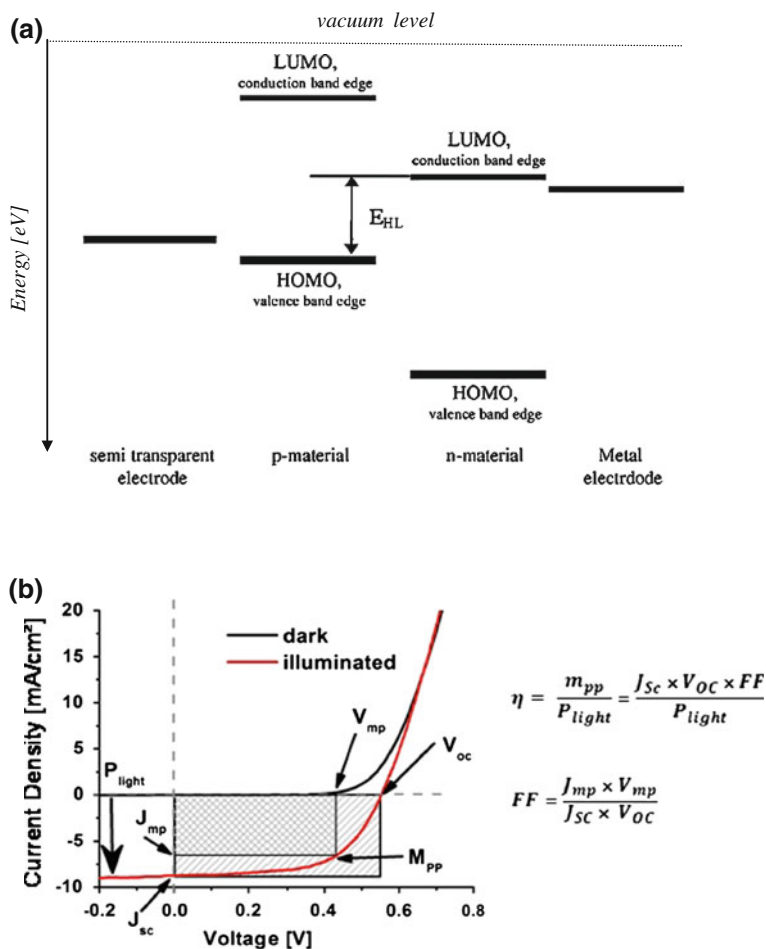


Fig. 2.2 **a** Energy band scheme of a bulk heterojunction solar cell. The V_{OC} is determined by the distance of the highest occupied molecular orbital (*HOMO*) level of the donor and the lowest unoccupied molecular orbital (*LUMO*) level of the acceptor (indicated as E_{HL}). **b** Characteristic J - V -curve of a solar cell in the dark (*upper curve*) and under illumination (*lower curve*). The parameters J_{sc} , V_{OC} , M_{PP} and the power of the incident light P_{light} are depicted. The ideal power of a solar cell is represented by the *dashed square*. The real maximum power is shown by the *checkered square*. Moreover, the relationship between device performance, V_{OC} , J_{sc} and FF is given

(*HOMO*) level of the donor and the lowest unoccupied molecular orbital (*LUMO*) level of the acceptor material, as shown in Fig. 2.2a (indicated as E_{HL}).

Under illumination a photo-induced charge transfer occurs. As the bulk absorbs photon energy, coulombically bound electron-hole-pairs (excitons) are generated, that dissociate at the donor-acceptor interface into electrons and holes. Charge transport to the opposite electrodes takes then place: holes are transported by the p-type material to the higher work function electrode (TCO) and electrons by the n-type material to the lower work function contact (metal), respectively. The short

circuit current density (J_{SC}) depends on the number of photogenerated charges collected by the electrodes. The J_{SC} is among others affected by the absorption of photons, the mobility of charge carriers within the active layer, recombination processes and the morphology of the active layer. The relationship between device efficiency, V_{OC} , J_{SC} and fill factor (FF) is shown in Fig. 2.2b on a typical J - V characteristics under illumination and in the dark. The FF is defined as the ratio of the actual maximum obtainable power, ($V_{mp} \times J_{mp}$) to the maximum theoretical power, ($J_{sc} \times V_{oc}$). The FF is limited by insufficient transport properties, increased series resistance R_s or reduced parallel resistance R_p . R_s and R_p can be determined by the inverse of the slope of the J - V characteristics in the points V_{oc} and J_{sc} respectively.

The performance of BHJ solar cells depends critically on the material properties and processing conditions. Depending on the printing technology the ink must fulfil certain requirements for a reliable printing and adequate film formation in terms of viscosity, boiling point, vapour pressure, polarity and surface tension. The selection of organic solvents is determined by solubility, drying characteristics, fluidity, surface tension and environmental and regulatory considerations. Therefore, the ink is formulated with respect not only to the solvent properties, but also to adapt the ink to the printing technology. The characteristic properties of the different printing methods applied to manufacture solar cells and the requirements on the inks will be extensively discussed in the Sect. 2.2.

Section 2.3 will concentrate on reliability and yield aspects of OPVs, while Sect. 2.4 will discuss accelerated lifetime test procedures and Sect. 2.5 will present a possible roadmap for printed solar cells.

2.2 Production Technologies of Organic Photovoltaics

In recent years significant progress has been made in the processing of organic bulk hetero-junction solar cells. In this section we discuss the different solar cell fabrication technologies such as doctor blading, screen printing, spray coating, inkjet printing, gravure and flexographic printing, curtain and slot-die coating as compared to the conventional spin-coating process. These various technologies can all enable roll-to-roll printing of organic solar cells. The high throughput and productivity (amount of generated energy per energy used during manufacturing) of roll-to-roll (R2R) printing is expected to enable low-cost commercial solar cells. Due to the high level of development and the variety of printing and coating methods available, high resolutions down to 20 microns as well as high layer qualities for a broad range of printable materials can be achieved [16]. A roll-to-roll process simplifies manufacturing scale-up and has significantly lower costs than other methods to make solar cells. Printing processes are non-toxic, environmentally friendly and, being compatible with low temperatures, are less energy intensive than 1st or 2nd generation photovoltaic technologies [17]. Another significant advantage of roll-to-roll processes is that they can be implemented using existing coating and printing equipment, and thus does not require the construction of a new infrastructure [17].

Before discussing the details of the individual printing methods, it is essential to recall that the quality of any printing method heavily depends on the degree of optimization of the ink formulation. Some of the key requirements for organic solar cells including uniform film quality with low density of defects (pinholes or line defects) over large areas necessitate ink formulations with appropriate rheological properties. The ink should provide a long shelf life and high consistency in concentration, temperature behaviour and viscosity. Moreover, the substrate should exhibit high uniformity and reliable surface properties and during the printing process the web speed and the tension at the point of ink deposition has to be uniform.

Another important aspect of ink formulation is the drying kinetics, which is actually quite independent of the specific printing technology used. In general, one is interested to work with fast drying inks, which allow high web speeds and shorter drying stages. For OPV production, requiring solid films in the range of tens or few hundreds of nanometers and a typical wet film thickness in the 10 micron regime, inks with high drying rates are preferred. Conversely, the use of high-boiling-point organic solvents, which can delay the drying process significantly, should be avoided.

2.2.1 Spin Coating

Early reported organic photovoltaic devices were fabricated by spin coating [18, 19]. Spin coating is a well-understood laboratory method to deposit organic semiconductor solutions onto substrates resulting in high quality thin films. The fluid is deposited at the centre of the substrates. Spinning of the substrate at high velocity (up to 10,000 rpm) causes centrifugal acceleration and thus, spreading of the fluid on the surface. The final film thickness depends not only on the nature of the fluid in terms of viscosity, drying rate, solid concentration and surface tension, but strongly on the spinning parameters such as spinning speed, acceleration and time interval. Most of the recent research efforts in the OPV field have focused on spin coating due to the film homogeneity and low defect density that this technique enables. Spin coated cells with high power conversion efficiencies over 6 % have been reported [9, 20–23]. Unfortunately though, this method is not scalable to large volume production. Each substrate has to be handled individually and patterning the layers would require costly subtractive patterning steps like lithography. In addition most of the applied solution is wasted and only a small amount of it is eventually used to cover the substrate.

2.2.2 Doctor Blading

A couple of years after the first published spin coated organic photovoltaics, doctor blading was used to obtain thin films from solution [24, 25]. A schematic representation is shown in Fig. 2.3a.

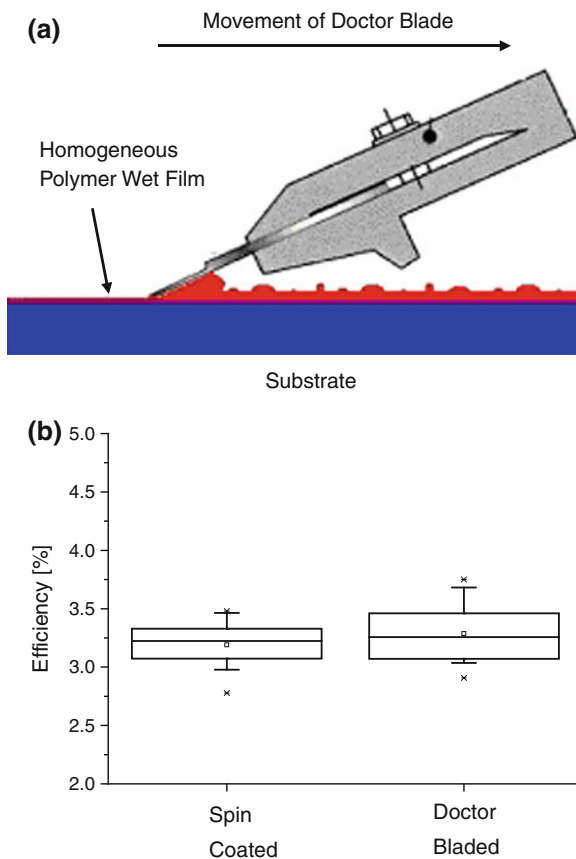


Fig. 2.3 **a** Principle of the film formation for films deposited by doctor blading. **b** Power conversion efficiencies of a series of organic solar cell devices by the state-of-the-art technique spin coating compared to the doctor blading method [26]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. Data are presented in box plots. The *horizontal lines* in the box denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The *two symbols below and above* the 5th/95th percentile error bar denote the highest and the lowest observed values, respectively. The *open square* inside the box denotes the mean value. The height of the box is the measure for the tolerance. Devices were illuminated with 100 mW cm^{-2} by a solar simulator. Efficiencies were corrected for the mismatch factor of the illumination source and represent AM1.5G values

Doctor blading basically uses a coating knife to apply a solution evenly over the substrate. A defined amount of the solution is applied either directly onto the substrate or, in case of low viscosities, in the gap between the substrate and the blade. Afterwards the knife is moved along the substrate with an adjustable velocity up to 70 mm s^{-1} . A wet thin film is left behind, which dries due to the evaporation of the solvent. Compared to spin coating, the loss of coating solution is strongly reduced. The different drying kinetics of the components may lead to distinct solid-state topographies in blend film morphologies [26]. The film

formation can also be influenced by a temperature control of the substrate obtained with a table heater. The blade can be located as low as 20 microns above the surface of the substrate. The target is to achieve a layer with a designated film thickness. In almost the same manner to spin coating, the designated film thickness is a result of the ink properties as well as the blading parameters such as slit height between substrate and knife, volume of the solution that is applied in the slit, temperature control of the substrate, and blading speed. This blading method is a large-area coating technique resulting in lateral resolutions in the sub-millimeter regime and in low material waste. An advantage of doctor blading is among others the large choice of organic solvents, thus little ink formulation work is required. While spin coating is incompatible with R2R processing, the transfer of doctor blading to a R2R process is rather straight forward. Optimized organic solar cells manufactured by doctor blading have been reported with performances comparable to those prepared by spin coating [26, 27]. A comparison of the power conversion efficiency (PCE) achieved by doctor bladed solar cells and spin coated ones, all prepared on glass substrates in our laboratories, is shown in Fig. 2.3b [26]. Three series, each with 16 solar cells, were compared to evaluate the quality of the blading process. As demonstrated in the box plots, the average performance of devices made with blading is slightly higher than the spin coated solar cells fabricated with the reference experiment. Furthermore, the reproducibility of the doctor blading is comparable to the reproducibility of the spin coating process. However, doctor bladed films usually show a small gradient in film thickness, which leads to different short circuit currents for cells fabricated from different areas of the film. Thus, along with a 10 % higher efficiency as compared to spin coated devices, the doctor bladed cells also show a larger variation in J_{SC} .

Similar quantum efficiencies for charge generation and charge separation in spin coated and doctor bladed OPVs are shown by external quantum efficiency (EQE)¹ measurements. An analysis of the current density–voltage (J – V) behaviour of bulk heterojunction solar cells was then carried out to examine the origin of the slight increase in device performance observed in doctor bladed devices compared to spin coated OPVs.

An equivalent circuit diagram representing the macroscopic model for describing a solar cell with one diode is presented in Fig. 2.4. The total current² I at a given voltage V is the algebraic sum of three contributions: the current through the diode, represented by the parameters n and J_0 , the current due to the shunt resistance R_P , and the photogenerated current $I_{photogenerated}$. The current is also influenced by the series resistance in the bulk of the semiconductor and in the connections, R_S . The standard replacement circuit shown in Fig. 2.4 leads to the I – V characteristics following the relations of the equation given in Fig. 2.4 as well. Herein, I represents the measured current throughout the whole device, J_0 stands

¹ External quantum efficiency (EQE) is the percentage of the number of electrons extracted out of a solar cell per incident photon.

² In this chapter, following the widespread convention, J is the symbol of a current density, while I stands for a current.

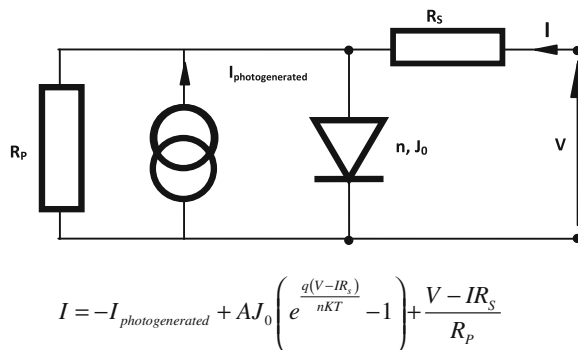


Fig. 2.4 Equivalent circuit diagram representing a macroscopic model for describing a solar cell with one diode. The total current at a given voltage V is the sum of different contributions: the current through the diode, which is represented by the parameters n and J_0 , the current due to the shunt resistance R_p , and the photogenerated current $J_{\text{photogenerated}}$. The series resistance limits the total current

for the saturation current density of the diode, and n is the ideality factor of the diode. V is the applied voltage, R_s , R_p the serial and parallel resistance, $I_{\text{Photogenerated}}$ the photogenerated current of the device, and A is the cross-section of the device.

According to the standard replacement circuit, the slope of the dark I - V curve in the voltage range between 0.2 and 0.7 V represents the diode behaviour as governed by the diode ideality factor n and the saturation current J_0 [28, 29]. The ideality factor n correlates with the number of distributed donor-acceptor interfaces within the blend [30], which is directly related to the morphology of the blend. Variations in the absolute values of n are related to different morphologies: $n = 1$ is typical of a bilayer system, while $n = 2$ represents an intimate mixing of the donor with the acceptor throughout the bulk. Values larger than two indicate more complex carrier recombination mechanisms [30]. The spin coated and doctor bladed devices based on pristine o-xylene solvent investigated in [26] and Fig. 2.3 show similar n , but different J_0 , which may indicate different quality of the interfaces in the different processing techniques [26]. The reduction in J_0 in bladed devices determines a slight increase in open circuit voltage (by 30–40 mV) and thus a slight PCE enhancement [26].

The distinct drying kinetics of the wet film processed by spin coating or doctor blading leads to different solid-state morphologies, without losing performance. In conclusion, doctor blading is a better technology approach to the manufacturing of OPVs than spin coating, considering that the former is compatible with roll-to-roll processing and results in comparable or slightly increased performance [26].

2.2.3 Screen Printing

Shaheen et al. [31] presented screen printing as a fabrication technique for organic photovoltaics. A screen is patterned with an image by closing selected areas. For the

deposition of the ink, the screen is located a couple of millimetres above the surface of the substrate and the ink is loaded onto the screen. Upon imprint, the squeegee transfers the ink through the open meshes onto the substrate by moving the squeegee with a velocity of several centimeters per second across the screen, momentarily touching the substrate. A wet film with designated structure/image is left behind that dries by the vaporization of the solvent formulation. Screen printing usually requires 10–100 times higher ink viscosities compared to spin coating or doctor blading. Screen printing inks show thixotropic behaviour: they are highly viscous in the resting state and become less viscous with applying a shear stress, rapidly recovering viscosity when the shear stress discontinues. To achieve such fluid behaviour, the commercial available screen printing pastes comprise among others thixotropic and viscosity modifiers, binders and thickeners to allow a reproducible and reliable screen printing process. Up to now there has been no report about the impact of these additives on the solar cell device performance. The major limitation of screen printing is defined by the ink requirements in terms of the high viscosity and stability of the ink formulation. Either a high molecular weight material with high solubility forming a stable solution is needed (which results in thicker films) or additives must be used to increase the viscosity of the ink. Nevertheless, the first organic solar cells on glass substrates with a screen printed photoactive layer were reported already in 2001 with a device performance in the range of 4.3 % PCE measured under monochromatic illumination [31]. Other groups presented screen printing as a deposition method for conjugated polymer based materials [32–34] and obtained a maximum power conversion efficiency of 1.25 % under AM1.5G spectra at 100 mW/cm² intensity [34].³ Recently, screen printing of anode and cathode materials with high resolution has also been reported [35, 36].

All these results prove the potential of screen printing for manufacturing OPVs. Moreover, screen printing is an elegant and fast technology that is compatible with roll-to-roll processing.

2.2.4 *Spray Coating*

Spray coating [37, 38] was recently reported as a convenient technique for the fabrication of BHJ devices. Vak et al. [39] showed that spray coating the active layer from chlorobenzene solutions gives efficient devices with 2.83 % PCE. Then, Green et al. presented spray deposited P3HT:PC₆₁BM films from a variety of common organic solvents with different boiling points [40]. Later, Steirer et al. reported on spray coated P3HT:PCBM OPVs using chlorobenzene instead of

³ Solar cells are typically measured at AM1.5G and a light intensity of 100 mW/cm². The “Air Mass” (AM) factor is defined as the quotient between the actual optical path length of sunlight and the optical path length when the sun is directly overhead; AM1.5G characterizes white light with a spectral intensity distribution matching that of the sun rising at a tilt angle of 37° on the earth’s surface.

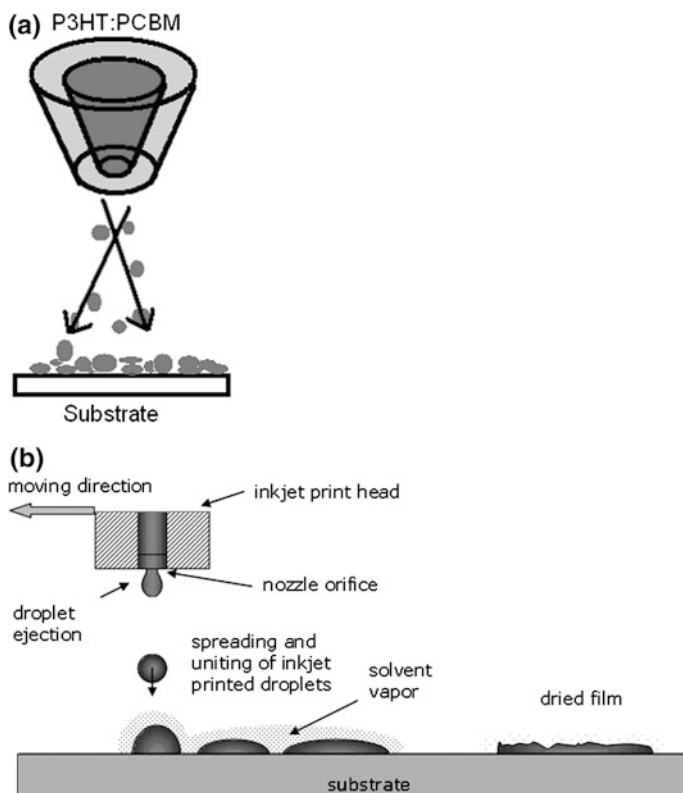


Fig. 2.5 Principle of the film formation for films deposited by (a) spray coating [43] and (b) inkjet printing [44]. Copyright Wiley–VCH Verlag GmbH & Co. KGaA. Reproduced with permission

p-xylene as solvent and found distinct morphologies for these two solvent formulations [41]. Recently, Giroto et al. investigated the influence of the airbrush settings on the surface topography of P3HT:PCBM films [42].

The film formation by spray coating is illustrated schematically in Fig. 2.5a [43]. In the spray coating technique organic thin films are generated stepwise. Single droplets are deposited by the transfer gas pressure with a high velocity onto the substrate. The droplets dry immediately when hitting the substrate surface. This results in a different morphology compared to more conventional technologies such as inkjet printing (Fig. 2.5b) [44], where the film formation is based on the spreading of droplets and combining with adjacent droplets, forming a liquid bulk that dries during vaporization of the solvent vehicle. The transfer of rather large droplets from microns to tens of microns via spray involves an individual drying of single droplets on the substrate and prevents the formation of a closed liquid film. Hence, the surface roughness of spray coated films is typically in the tens of nanometers compared to significantly smoother spin coated or doctor bladed films, which are typically in the range of few nanometers.

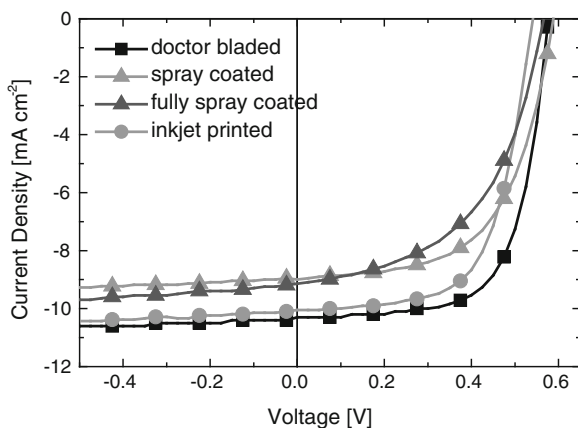


Fig. 2.6 Current–voltage behaviour of representative organic solar cells manufactured by doctor blading (*squares*) [64], spray coating (*triangles*) [45] and inkjet printing (*circles*) [63]. A fully spray coated solar cell device with spray coated PEDOT:PSS and spray deposited P3HT:PCBM is shown by the *dark triangles* [45]. Current density–voltage behaviour and device performance parameters of solar cell devices are studied with AM1.5G illumination with 100 mW cm^{-2}

To achieve rapid drying, the semiconductor ink must fulfil specific requirements, which are primarily defined by the solvent properties, such as boiling point, vapour pressure, viscosity and surface tension. Beyond this, the ink has to be compatible with the nozzle of the airbrush system: coating fluids for spray application need to be weakly viscous at ambient conditions since the inks are not heated during the spray deposition [45]. Highly viscous inks would require higher application temperatures to decrease the viscosity.

At constant nozzle-to-substrate distances, the liquid droplets of low drying-rate inks are immediately pushed sideward by the pressure gas of the airbrush. This leads to non-uniform wetting. On the other hand, spray coated droplets based on very quickly evaporating organic solvents may dry before reaching the substrate surface, preventing the formation of homogeneous films.

“Low wets high” is a guideline for printing. In fact low surface tension for the blended semiconductor solutions guarantees reasonable wetting on many substrates. For instance, PEDOT:PSS surfaces show high surface energies due to the hygroscopic behaviour of PEDOT:PSS and thus the P3HT:PCBM ink should have surface tensions in the 30 mN m^{-1} regime for adequate wetting [45]. Recently, two ink formulations for spray coating based on either pristine organic solvent chlorobenzene or on a two component solvent mixture comprising 68 % oDCB and 32 % mesitylene were studied. These inks have a different drying behaviour due to their vapour pressures [45]. More details on the development of the ink formulation can be found in [44]. Here an organic photovoltaic device based on the improved ink formulation using oDCB/mesitylene is discussed. Despite the high surface roughness, the spray deposited devices on glass based on oDCB/mesitylene show high device performance (Fig. 2.6—“spray coated” line), a V_{oc} of

588 mV, J_{sc} of 9.0 mA cm^{-2} , and a high FF of 0.59 corresponding to a PCE of 3.1 %.

This good photovoltaic performance proves the potential of spray coating as a deposition method for P3HT:PCBM blends. The J - V characteristics under illumination of spray coated devices compared to solar cells prepared by doctor blading or inkjet printing (which will be discussed in the next section) are depicted in Fig. 2.6. The spray coated solar cell shows reduced J_{SC} and FF compared to doctor bladed ones. The lower FF is attributed to increased series resistance R_s , whereas the reduced J_{SC} is related to different semiconductor film morphologies.

To further verify the potential of spray coating, the authors in [45] demonstrated a fully spray-deposited solar cell on glass comprising a spray coated PEDOT:PSS film together with a spray coated photoactive P3HT:PCBM layer, still resulting in a good device performance. The current-voltage behaviour under illumination is also illustrated in Fig. 2.6. The fully spray deposited solar cell has $V_{oc} = 560 \text{ mV}$, $J_{sc} = 9.1 \text{ mA cm}^{-2}$ and $FF = 0.52$. This corresponds to a power conversion efficiency of 2.7 % [45]. The lower device performance of the fully sprayed solar cells compared to devices fabricated with doctor bladed PEDOT:PSS film and spray coated P3HT:PCBM dissolved in oDCB/mesitylene is attributed to the fact that the sprayed PEDOT:PSS film decreases the V_{oc} (5 % lower), and strongly worsens the FF (which is 13 % lower for the fully sprayed devices). The J_{SC} is comparable in the different devices. The decreased FF is related to increased surface roughness of the spray deposited PEDOT:PSS film ($rms = 20.7 \text{ nm}$) and hence, to a poor interface [45]. Despite the higher surface roughness of spray coated films, this method might be a feasible technology to deposit multiple functional layers resulting in well performing photovoltaic devices. In addition, Hau et al. and Giroto et al. also reported on the use of spray coating to manufacture the electrode of OPVs using silver (Ag) nanoparticles dispersed in solution [46, 47]. These promising results on spraying all functional layers of organic solar cells prove the potential of spray coating as a convenient manufacturing method for large area and high throughput roll-to-roll production of solar cells.

2.2.5 Inkjet Printing

In the past few years, inkjet printing has evolved as an important patterning method, not only in the paper industry. Nowadays inkjet printing is probably the most widely used method for organic electronics. Inkjet printers can be divided into three categories: continuous inkjet, drop on demand (DOD) inkjet and bubble jet, all differing in the formation of droplets [48]. The DOD approach is commonly used for accurate deposition of inks on defined spots. This technology eliminates the need for post-patterning the coated films and allows a precise printing with micrometric resolution due to the formation of droplets in the picoliter regime. The use of inkjet printing has been extensively implemented in the field of organic field effect transistors [49–56] and organic light emitting diodes [49, 57–59], but only

little work is found on inkjet printed organic photovoltaics [44, 60–64]. The application of the inkjet printing technology as a fabrication tool for organic devices is very promising due to the compatibility with various substrates. As shown in the schematic representation in Fig. 2.5b [44], the ink is transferred from a writing head to the substrate without direct contact with the surface [65]. A droplet is ejected at the nozzle orifice. As it hits the surface of the substrate, the droplet spreads and wets the substrate. Spreading and wetting depends on the surface tension of both the fluid and the substrate. Film formation occurs by the coalescence of adjacent droplets. A liquid bulk is built that shows particular drying kinetics controlled by the solvent properties. The viscosity needs to be in a range of 1–10 mPas. Higher viscosities up to 40 mPas can be printed with high frequencies by heatable ink reservoirs or temperature controlled print heads to decrease the viscosity for the droplet formation at the nozzle. The droplet formation at the jet and the jetting behaviour may be critical for higher viscosities. High concentrated solutions or particle dispersions may cause jetting problems which lead to nozzle clogging. This can be overcome by using appropriate solvent formulations which extend the ink shelf life.

The homogeneity of the inkjet printed films is, among other factors, determined by the substrate temperature. Most of the vendors offer tools equipped with a heated substrate holder to increase the drying rate of the inkjet printed film.

The vapour pressure of organic solvents plays an important role in the design of inkjet fluids. Since the nozzle orifice is open to the atmosphere when not printing, the solvent will evaporate. This causes an increase of the viscosity at the nozzle orifice. Consequently, the droplet characteristics in terms of velocity, volume and angularity (angle deviation) are affected. This phenomenon is more distinct for high vapour pressure solvents.

During the vaporization of low boiling solvents at the nozzle orifice, the solid blend materials may precipitate in the jet resulting in clogged nozzles [44].

The surface tension of the ink plays a major role in controlling the spreading and wetting on the substrate as well as the interaction with the printhead. A 10 picoliter droplet has a calculated diameter of 27 microns.

The ability of the ink formulation to give excellent droplet formation for photovoltaic applications is strongly dependent on the rheology of the polymer-fullerene solution and on the driving conditions of the print head. Inkjet printing requires significant efforts to properly design an ink formulation for reliable jetting and optimized film quality. In parallel, an optimized drive waveform is responsible for reliable jetting behaviour. A droplet ejected by the piezo-driven print head has a velocity of a few meters per second. Prior to the impact on the substrate, the droplet should afford a round shape avoiding tails and satellites. Such tails and satellites lead to serious problems in printing small structures, e.g. printing of materials emitting different colours in small pockets on tiles for OLED display applications or printing metal electrode grids on OPVs, where high resolution is a prerequisite for reasonable performance.

A variation in the droplet volume results in different film thickness. A method to adapt the droplet volume is to modulate the driving voltage. Higher voltages

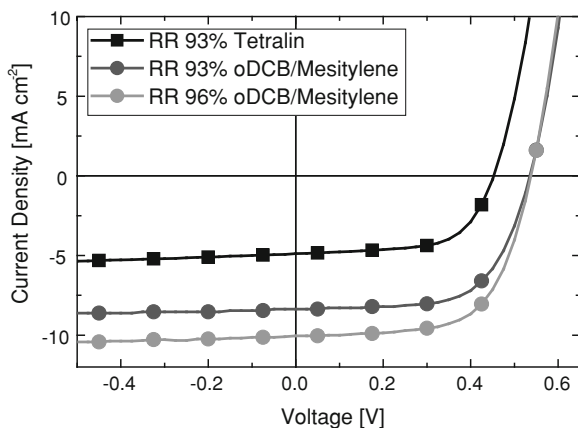


Fig. 2.7 Current–voltage behaviour of inkjet printed organic solar cells. The solvent formulation and the polymer material properties strongly impact the solar cell device performance [44, 63, 64]. Reproduced by permission of the Royal Society of Chemistry. Current density–voltage behaviour and device performance parameters of solar cell devices are studied with AM1.5G illumination with 100 mW cm^{-2}

result in larger droplets and thus, with equal droplet spacing, the printed film thickness can be increased. On top of this, film thickness can be controlled by modifying the droplet spacing or printing multiple drops per spot.

The investigations in [44] report on two ink formulations for OPVs differing in the drying behaviour due to their vapour pressures. These formulations are based on either pristine organic solvent tetrahydronaphthalene (tetralin) or on a two component solvent mixture comprising 68 % ortho-dichlorobenzene (oDCB) and 32 % 1,3,5-trimethylbenzene (mesitylene) [44]. Tetralin vaporizes and dries slower due to the lower vapour pressure (0.18 mmHg) and higher boiling point (207 °C). In contrast the mixture of oDCB and mesitylene results in homogeneous drying kinetics. Mesitylene features not only a higher vapour pressure (1.86 mmHg) and lower boiling point (165 °C) for rapid drying, but also a lower surface tension ($28.8 \text{ dynes cm}^{-1}$). This allows better spreading and wetting behaviour with positive effects on the film formation and film quality. In [44] the authors investigate the morphological properties of the photoactive layer made with an inkjet printed polymer–fullerene blend and highlight the better device performance achieved using an optimized oDCB/mesitylene inkjet formulation instead of the pristine tetralin solvent. In this reference it is shown that solvent mixtures based on oDCB/mesitylene enhance the device performance of inkjet printed solar cells due to improved morphology, decreased first order recombination and reduced surface roughness. Accordingly, a calibrated power conversion efficiency of about 3 % was obtained for the new solvent choice (see Fig. 2.7—93 % oDCB/mesitylene trace) [44]. The main electrical performances of this device are: $V_{oc} = 540 \text{ mV}$, $J_{sc} = 8.4 \text{ mA cm}^{-2}$ and $FF = 0.64$. The chemical material properties of the conjugated polymer such as regioregularity (RR)

together with solvent formulations and their impact on printing reliability, film morphology and device performance are studied in detail in [63, 64]. The J - V curves obtained in that reference are also depicted in Fig. 2.7.

By using a combination of a 96 %-RR P3HT and a suitable solvent mixture oDCB/mesitylene to control the drying and film formation, the authors were able to achieve extended gelation time and further improved morphological properties of the active layer, resulting in a very high PCE of 3.5 % with V_{oc} of 537 mV, J_{sc} of 10.05 mA cm⁻² and a FF of 0.64 for an inkjet printed conjugated polymer-fullerene bulk heterojunction solar cell.

These results evidence a strong dependency of the inkjet device performance on the solvent formulation, on its stability and on the chemical material properties of the donor materials. Therefore, it is important to make an effort on formulation work for high ink shelf life and performance, and adapt the ink to the printing tool. The development of suitable ink formulations for functional materials to control the morphology and printing reliability and achieve efficient devices is an essential step towards the commercial exploitation of organic photovoltaics.

2.2.6 Gravure Printing and Flexographic Printing

Gravure printing is one of the simplest printing technologies. The printing setup (Fig. 2.8a [66]) is based on an engraved printing roll, an ink bath, a coating knife and a counter pressure roll. The printing pattern is engraved into the printing cylinder, meaning that new patterns require new engraved rolls, leading to higher costs. The engraved cells are filled with ink by rotating the roll in an ink bath. The excessive ink is peeled off by a flexible coating knife (doctor blade) prior to contacting the substrate. Ink remains in the engraved pattern and is directly transferred onto the flexible substrate. During imprinting, the substrate takes up the ink from the engraved cells [66]. This method requires inks in the low viscosity regime. Gravure printing can result in high throughput and can be a cost-effective roll-to-roll printing technology. Gravure printing is capable of printing thin films in the range of 1–50 microns and patterns with line width smaller than 100 microns at high speeds up to 15 m/s [67]. These properties in combination with low temperature processing make this technology one of the most promising methods for the mass production of organic photovoltaics. The thickness of gravure printed films is proportional to the area and the depth of the engraved cells, and depends on the line speed, on the roll (cylinder) speed and on the nature of the ink in terms of concentration and rheological properties. Gravure printed organic solar cells were published in 2006 [66]. The authors reported excellent film qualities for 100 nm thick gravure printed P3HT:PCBM layers. A surface roughness of 1.58 nm rms was found for the gravure printed films, while spin coated films from the same solutions showed only slightly lower surface roughness values of 1.26 nm rms. Such a high quality print of thin films with low viscous inks is very encouraging. Beyond high film quality, the gravure printed photovoltaic device

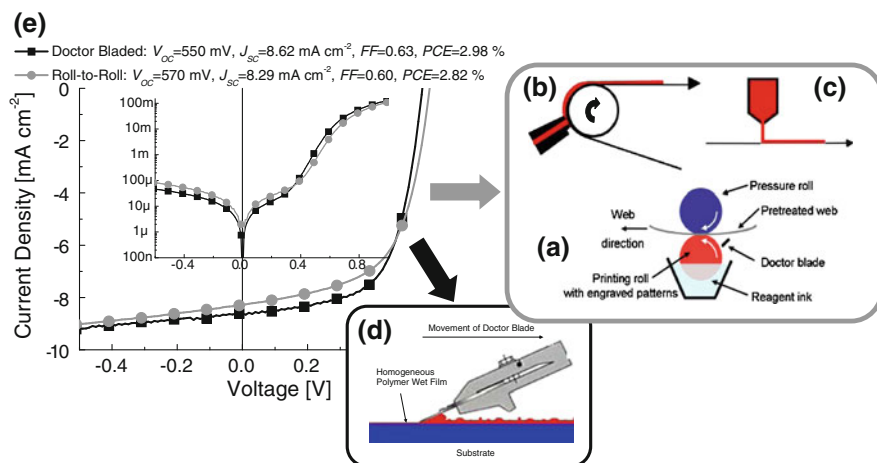


Fig. 2.8 Schematic representation of different fabrication technologies: **a** gravure printing [66], **b** slot die coating, **c** curtain coating [71] and **d** doctor blading. **e** Current–voltage behaviour of a lab-scale doctor bladed device (black squares) compared to a solar cell manufactured by a roll-to-roll process (grey circles). The inset shows the J – V characterization in the dark [Hoth et al. (2008) “unpublished”]. Current density–voltage behaviour and device performance parameters of solar cell devices are studied with AM1.5G illumination at 100 mW cm^{-2} intensity

showed good diode properties. The short circuit current density of these first gravure printed solar cell devices [66] was on the lower side for P3HT:PCBM composites, which might reflect the formation of an unfavourable morphology during the drying kinetics. These initial morphological problems seem to be overcome as Tuomikoski et al. recently demonstrated more than 2 % PCE for gravure printed solar cells under AM1.5G spectra. Similar encouraging results were obtained by Ding et al., who demonstrated printed flexible solar cell devices with a gravure printed hole-transporting layer as well as gravure printed photo-active layer (P3HT:PCBM). Power conversion efficiencies as high as 1.68 % under AM1.5G illumination have been reported for these fully printed solar cells [68]. These results demonstrate the feasibility of gravure printing for roll-to-roll manufacturing of organic solar cells. Gravure printing is able to meet all specifications with respect to layer homogeneity, surface roughness, resolution as well as production speed.

A printing method similar to gravure printing is flexographic printing, where the ink is transferred via flexible printing plates. A typical flexographic printing unit consists of 4 rolls: the fountain roll fills the Anilox roll (roll with engraved pattern). This roll feeds the printing roll with ink and the latter roll applies the ink to the substrate. The substrate is controlled by a back-up roll [69]. Flexographic printing plates lead to a broadening of the image resulting in reduced resolution and film quality. Flexographic printing allows the deposition of layers with comparatively high thicknesses up to several microns. Relatively low viscous inks can be handled at low transfer pressures.

The use of flexographic printing for organic electronic applications was discussed and demonstrated in great detail by Huebler et al. [70]. This group reported flexo-printed hole-transport layers as well as semiconductor layers with good homogeneity and sufficient resolution. However, so far, this printing method was used predominantly for organic electronic applications other than solar cells. Nevertheless, also flexographic printing has the potential to meet the production specifications for organic solar cells, similarly to gravure printing. Edge resolution may be lower than for gravure printing, but, organic photovoltaics won't need resolution better than a few hundreds of micrometers according to the first module designs.

2.2.7 *Curtain Coating and Slot Die Coating*

Curtain and slot die coating have evolved to promising printing methods for the manufacturing of organic solar cells using the roll-to-roll approach. In the curtain coating technique (Fig. 2.8c [71]), a gravity fed slot orifice is used to apply a coating by a falling ink curtain onto the substrate. The coating thickness depends on the die gap, the coating speed and certainly on the rheology of the coating fluid. Curtain coating can produce high quality films with a low number of physical defects at extremely high line speeds up to 1,000 m/min. Despite the importance of the volume flow density, which is of fundamental interest to achieve a stable curtain formation during coating, this method requires specifically designed ink formulations with high ink momentum to prevent defects. For the stability of the curtain, minimum line speeds are required.

In slot die coating inks are *squeezed* via a slot onto the substrate. In case of a 100 % solid coating, this process is called extrusion. An ink or coating is directly applied through a pump-fed slot orifice to a web supported by a backup roll, as shown in Fig. 2.8b. Both curtain and slot coating are rather comparable to doctor blading (Fig. 2.8d). Similar to doctor blading, the final film thickness in slot die coating depends not only on the nature of the ink, but on the coating parameters such as the die gap, the distance and angle between the die and the web, the pump speed, the web line speed and ultimately the temperature control of the flexible substrate. The application of slot die coating to either deposit the hole collecting PEDOT:PSS layer or the photoactive layer P3HT:PCBM were already discussed in [72, 73]. Recently, the first successful demonstration of fully slot-die-coated OPV cells was reported [74]. The functional layers were coated with a speed of 2 m/min and a coating width of 20–50 mm on ITO coated polyester film. An aluminium cathode was vacuum deposited onto small areas of the web coated film to complete the photovoltaic device resulting in power conversion efficiencies up to 1.74 % [74].

Slot die coating allows the usage of inks over a wide range of viscosities. However, the upper limit of the viscosities depends on the pump. The adjustment of the pump pressure is one critical parameter for slot die coating. At higher web speeds the material loss may increase, and the high costs of the die systems are

another disadvantage. Nevertheless, the good homogeneity of coated films and the potential for high web speeds qualify slot die coating as a promising production technology for flexible organic photovoltaics [74]. Today's biggest drawback of slot die coating is its incompatibility with patterning. Production of OPV modules requires patterning the hole-transport as well as the semiconductor layer with sub-mm resolution and registration. Till today, it is not clear how to achieve this with classical coating methods. Post-patterning of thin organic layers, which was mentioned recently [75], might be a concept to allow exploring slot die coating for practical OPV module production.

2.2.8 Characterization of Proprietary Roll-to-Roll Printed Devices

To assess the quality of roll-to-roll processed films, our group investigated the impact of a proprietary roll-to-roll processing on the morphology and topography of roll-to-roll fabricated solar cells [Hoth et al. (2008) "unpublished"]. The device performance of a roll-to-roll deposited organic photovoltaic device compared to a sheet based doctor bladed solar cell fabricated at the laboratory scale is shown in Fig. 2.8e. Both types of solar cells had identical device architectures and were produced from identical materials onto an ITO coated polyester substrate. The J - V characteristics of the roll-to-roll processed solar cell have a V_{oc} of 570 mV, a J_{sc} of 8.29 mA cm⁻², a FF of 0.60 and a PCE of 2.82 %, all performances which are very similar to the doctor bladed device (V_{oc} of 550 mV, J_{sc} of 8.62 mA cm⁻² and a FF of 0.63, corresponding to a PCE of 2.98 %). The inset in Fig. 2.8e represents the dark J - V curves. Both device types, despite being processed by different processing techniques, have similar values of the ideality factor n (1.6) and similar saturation currents J_0 , indicating a very similar bulk morphology of the P3HT:PCBM composite. Accordingly, the domain size of the phase aggregation throughout the bulk must be of the same order. The lower V_{OC} of the doctor bladed solar cell is partly attributed to slightly higher injection currents over the roll-to-roll fabricated device. Furthermore, the decreased J_{SC} of the roll-to-roll device is explained by the slightly lower $\mu\tau$ -product⁴ compared to the doctor bladed reference solar cell. Nevertheless, the overall performance of the roll-to-roll processed organic solar cell is in good accordance with the lab-scale doctor bladed device and confirms the high quality of roll-to-roll processing as the method of choice for the production of OPV. Figure 2.9 [Hoth et al. (2008) "unpublished"] shows an overview of power conversion efficiencies achieved with different fabrication methods either on glass (black boxes) or flexible substrates (grey boxes).

In this section a selection of the most promising printing and coating methods for organic photovoltaic devices was investigated. Despite the differences of fluid

⁴ The charge transport is field driven and the relevant transport parameters are the carrier mobility μ , carrier lifetime τ and internal electric field E .

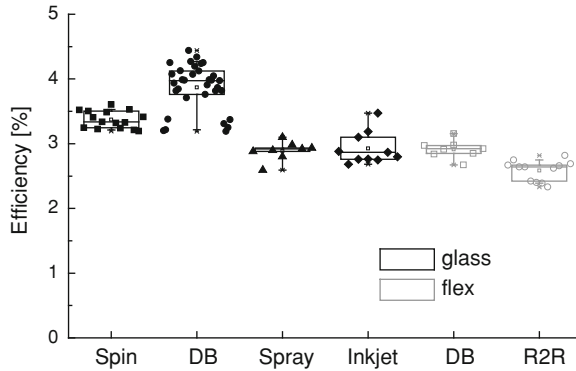


Fig. 2.9 Overview of power conversion efficiencies for different processing techniques for OPVs: spin coating (*Spin*) [26], doctor blading (*DB*) [26, 63, 64], spray coating (*Spray*) [45] and inkjet printing (*Inkjet*) [44, 63, 64], prepared on glass substrates (*black*). The *grey box plots* show doctor bladed (*DB*) and roll-to-roll processed (*R2R*) OPVs on flexible plastic carriers [Hoth et al. (2008) “unpublished”]. All solar cell devices were fabricated at the Konarka research and development facilities

handling and drying in the different methods and their different requirements with respect to ink formulation, we could show that all of the investigated technologies allow manufacturing cells and modules with nearly identical performance. This encourages to further develop new functional materials and ink formulations and to produce OPVs using large-scale printing or coating procedures.

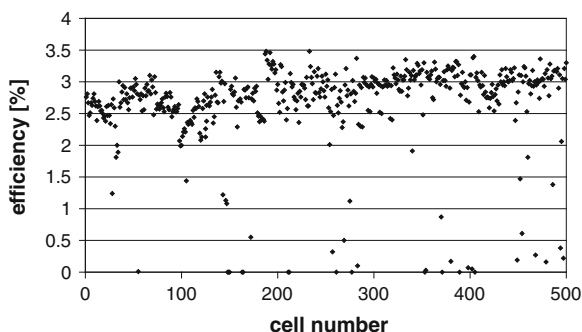
2.3 Reliability and Yield of the Manufacturing Process

One fundamental requirement to a production technology which would be suitable for the market is a high degree of reliability and reproducibility of the results. To establish a baseline of efficiency and prove the reliability of standard manufacturing processes, the fabrication of OPVs by doctor blading was repeated multiple times. Figure 2.10 shows the efficiency evolution of a number of devices fabricated over several months under standard measurement conditions.

The baseline evidences the stable device performance of doctor bladed solar cells over several months. A standard sheet-based device process is thus extremely reliable and results in good-quality working devices with an observed yield reaching 90 %. The lower processing speed and the reduced throughput of the sheet based methods is not a drawback for laboratory operation, where a stable device performance baseline plays a major role for lifetime and degradation investigations and for any optimization approaches.

Similar yield levels close to 90 % are observed for roll-to-roll processing. The high yield of these processes is ascribed to the high degree of reliability of roll-to-roll technologies, and to the reproducibility and homogeneity of the functional films obtained [74].

Fig. 2.10 Efficiency baseline shows the reproducibility of a sheet-fed coating process for flexible OPV cells. The efficiency is plotted vs. the number of manufactured cells



2.4 Accelerated Lifetime Test

The competitive position of OPVs in the energy market and their field of application is a function of efficiency, lifetime and in particular of cost per kWh. The potential of organic photovoltaics has to be assessed by these key parameters as well. This section will focus on lifetime and degradation of organic photovoltaics.

No matter the specific product application, lifetime characterization and understanding the degradation mechanisms is of great interest for a successful product. Degradation of solar cells is normally quantified by the time it takes for a given OPV to drop in power output to 80 % of the initial value [76, 77]. In the past, qualitative experiments to determine the lifetime showed that parameters such as temperature, humidity, electrical stress and irradiation are limiting the long-term stability and thus, accelerating the degradation of organic photovoltaic devices. To study degradation, obtain information about the parameters influencing lifetime, and to quickly characterize degradation mechanisms, accelerated lifetime testing is performed on organic solar cells which are exposed to stress conditions. Such stress conditions are realized in climate chambers with temperatures of 65 or 85 °C, in humid or dry atmosphere and exposing or not the device to 1 sun illumination (corresponding to a 100 mW/cm² intensity). Lifetime studies are also carried out with outdoor exposure. The determination of acceleration factors and, consequently, the use of accelerated lifetime models is an adequate instrument for predicting the lifetime of organic solar cells. The mechanism of the accelerated lifetime degradation at elevated temperatures and stress conditions can be described by an Arrhenius model [78]. Once the acceleration factor is determined at a certain stress condition, the lifetimes of the organic solar cell devices can be predicted.

Only limited data are available on the stability of organic solar cells [76, 77]. Hauch et al. reported on the stability of flexible organic solar cells, which were packaged with a low-cost and rather high water vapour transmission rate (WVTR) food-packaging barrier before exposing to 1 sun illumination at a temperature of 65 °C. In parallel, cells and modules with the same architecture and material combination were investigated at an outdoor rooftop setup in Lowell, MA (USA) to determine the lifetime in operative conditions [76]. The flexible polymer solar

cells survived 1,000 h under accelerated light soaking conditions indicating a high light stability, with hero cells showing less than 20 % degradation after 6,000 h. The good environmental stability measured in accelerated experiments was confirmed by the outdoor data, where flexible modules located at the rooftop did not show performance losses after being operated for 1 year. Figure 2.11a shows the normalized power output (black diamonds) of a solar cell module exposed to outdoor conditions on the rooftop over a period of more than 1 year. The grey squares indicate the air temperature at the time of measurement. Immediately after positioning the module on the rooftop, the efficiency increased by 40 %. Afterwards, there is a strong correlation between efficiency and outdoor temperatures. In May 2007 a linear degradation trend sets in, resulting in a power output of 80 % of its initial value at the end of the experiment, after about 13 months. Re-measuring the J - V characteristics of the solar module after terminating the rooftop experiment indicates a slight increase in the power conversion efficiency due to a relative increase in FF , together with a slight decrease in V_{oc} , resulting in an overall slightly enhanced PCE. Due to the fact that the current density remains constant over the period of outdoor exposure, there is no hint for bleaching of the photoactive layer. The drop in the power output measured on the rooftop was thus only attributed to a shift in the maximum power point (MPP) of the module [76], which can be determined on J - V characteristics as indicated in Fig. 2.2b.

The impact of the WVTR of the packaging for flexible OPVs was also studied [77]. In this report, organic solar cells were encapsulated with a low-cost food package barrier film and exposed to three different climate conditions, 65 °C (high temperature storage), 65 °C illuminated with 1 sun (sun soaking) and 65 °C with 85 % relative humidity (damp heat). An abrupt 5 % drop in the V_{oc} , occurring within the first 100–200 h, is observed for the damp heat condition and may be attributed to a “soaking effect” of the device, i.e. the active layers are assumed to be saturated of humidity and in equilibrium with their surroundings. After a period where V_{oc} is stable in humid air until about 1,250 h, the cell rapidly fails [77]. The stability in V_{oc} hints to stable interfaces between the active layer and the electrode.

A strong degradation in J_{sc} is observed for the sun soaking conditions, while high temperature storage in dark and damp heat show better J_{sc} stability. The FF decreases constantly for all three conditions. The FF is more stable for the illuminated devices, while in dark FF degradation is more pronounced. The efficiency performance of the devices exposed to different climate conditions over time is plotted in Fig. 2.11b [77]. From these results it is clear that different kind of environmental stress lead to different types of degradation behaviour. Damp heat is the most damaging environmental condition when considering the time needed to drop to 80 % of the initial power output. Comparing the results of this study [77] with previously published data on accelerated lifetime measurements [76], the operational lifetime for flexible organic photovoltaic devices with an appropriate package under outdoor conditions can be predicted to be nowadays in the range of 3–5 years. Higher lifetimes are expected to come in quickly, either using intrinsically more stable materials or using packaging materials with better barrier properties.

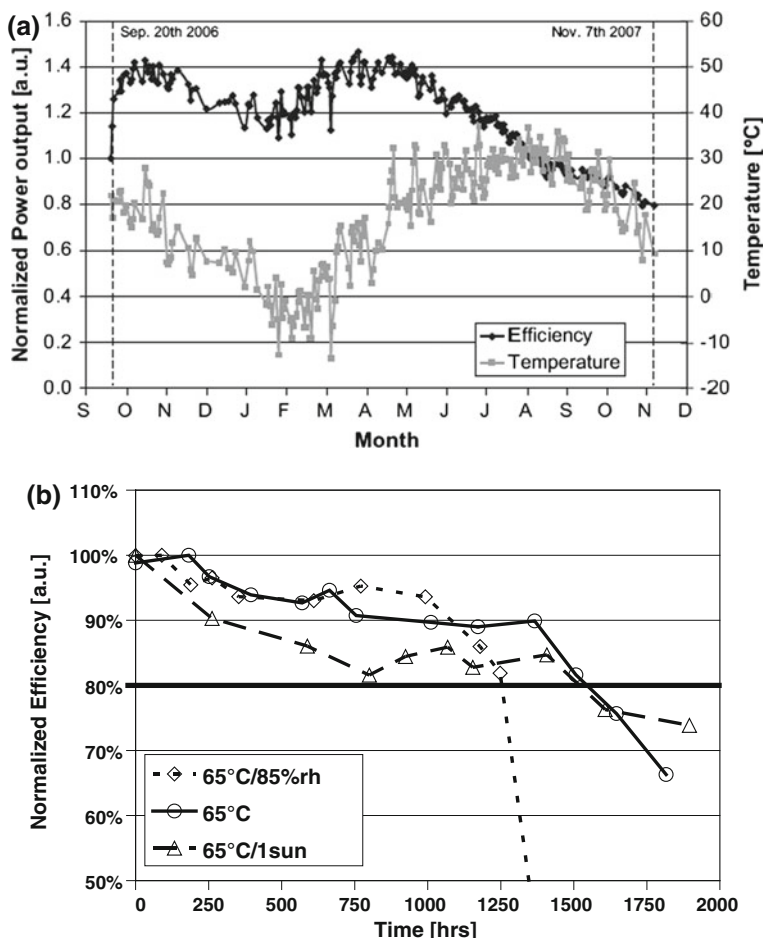


Fig. 2.11 Accelerated lifetime test. **a** Normalized power output (black diamonds) of a solar cell module on the rooftop over time in months. The grey squares indicate the air temperature at the time of measurement. Reproduced with permission by Elsevier from [76]. **b** Degradation in PCE (normalized) of flexible encapsulated organic solar cells exposed to three different climate conditions: 65 °C (circles), 65 °C illuminated with 1 sun (triangles) and 65 °C with 85 % relative humidity (diamonds). Reprinted with permission from [77]. Copyright 2008, American Institute of Physics

2.5 Application Aspects and Product Roadmap

In a market study [79], it has been predicted that organic semiconductor solar cells will have annual growth rates of 40 % or more after market introduction. This work also states that the “Development of high-efficiency organic solar cells would be the single most important factor in the emergence of ultra-portable applications like electronic textiles. Integrated solar cells would allow organic

semiconductor devices to achieve their full flexibility and potential.” Generally speaking, the short term vision for organic solar cell applications is to support market adoption of other organic semiconductor devices by supplying a portable, non-bulky power source. Unfortunately, the performance of organic semiconductor technology in general and the organic photovoltaic technology specifically, has been till recently inadequate for most applications. With the enormous progress made in recent years in OPV performance and production technology many of these applications can now be accessed.

Organic photovoltaics are expected to play a role also in applications beyond consumer electronics and remote power supplies. The scope and impact of the overall solar energy industry has been limited to date by the inability to achieve meaningful breakthroughs in efficiency and cost. In spite of this, the PV industry has been growing at a staggering annual rate of 44 % since 2002, with a total of just over 3 GW shipped in 2007. At an average price of \$3/W, this represented in the same year a market of over \$9 billion for modules and \$18 billion for the total industry. After declining for 50 years, the cost of PV began to rise in 2003 due to a silicon feedstock shortage. These material issues present a longer term threat to the economic viability of conventional photovoltaics, and highlight the importance of developing non-silicon based solar technologies.

The first value proposition of organic PVs and the associated technology is large-scale continuous roll-to-roll production of solar modules achieving costs below \$1/W peak, which is the price at which PV becomes truly competitive with grid-supplied electricity. OPVs’ second value proposition is the flexible, conformable format, enabling integration into products never before accessible by PV, which would include, but not be limited, to anything that currently uses a battery for power. Further anticipated increase in efficiency and lifetime will enable manufacturing highly efficient flexible and light-weight power sources that can be integrated into products, ranging from handheld electronics to rooftops and facades.

Quality of life, environmental and health benefits related to a reduced consumption of fossil fuels are interrelated and will determine the market size of photovoltaics.

Due to its form factor, the colours and the rather high performance of semi-transparent cells, building integrated PVs (BIPV), and especially window integrated PVs, are one of the big opportunities for OPV. Assuming only 30 % of the US based existing housing stock is accessible for building and window integrated PV, and that 2 kW can be installed per structure, the longer-term building-integrated application would generate significant emissions reductions, with the potential for over 70 GW of power generation in the housing market alone. Assuming that 70 GW of PVs are installed by 2020 and produce power for 6 h (a rather optimistic guess) a day, 153 billion kWh per year would be generated. Using Annual Energy Outlook 2008 data, this represents 5 % of total projected US electricity consumption in 2020, and would eliminate 148 million tons of CO₂, 192,000 tons of SO₂, 108,000 tons of NO_x, and 990,000 tons of mercury emissions per year.

Sensors and indoor applications are a second key market for OPVs. Typical fire, smoke, and heat detectors used as safety devices in virtually all residences are an



Fig. 2.12 Application aspects and product roadmap

example of such products. Despite the high level of market penetration, this is still a \$550M annual market just for North America, driven by retrofits and new construction [80]. Today, these devices are either hardwired to the site electricity or battery powered. Many of these devices are in normally occupied areas of the residence, providing a relatively reliable source of ambient light. By implementing OPV panels (which were proven to function very well indoors as well as outdoors, unlike crystalline silicon) directly into the housing of the detector, the expense and inconvenience of hardwiring could be avoided, and the need for disposable batteries eliminated.

The rooftop market will be pursued last, as it is currently dominated by crystalline silicon technology with higher conversion efficiency, despite other limitations such as weight and fragility. Once the OPV technology achieves module efficiencies beyond 7 %, the technology is expected to be able to compete with crystalline technology in rooftop markets based on other consumer parameters, such as aesthetics, cost, ease of installation and weight [81].

Summarizing, the roadmap to market introduction that can be foreseen nowadays is shown in Fig. 2.12. The initial product focus is on the battery charging market, followed by consumer products (lighting, sensors, communications, computing), remote power applications (tents, awnings, shading elements) and finally building-integrated and grid connected PVs. This roadmap follows the increasing economy of scale from the pilot lines stage to the large-quantity production of OPV modules.

2.6 Conclusion

The encouraging results for printed organic solar cells strongly suggest that roll-to-roll fabrication is the most economical way to realize a mass production of photovoltaics. Organic photovoltaics, i.e. solar cells based on solution processable semiconductors, can be mass manufactured by sheet-fed and roll-to-roll printing/

coating technologies. In this chapter we have investigated in detail several printing and coating methods suitable for a P3HT: PCBM bulk heterojunction composite. Despite the differences of fluid handling and drying in the described methods and their different requirements with respect to ink formulation, we could show that all of the investigated technologies enable manufacturing cells and modules with nearly identical performance. An overview of these devices and their performance is shown in Fig. 2.9.

Significant technological developments have been reported on the printing and manufacturing of organic photovoltaics over the last years. Further progress is expected from continuously improved ink formulation, material development, process optimization, development of inline quality control methods and packaging methods. In parallel, with higher efficiencies and longer lifetimes OPV will become able to contribute to the world's energy supply, while first OPV products for consumer electronics, BIPV and remote power applications have entered the market starting in the last quarter of 2009 [82, 83].

References

1. Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, Spiering AJH, Janssen RAJ, Meijer EW, Herwig P, de Leeuw DM (1999) Two-dimensional charge transport in self-organized, high-mobility conjugated polymers. *Nature* 401:685
2. Brown AR, Pomp A, Hart CM, de Leeuw DM (1995) Logic Gates Made from Polymer Transistors and Their Use in Ring Oscillators. *Science* 270:972
3. Brabec CJ, Dyakonov V, Parisi J, Sariciftci NS (eds) (2003) Organic photovoltaics: concepts and realization. Springer series in materials science, vol 60. Springer, London
4. Gur I, Fromer NA, Geier ML, Alivisatos AP (2005) Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science* 310(5474):462–465
5. Kapur V, Kemmerle R, Bansal A, Haber J, Schmitzberger J, Le P, Guevarra D, Kapur V, Stempien T (2008) Manufacturing of 'ink based' CIGS solar cells/modules. Conference record 33rd IEEE photovoltaic specialists conference, IEEE, Piscataway, NJ
6. Sang B, Adurodija F, Taylor M, Lim A, Taylor J, Chang Y, McWilliams S, Oswald R, Stanbery BJ, Van Hest M, Nekuda J, Miedaner A, Curtis C, Leisch J, Ginley D (2008) Low cost copper indium gallium selenide by the FASST[®] process. Conference record 33rd IEEE photovoltaic specialists conference, IEEE, Piscataway, NJ
7. Reyes-Reyes M, Kim K, Carroll DL (2005) High-efficiency photovoltaic devices based on annealed poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 blends. *Appl Phys Lett* 87:083506
8. Ma W, Yang C, Gong X, Lee K, Heeger AJ (2005) Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv Funct Mater* 15:1617
9. Li G, Shrotriya V, Huang J, Yao Y, Moriarty T, Emery K, Yang Y (2005) High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends. *Nat Mater* 4:864
10. Mühlbacher D, Scharber MC, Morana M, Zhu Z, Waller D, Gaudiana R, Brabec CJ (2006) High Photovoltaic Performance of a Low-Bandgap Polymer. *Adv Mater* 18:2884
11. Zhu Z, Waller D, Gaudiana R, Morana M, Mühlbacher D, Scharber MC, Brabec CJ (2007) Panchromatic Conjugated Polymers Containing Alternating Donor/Acceptor Units for Photovoltaic Applications. *Macromolecules* 40:1981

12. Peet J, Kim JY, Coates NE, Ma WL, Moses D, Heeger AJ, Bazan GC (2007) Efficiency enhancement in low-bandgap polymer solar cells by processing with alkanedithiols. *Nat Mater* 6:497–500
13. Soci C, Hwang IW, Moses D, Zhu Z, Waller D, Gaudiana R, Brabec CJ, Heeger AJ (2007) Photoconductivity of a Low-Bandgap Conjugated Polymer. *Adv Funct Mater* 17:632
14. Morana M, Wegscheider M, Bonanni A, Kopidakis N, Shaheen S, Scharber MC, Zhu Z, Waller D, Gaudiana R, Brabec CJ (2008) Bipolar charge transport in PCPDTBT-PCBM bulk-heterojunctions for photovoltaic applications. *Adv Funct Mater* 18:1757–1766
15. NREL certificate Konarka, 8.29 % PCE (thickness > 200 nm, device area 1.031 cm²) under ASTM G173 global spectrum, 17 November 2010
16. Blayo A, Pineaux B (2005) Printing Processes and their Potential for RFID Printing. Joint sOc-EUSAI conference, Grenoble
17. Konarka technologies, homepage www.konarka.com
18. Yu G, Heeger AJ (1995) Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions. *J Appl Phys* 78:4510
19. Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ (1995) Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* 270:1789
20. Shaheen SE, Brabec CJ, Sariciftci NS, Padinger F, Fromherz T, Hummelen JC (2001) 2.5% efficient organic plastic solar cells. *Appl Phys Lett* 78:841
21. Padinger F, Rittberger RS, Sariciftci NS (2003) Effects of postproduction treatment on plastic solar cells. *Adv Funct Mater* 13:85
22. Ma W, Yang C, Gong X, Lee K, Heeger AJ (2005) Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv Funct Mater* 15:1617
23. Konarka homepage (www.konarka.com), press release 19 May 2009, NREL certificate 6.4 % PCE
24. Brabec CJ, Padinger F, Hummelen JC, Janssen RA, Sariciftci NS (1999) Realization of Large Area Flexible Plastic Solar Cells Based on Conjugated Polymers and Fullerenes. *Synth Metals* 102:861
25. Padinger F, Brabec CJ, Fromherz T, Hummelen JC, Sariciftci NS (2000) Fabrication of Large Area Photovoltaic Devices Containing various blends of Polymer & Fullerene Derivatives by Using the Doctor Blade Technique. *Optoelectron Rev* 8(4):280
26. Schilinsky P, Waldauf C, Brabec CJ (2006) Performance analysis of printed organic solar cells. *Adv Funct Mater* 16:1669
27. Chang Y-H, Tseng S-R, Chen C-Y, Meng H-F, Chen E-C, Horng S-F, Hsu C-S (2009) Polymer solar cell by blade coating. *Org Electron* 10(5):741–746
28. Waldauf C, Schilinsky P, Hauch JA, Brabec CJ (2004) Material and device concepts for organic photovoltaics: towards competitive efficiencies. *Thin Solid Films* 451–452:503–507
29. Schilinsky P, Waldauf C, Hauch JA, Brabec CJ (2004) Simulation of light intensity dependent current characteristics of polymer solar cells. *J Appl Phys* 95:5
30. Waldauf C, Scharber MC, Schilinsky P, Hauch JA, Brabec CJ (2006) Physics of organic bulk heterojunction devices for photovoltaic applications. *J Appl Phys* 99:104503
31. Shaheen SE, Radspinner R, Peyghambarian N, Jabbour GE (2001) Fabrication of bulk heterojunction plastic solar cells by screen printing. *Appl Phys Lett* 79:2996
32. Krebs FC, Alstrup J, Spanggaard H, Larsen K, Kold E (2004) Production of large-area polymer solar cells by industrial silk screen printing, lifetime considerations and lamination with polyethyleneterephthalate. *Sol Energy Mater Sol Cells* 83:293
33. Krebs FC, Spanggaard H, Kjaer T, Biancardo M, Alstrup J (2007) Large area plastic solar cell modules. *Mater Sci Eng B* 138:106
34. Aernouts T, Vanlaeke P, Poortmans J, Heremans P (2005) Polymer solar cells: screen-printing as a novel deposition technique. *Mater Res Soc Symp Proc* 836, art. no. L3.9, 81

35. Aernouts T, Vanlaeke P, Geens W, Poortmans J, Heremans P, Borghe S, Mertens R, Andriessen R, Leenders L (2004) Printable anodes for flexible organic solar cell modules. *Thin Solid Films* 451–452:22
36. Krebs FC (2008) Air stable polymer photovoltaics based on a process free from vacuum steps and fullerenes. *Sol Energy Mater Sol Cells* 92:715–726
37. Ishikawa T, Nakamura M, Fujita K, Tsutsui T (2004) Preparation of organic bulk heterojunction photovoltaic cells by evaporative spray deposition from ultradilute solution. *Appl Phys Lett* 84:2424
38. Mo XL, Mizokuro T, Mochizuki H, Tanigaki N, Hiraga T (2005) Polymer Solar Cell Prepared by a Novel Vacuum Spray Method. *Jpn J Appl Phys, Part 1*, 44: 656
39. Vak D, Kim S, Jo J, Oh S, Na S, Kim J, Kim D (2007) Fabrication of organic bulk heterojunction solar cells by a spray deposition method for low-cost power generation. *Appl Phys Lett* 91:081102
40. Green R, Morfa A, Ferguson AJ, Kopidakis N, Rumbles G, Shaheen SE (2008) Performance of bulk heterojunction photovoltaic devices prepared by airbrush spray deposition. *Appl Phys Lett* 92:033301
41. Steirer KX, Reese MO, Rupert BL, Kopidakis N, Olson DC, Collins RT, Ginley DS (2009) Ultrasonic Spray Deposition for Production of Organic Solar Cells. *Sol Energy Mater Sol Cells* 93:447–453
42. Giroto C, Rand BP, Genoe J, Heremans P (2009) Exploring spray coating as a deposition technique for the fabrication of solution-processed solar cells. *Sol Energy Mater Sol Cells* 93:454–458
43. Hoth C (2009) Ink Formulations for Organic Photovoltaics and their Processing with Printing and Coating Technologies. Carl von Ossietzky Universität Oldenburg, Fakultät V, EHF, PhD thesis
44. Hoth CN, Choulis SA, Schilinsky P, Brabec CJ (2007) High Photovoltaic Performance of Inkjet Printed Polymer:Fullerene Blends. *Adv Mater* 19:3973
45. Hoth CN, Steim R, Schilinsky P, Choulis SA, Tedde SF, Hayden O, Brabec CJ (2009) Topographical and morphological aspects of spray coated organic photovoltaics. *Org Electron* 10:587–593
46. Hau SK, Yip H-L, Leong K, Jen AK-Y (2009) Spray coating of silver nanoparticle electrodes for inverted polymersolar cells. *Org Electron* 10:719–723
47. Giroto C, Rand BP, Steudel S, Genoe J, Heremans P (2009) Nanoparticle-based, spray-coated silver top contacts for efficient polymer solar cells. *Org Electron* 10:735–740
48. Gamota DR, Brazis P, Kalyanasundaram K, Zhang J (2004) Printed Organic and Molecular Electronics. Kluwer Academic Publishers, T. Claypole, pp 320–322
49. Calvert P (2001) Inkjet Printing for Materials and Devices. *Chem Mater* 13:3299–3305
50. Liu Y, Varahramyan K, Cui T (2005) Low-Voltage All-Polymer Field-Effect Transistor Fabricated Using an Inkjet Printing Technique. *Macromol Rapid Commun* 26:1955–1959
51. Kim D, Jeong S, Lee S, Park BK, Moon J (2007) Organic thin film transistor using silver electrodes by the ink-jet printing technology. *Thin Solid Films* 515:7692–7696
52. Song DH, Choi MH, Kim JY, Jang J (2007) Process optimization of organic thin-film transistor by ink-jet printing of DH4T on plastic. *Appl Phys Lett* 90:053504
53. Mannerbro R, Rånlöf M, Robinson N, Forchheimer R (2008) Inkjet printed electrochemical organic electronics. *Synth Metals* 158:556–560
54. Sirringhaus H, Kawase T, Friend RH, Shimoda T, Inbasekaran M, Wu W, Woo EP (2000) High-Resolution Inkjet Printing of All-Polymer Transistor Circuits. *Science* 290:2123
55. Kawase T, Sirringhaus H, Friend RH, Shimoda T (2001) Inkjet Printed Via-Hole Interconnections and Resistors for All-Polymer Transistor Circuits. *Adv Mater* 13:1601
56. Kawase T, Shimoda T, Newsome C, Sirringhaus H, Friend RH (2003) Inkjet printing of polymer thin film transistors. *Thin Solid Films* 438:279–287
57. Xia Y, Friend RH (2006) Polymer bilayer structure via inkjet printing. *Appl Phys Lett* 88:163508

58. Xia Y, Friend RH (2005) Controlled phase separation of polyfluorene blends via inkjet printing. *Macromolecules* 38:6466–6471
59. Shimoda T, Morii K, Seki S, Kiguchi H (2003) Inkjet Printing of Light-Emitting Polymer Displays. *MRS Bull* pp 821–827
60. Shah VG, Wallace DB (2004) Low-cost Solar Cell Fabrication by Drop-on-Demand Ink-jet Printing. Proceedings of IMAPS 37th annual international symposium on microelectronics, Long Beach, CA, 14–18 Nov 2004, pp 1
61. Marin V, Holder E, Wienk MM, Tekin E, Kozodaev D, Schubert US (2005) Ink-Jet Printing of Electron Donor/Acceptor Blends: Towards Bulk Heterojunction SolarCells. *Macromol Rapid Commun* 26:319–324
62. Aernouts T, Aleksandrov T, Giroto C, Genoe J, Poortmans J (2008) Polymer based organic solar cells using ink-jet printed active layers. *Appl Phys Lett* 92:033306
63. Hoth CN, Schilinsky P, Choulis SA, Brabec CJ (2008) Printing highly efficient organic solar cells. *Nano Lett* 8:2806–2813
64. Hoth CN, Choulis SA, Schilinsky P, Brabec CJ (2009) On the effect of poly(3-hexylthiophene) regioregularity on inkjet printed organic solar cells. *J Mater Chem* 19(30):5398–5405
65. Nie Z, Kumacheva E (2008) Patterning surfaces with functional polymers. *Nature Mater* p 7
66. Tuomikoski M, Suhonen R (2006) Technologies for Polymer Electronics. Proceedings of TPE06, 2nd international symposium technologies for polymer electronics, Rudolstadt, vol 83
67. Yin X, Kumar S (2006) Flow visualization of the liquid-emptying process in scaled-up gravure grooves and cells. *Chem Eng Sci* 61:1142–1152
68. Ding JM, De la Fuente Vornbrock A, Ting C, Subramanian V (2009) Patternable polymer bulk heterojunction photovoltaic cells on plastic by rotogravure printing. *Sol Energy Mater Sol Cells* 93:459–464
69. Krebs FC (2009) Fabrication and processing of polymer solar cells: A review of printing and coating techniques. *Sol Energy Mater Sol Cells* 93:394–412
70. Hübler AC, Kempa H (2008) Flexo printing in organic electronics. In: Brabec CJ, Dyakonov V, Scherf U (eds) *Organic photovoltaics*. Wiley VCH, New York
71. Santurri P, Chemsultants, Inc., (2007) Coating methods for producing polymer films & membranes 3rd MEA Manufacturing symposium, Dayton, Ohio
72. Schultheis K, Blankenburg L, Sensfuss S, Schrödner M (2007) Polymer photo-voltaics: first steps to large scale R2R-production using wet coating techniques. Proceedings of the Cintelliq conference, Frankfurt
73. Schrödner M, Schultheis K, Blankenburg L, Schache H, Sensfuss S (2008) Reel-to-reel film coating technique for production of functional layers for polymer photovoltaics and electronics. International symposium TPE08, Rudolstadt
74. Blankenburg L, Schultheis K, Schache H, Sensfuss S, Schrödner M (2009) Reel-to-reel wet coating as an efficient up-scaling technique for the production of bulkheterojunctionpolymer solar cells. *Sol Energy Mater Sol Cells* 93:476–483
75. Tipnis R, Bernkopf J, Jia S, Krieg J, Li S, Storch M, Laird D (2009) Large-area organic photovoltaic module - fabrication and performance. *Sol Energy Mater Sol Cells* 93:442–446
76. Hauch JA, Schilinsky P, Choulis SA, Childers R, Biele M, Brabec CJ (2008) Flexible organic P3HT:PCBM bulk-heterojunction modules with more than 1 yearoutdoor lifetime. *Sol Energy Mater Sol Cells* 92:727–731
77. Hauch JA, Schilinsky P, Choulis SA, Rajoelson S, Brabec CJ (2008) The impact of water vapor transmission rate on the lifetime of flexible polymer solar cells. *Appl Phys Lett* 93:103306
78. Schuller S, Schilinsky P, Hauch JA, Brabec CJ (2004) Determination of the degradation constant of bulk heterojunction solar cells by accelerated lifetime measurements. *Appl Phys A* 79:37
79. Derbyshire K (2003) The future of organic semiconductors. Pira International, Surrey

80. Frost & Sullivan (2004) Security technology—North American trends and developments in video surveillance D288
81. Dennler G, Brabec CJ (2008) In: Brabec CJ, Dyakonov V, Scherf U (eds) Organic photovoltaics: Materials, device physics & manufacturing technologies. Organic photovoltaics. Wiley VCH
82. Press release, Konarka Homepage (www.konarka.com), Eröffnung der New Bedford Produktionsanlage, 2008
83. Konarka homepage (www.konarka.com), power plastics, products and applications