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[Continued on next page]

(54) Title: METHOD FOR THE PRODUCTION OF A LAYER OF ORGANIC MATERIAL

(a)



(b)



(57) Abstract: The present invention provides a method for producing a layer of organic material. The method comprises a. providing a substrate; b. providing, onto said substrate, under deposition conditions, a layer of a solution comprising said organic material dissolved in a solvent; c. optionally partially drying said layer of solution; thereafter d. reflowing said layer, said reflowing being applied before said layer has been dried out completely and said reflowing further being limited in time such that said layer is not dried out completely during the reflowing; and e. thereafter controlling drying out of the layer so that drying is performed slower than it would be under deposition conditions. The resulting layer of organic material shows an improvement of both the micro quality and the macro quality, leading to obtaining a fully continuous film with minor surface roughness and an accurate line resolution and edge definition.

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Method for the production of a layer of organic material.

Field of the invention

The present invention relates to the field of organic materials for use in
5 photovoltaic applications. With organic materials is meant materials comprising carbon.

Background of the invention

Photovoltaic applications based on organic materials are known from
10 numerous publications. More specifically a device concept in which the photovoltaic active layer comprises a mixture of an electron donating and an electron accepting material sandwiched between two electrodes is attracting much attention.

Compounds forming this mixture for the photovoltaic active layer are manifold.
15 Well-known electron acceptor materials are fullerenes and/or fullerene derivatives. However, other compounds like, for example, cyano-substituted conjugated polymers or perylene based small molecules are also considered as electron acceptors. Well-known electron donating materials are conjugated polymers like, for example, poly(phenylene-vinylene)s, poly(fluorene)s,
20 poly(thienylene-vinylene)s or poly(thiophene)s. However, other organic polymers as well as numerous amounts of small molecules are also considered as electron donating materials.

Many material combinations are therefore studied but mixtures involving polymeric materials are attracting much attention because they are assumed to
25 be more suitable for large area processing.

A combination of poly(thiophene) polymers with fullerene derivatives as photovoltaic active layer is well-known. Especially the ability of having regioregular poly(thiophene) incorporated in the active compound mixture can lead to a better overlap of the absorption characteristics of the photovoltaic
30 active layer with the solar spectrum. A shift of the absorption of such a photovoltaic active layer into the longer wavelength range has been described to be beneficial for the performance of the final solar cell. It can be achieved by incorporating an additional treatment into the device production process, as

shown in WO 2004/025746 and in "Effects of Postproduction Treatment on Plastic Solar Cells", Franz Padinger et al., Adv. Funct. Mater. 2003, 13, No. 1, January.

These treatments are however applied after finalizing the deposition of the active layer or even the full device.

In US2005/0276910 an organic material is deposited on a lower electrode layer of an organic electronic device prior to fabrication of organic layers. The organic layer is allowed to dry into a film. The device is subjected to post-processing at high temperature and/or high humidity environment to induce reflow of the film. Alternatively, the conductive polymer layer is deposited on the substrate and as it is drying, the substrate is exposed to high temperature and/or high humidity.

Otherwise, in "Device annealing effect in organic solar cells with blends of regioregular poly(3-hexylthiophene) and soluble fullerene", Youngkyoo et al., Applied Physics Letters 86, 063502 (2005) suggestions have been made to obtain similar effects by optimized deposition control of the photovoltaic active mixture.

Since the photovoltaic active layer of these devices generally has a thickness below 1 micrometer and is sandwiched in between two metallic contacts or contact layers, high accuracy on the deposition of this layer is required. Especially the need to achieve a fully continuous film between the electrodes with a well-controlled thickness and minor surface roughness is high. If the thickness of the film is not uniform, the collection of the photo-generated current through the thinner parts of the film is more efficient than through the thicker parts of the film. This would leave less of the film that is actually usable in terms of device performance. Moreover, non-uniformities in the film due to high surface roughness or discontinuities in the film due to pinholes can act as low resistance paths and result in high leakage currents. This high degree of film continuity and uniformity is generally achieved by solution processing via spin coating. Therefore, the compounds of the film have to be dissolved in a solvent or a mixture of solvents. Several processing drawbacks can however be associated with this coating technique like high material consumption and limited substrate sizes. The application of linear casting techniques like, for

example, doctor blading or roll-casting can overcome these problems. However, they still lack the possibility of direct patterning of the deposited layer. This patterning can be beneficial for integration of the photovoltaic structures into larger applications or to produce monolithic modules of photovoltaic devices. There, the patterning of the deposited layer offers the possibility to construct several photovoltaic devices onto a single substrate to be connected with each other. Printing techniques like, for example, inkjet, screen, gravure, flexo or offset printing can resolve these process limitations. In "Production aspects of organic Photovoltaics and their Impact on the commercialisation of devices", C. Brabec et al, MRS Bulletin, Volume 30, January 2005, printing is shown for the production of organic photovoltaic devices.

However, it is not obvious with these techniques to deposit a photovoltaic active layer with limited thickness and to achieve at the same time the requested high quality of a fully continuous film with minor surface roughness. For a good integration of the photovoltaic structures into other applications or to construct several photovoltaic devices onto a single substrate to be connected with each other, accurate line resolution and edge definition also have to be obtained.

Furthermore, the above different deposition techniques have rather diverse requirements with respect to the physical properties of the dissolved active layer compounds. For some of them it is for example more appropriate to have a low viscosity of the dissolved active layer compounds whereas other deposition techniques require high viscosity levels of the dissolved active layer compounds.

Aim of the invention

It is an aim of this invention to provide for a method for producing an organic layer that can be used e.g. as photo-active layer in organic photovoltaic devices, which alleviates or avoids the problems of the prior art.

Summary of the invention

The present invention has been made in view of the above and an object of the present invention is therefore to provide a method to deposit an organic layer with a thickness suitable for photovoltaic applications. The deposition
5 may be performed by a linear technique, a linear casting or linear printing technique. At the same time, when applying a method in accordance with embodiments of the present invention, the requested high quality of a fully continuous film with minor surface roughness is obtained. Moreover, the line resolution and edge definition of the deposited film are substantially improved.

10 The need for additional treatments of the photovoltaic layer to optimize the performance of the final photovoltaic device is not disregarded by this novel method according to the present invention.

A method according to embodiments of the present invention comprises the application of an anneal step on an applied photovoltaic active layer, i.e. layer
15 of organic material, before the layer of organic material has dried out completely, e.g. preferably right away or as soon as possible after the deposition of this layer onto the substrate under deposition conditions and before the solvent has completely evaporated from the deposited layer. By this anneal step, the layer of organic material is made to reflow. "Reflow" may be
20 defined as the redistribution of material on the deposition surface i.e. the substrate. This considerably improves the macro quality of the film, leading to obtaining a fully continuous film with minor surface roughness and an accurate line resolution and edge definition. The "macro quality" is a measure for the surface roughness and line resolution accuracy. The surface roughness of the
25 film can be defined by the average thickness deviation (average of the absolute value of the amplitude) of a line drawn along the surface of the film from the intended surface of the film. The surface roughness can be below 1 micron, below 100 nm, below 10 nm. The resolution accuracy of the film can be defined by an average deviation (average of the absolute value of the
30 amplitude) of the edge profile from the intended edge profile. The resolution accuracy of the film can be below 1mm, below 100 micron, below 10 micron, below 1 micron. After the anneal step, according to the present invention, the film is further dried in a controlled way, i.e. in such a manner that the drying is

slowed down with respect to drying under the deposition conditions. This may be obtained by changing the conditions for drying with respect to the deposition conditions or standard drying conditions, such as e.g. changing the drying temperature, the drying pressure, or performing drying in a saturated atmosphere. It is advantageous to keep the anneal step as short as possible, i.e. sufficient to cause the layer to reflow, but substantially not longer. In preferred embodiments, the anneal step is performed during less than 60 seconds, preferably less than 30 seconds, still more preferred less than 10 seconds. In more preferred embodiments, the anneal step is performed during a time period not longer than a few seconds, preferably between 0.1 and 10 seconds. In view of the limited duration of the anneal step, it does not interfere with additional treatments of the photovoltaic layer to optimize the performance of the final photovoltaic device. The drying performed after the anneal can preferably follow a predetermined drying scheme, comprising at least 1 deceleration of the evaporation of the solvent, and thus dry-out of the film, but optionally also followed by a number (1 or more) of accelerations and decelerations. The drying scheme can be optimized in order to provide an appropriate light absorption spectrum of the organic layer.

In certain embodiments the deceleration takes until an optimum value has been reached for the absorption spectrum of the layer. This considerably improves the micro quality of the film. Micro-quality is related to the internal structure of the layer, i.e. how molecules align. The high micro-quality obtained is a high degree of alignment of molecules in the layer, leading to obtaining a microcrystalline film.

An aspect of the invention is also to provide a method to control the viscosity of the dissolved active layer compounds in the solvent. The viscosity of the dissolved active layer compounds in the solvent is controlled via temperature, choice of solvent, stirring or in any other suitable way. In this way, a solution of the photovoltaic active layer material dissolved in a solvent or solvent mixture can be made suitable for different linear casting or printing techniques. The application of the aforementioned anneal step to improve the film quality can also be done on photovoltaic active layers resulting from a deposition of such viscosity controlled solutions.

The present invention also provides a method to induce an increase of the absorption of the photovoltaic layer in the longer wavelength range, described to be beneficial for the performance of the final solar cell. Dissolving the active layer materials in appropriate solvent or solvent mixtures, i.e. solvents or
5 solvent mixtures in which the active layer materials easily dissolve, in combination with a deposition technique like linear casting or printing and controlling its parameters, can thereby make aforementioned additional treatments, e.g. as disclosed in WO 2004/025746, obsolete. The application of the aforementioned anneal step followed by a slow drying step in accordance
10 with the present invention to improve the film quality can still be combined, without deteriorating the final result.

In a first aspect of the present invention, a method for producing a layer of organic material is disclosed, the method comprising

1. providing a substrate;
- 15 2. providing a solution, comprising the organic material dissolved in a solvent;
3. providing under deposition conditions a layer of the solution onto the substrate, e.g. by means of a linear casting or printing technique;
4. optionally partially drying said layer of solution; thereafter
- 20 5. reflowing the layer, the reflowing being applied before the layer has been dried out completely and the reflowing further being limited in time such that the layer is not dried out completely during the reflowing; and there after
6. controlling complete drying out of the layer so that drying is
25 performed slower than it would be under deposition conditions

The deposition conditions can be normal atmospheric conditions as e.g. in air at atmospheric pressure and room temperature. Deposition can e.g. also be performed in an N₂ atmosphere at atmospheric pressure and room temperature.

30 With organic material is meant carbon containing material. The organic material used for the layer can comprise materials which are electron acceptors and/or materials which are electron donors. The organic material may be a mix or combination of electron acceptor and electron donor

materials. The layer of organic material may be suitable for being used in solar cell applications, but also for OLED transistors, lasers, phototransistors, photodetectors, optocouplers. The organic material should be a material suitable for the application aimed at. In embodiments of the present invention,

5 the organic material is soluble in tetraline (THN). The organic material may comprise or may be a conjugated polymer. It can comprise or be a regio-regular material. The organic material can comprise or be a poly(thiophene). The organic material can further comprise fullerenes and/or fullerene derivatives. The organic material can further comprise conjugated additives.

10 The organic material can further comprise non-conjugated additives. Conjugated additives can have an electrical function, e.g. providing electrical conductivity. Non-conjugated additives can have function e.g. with regard to printing techniques. They can for instance be used to control the rheology, i.e. characteristics related to deformation and flow of the matter, as e.g. viscosity

15 of the solution, or for instance to allow UV curing of the deposited solution. They can further affect the contact angle, affinity, drying, dilution and so on of the deposited film.

Preferred solvents have a high boiling point, because the higher the boiling point of the solvent, for a same temperature and atmosphere, the slower the

20 evaporation and thus the eventual drying out of the film will be. The solvent can comprise tetralin. The solvent can be a mixture of individual solvents. Individual solvents can comprise tetralin, tetrahydrofurane, xylene, toluene, chloroform, chlorobenzene and the like.

In preferred embodiments, the solution has a viscosity high enough to prevent

25 bleed through of the solution in a screen printing process, for example a viscosity higher than 0.5 Pa.s.

In preferred embodiments, the solution is produced by dissolving the organic material in the solvent and waiting until the solution attains a viscosity high enough to prevent bleed through of the solution in a screen printing process,

30 for example a viscosity higher than 0.5 Pa.s.

The ratio of weight of organic material per volume of solution (w/v) is preferably in the range between, as a bottom limit, 0.5% or 1% or 2% and, as a top limit, 5% or 6% or 7% or 8% or 9% or 10% or 15%.

Providing the layer of solution may preferably be performed by a linear technique, in particular a linear casting technique. In preferred embodiments the linear casting technique is a doctor-blading technique or a roll-casting technique or a printing technique like, but not limited to, inkjet printing, screen printing, gravure printing, flexographic printing, offset printing. Such techniques can, and preferably do, produce a pattern comprising a top surface and side surfaces, i.e. a three-dimensional pattern.

In advantageous embodiments the layer is for example provided by a doctor blading technique.

- 10 The reflowing may comprise a temperature increase of the layer of organic material. Said reflowing may comprise a temperature increase preferably above the deposition temperature, and up to any temperature lower than the boiling point of the solvent or mixture of solvents, e.g. up to 99%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20% of the boiling point temperature in degrees
15 Celcius of the solvent.

The reflow can have a duration between, as a lower limit, 0.1 or 1 or 2 or 3 or 4 or 5 seconds and, as an upper limit, 6 or 7 or 8 or 9 or 10 or 15 or 20 or 30 or 60 seconds. The optimum duration will be dependent upon factors such as the chemical and physical properties of the material under reflow, and the
20 environmental conditions during reflow, such as temperature, humidity and pressure conditions, and can be determined by experimentation. The duration of the reflow is of course dependent on the temperature increase: the higher the temperature increase, the faster the layer of organic material will dry out, and the shorter the reflow step should be. It is preferable to have a shorter
25 reflow step at higher temperature, rather than a longer reflow step at lower temperature. It is preferable to have a higher reflow temperature rather than a lower reflow temperature. The duration of the reflow is of course also dependent on the humidity: the larger the humidity, the faster the layer of organic material will reflow.

- 30 The reflow can be such that an already partially crystallised organic film, i.e. where the polymer chains are partially lined up in ordered crystals, is again transformed into an amorphous film, i.e. where the polymer chains have no ordered arrangement. Preferably, the reflow is performed as early as possible

after deposition of the layer, in order to be able to change the roughness thereof, preferably immediately after deposition of the layer.

According to the present invention, the dry out time of the layer, or the evaporation time or evaporation speed of the solvent, after the reflow, is
5 controlled. This can be done by state of the art techniques, such as for instance drying out the film in a reduced-temperature environment or in a solvent-saturated environment, or by choosing a specific linear casting technique. With linear casting techniques the film is typically dried out after deposition, while with a classical spin-on technique those processes are at
10 least partially occurring contemporaneously.

Temperature, pressure, humidity are examples of parameters which may be controlled in order to control the dry-out time of the layer.

Controlling the dry-out time of the layer can advantageously be performed by reducing the evaporation speed of the solvent, when compared to the
15 evaporation speed of the solvent at deposition conditions.

The drying performed after the anneal can preferably be controlled by following a predetermined drying scheme, comprising at least 1 deceleration of the evaporation of the solvent, and thus controlling the drying-out of the film, but the at least 1 deceleration can optionally also be followed by a number (1 or
20 more) of accelerations and decelerations. The drying scheme can be optimized in order to provide an appropriate light absorption spectrum of the organic layer.

In certain embodiments the deceleration of the evaporation of the solvent, or thus the drying-out of the film under conditions so that it dries out slower than it
25 would do under deposition conditions, takes place until an optimum value has been reached for the absorption spectrum of the layer. The drying scheme can be determined such that the micro quality (quality of microstructure) of the layer is optimised.

In embodiments of the present invention, the term "substrate" may include any
30 underlying material or materials that may be used, or upon which a device, a circuit or an epitaxial layer may be formed. The substrate can be transparent, semi-transparent or opaque. The substrate can comprise glass, quartz, semiconductors (such as silicon, germanium, gallium arsenide, and the like),

metals (such as platinum, gold, palladium, indium, silver, copper aluminium, zinc, chromium nickel, and the like), stainless steel, plastic. The substrate may include for example, an insulating layer such as a SiO_2 or a Si_3N_4 layer in addition to the previously described substrate materials. The substrate may

5 include in addition to previously described substrate materials electrode materials like metals (such as platinum, gold, palladium, indium, silver, copper aluminium, zinc, chromium nickel, and the like), metal oxides (such as lead oxide, tin oxide, indium tin oxide, and the like), graphite, doped inorganic semiconductors (such as silicon, germanium, gallium arsenide, and the like)

10 and doped conducting polymers (such as polyaniline, polypyrrole, polythiophene, and the like). The term "substrate" is thus used to define generally the elements for layers that underlie a layer or portions of interest. Also, the "substrate" may be any other base on which a layer is formed, for example a glass or metal layer.

15 The method according to embodiments of the present invention can be used for the production of an organic layer as part of a photovoltaic cell, a light-emitting diode, a photodetector, a transistor, a laser or a memory element.

The layer of organic material produced by a method according to embodiments of the present invention, can advantageously be used for the production of a

20 solar cell.

Such a method for production of a solar cell preferably comprises:

1. providing a substrate;
2. providing first electrodes on the substrate;
3. providing onto the substrate and the electrodes, under deposition
- 25 conditions, a layer of solution comprising organic material dissolved in a solvent;
4. reflowing said layer of solution, said reflow being applied before said layer has been dried out completely and said reflowing further being limited in time such that said layer is not dried out completely during
- 30 the reflowing;
5. thereafter controlling drying out of the layer so that drying is performed slower than it would be under deposition conditions; and

6. providing second electrodes on top of the dried out layer of organic material.

Description of the figures

- 5 Fig. 1 illustrates films, after full evaporation of the solvent, of P3HT, screen printed onto a substrate (a) without reflow treatment in accordance with prior art methods, and (b) with a reflow treatment in accordance with embodiments of the present invention, the reflow treatment having a duration of 2 seconds at a temperature of 100°C.
- 10 Fig. 2 shows optical absorption spectra (UltraViolet-Visual spectra) of a spin coated and a doctor bladed film containing a mixture of the regio-regular conjugated polymer P3HT and the molecule PCBM.

Description of illustrative embodiments

- 15 The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. The drawings described are only schematic and are non-limiting. In the drawings, the size of some of the elements may be exaggerated and not drawn on scale for illustrative purposes.
- 20 Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are
- 25 capable of operation in other sequences than described or illustrated herein. Moreover, the terms top, bottom, over, under and the like in the description and the claims are used for descriptive purposes and not necessarily for describing relative positions. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of
- 30 the invention described herein are capable of operation in other orientations than described or illustrated herein.

Aspects of the invention concern a temperature treatment, also called anneal step, of a wet layer comprising organic material, in order to obtain a reflow

effect of a layer deposited by linear casting or printing techniques. This has as advantage that it enhances the film quality so as to obtain a fully continuous film with minor surface roughness and accurate line resolution and edge definition. More specifically it has been shown beneficial for the production of
5 active layers for organic material based solar cells.

The anneal step is followed by a controlled drying step of the layer of organic material, so that the drying of the layer is slowed down with regard to drying under deposition conditions, at least during a pre-determined period in time.

An organic material has been dissolved in a solvent. Deposition of this solution
10 onto a substrate by use of the linear casting or printing technique can yield a thin, inhomogeneous film with a thickness below 1 micron, the film having poor resolution definition after evaporation of the solvent, i.e. the film showing a deviation from the required pattern which is larger than 1 mm. Temperature curing of such a film while it is still wet, preferably directly after deposition, and
15 prior to complete evaporation of the solvent in accordance with embodiments of the present invention resulted in a reflow effect that yields a fully continuous film with minor surface roughness and accurate line resolution and edge definition. Moreover, this annealing procedure can be restricted to a short time interval, i.e. 60 seconds or less, preferably only a few seconds, to achieve this
20 beneficial effect. Therefore, the curing procedure does not at all have to result in a fast and complete evaporation of the solvent. This makes it highly compatible with subsequent treatments in the production of certain polymer based devices.

Furthermore, this anneal step is highly compatible with the next step of
25 controlled drying of the film, in such a way that the drying is performed slower than it would be performed under deposition conditions. This means that, after the anneal step, the system is not brought back to deposition conditions, but to drying conditions different from the deposition conditions so as to control the drying of the film. The drying conditions may differ from the deposition
30 conditions e.g. in temperature, pressure, humidity or saturation or the environment.

The idea has been shown to be interesting for the deposition of active layers of organic solar cells based on polythiophenes like poly(3-hexyl thiophene).

Dissolving this material in a high boiling point solvent like tetrahydronaphthalene (THN, tetralin – having a boiling point of about 206°C) in a concentration of a weight per volume (w/v) percentages in the range between 1% and 5%, it is possible to deposit this solution onto a substrate by screen printing. However, the discontinuous nature of the process whereby the solution has to be pushed through separate holes of the screen to form a continuous layer in the end, as well as a possibly low viscosity of the solution results in an overall poor quality of the layer after evaporation of the solvent. A temperature curing of approximately 100°C during ~2s is then performed in accordance with embodiments of the present invention, the temperature curing being applied after deposition of the solution onto the substrate, and before the solution is completely dried out, preferably the temperature curing being applied immediately after deposition of the solution onto the substrate. The temperature curing is performed under conditions and during a time sufficient to make the layer reflow. Preferably the conditions are such that the time of the temperature curing may be as short as possible, less than 60 seconds preferably less than 20 seconds, still more preferred only a few seconds, i.e. between 0.1 and 10 seconds. In accordance with the present invention, the temperature curing is followed by a controlled drying of the applied film, so that the film dries slower than it would do if it would dry under deposition conditions. This may e.g. be obtained by changing one or more of the environmental parameters such as temperature, pressure, humidity or saturation. The method of the present invention yields a substantial improvement of the layer quality, both of the macro and of the micro structure. The surface roughness of the film is reduced, the edge definition of the pattern is considerably better, and on a micro-scale the film shows an improved alignment of molecules compared to conventional methods of applying such films, as shown in Fig. 1 by digital scans of the layers processed without (Fig. 1(a)) or with Fig. 1(b)) this annealing procedure, after full evaporation of the solvent.

Similar results can be obtained for a solution of P3HT in THN in which also materials like fullerene-derivatives are additionally dissolved. The material

combination of P3HT and the fullerene-derivative PCBM in a solid state active layer is well-known to result in very good performing organic solar cells.

The regioregularity of polythiophenes, which accounts for the specific orientation of sidechains onto a polymer backbone, can result in a specific interaction of the separate polymer chains with each other. This can also occur in solution and it simply proceeds over time. The process can be monitored by a distinct red-shift of the colour of the solution. It is accompanied by an increase of the viscosity of the solution over time. A viscosity level can thereby be obtained such that bleed through of the solution in a screen printing process can be prevented. This procedure makes the solution more suitable for processing with a technique like screen printing. The procedure can be reversed simply by heating the solution to obtain again the initial lower viscosity. This reversing of the effect results in a viscosity level of the solution that can be more suitable for other deposition techniques than screen printing.

The reversing is accompanied by a disappearance of the red-shifted colour of the solution. The application of the earlier-described annealing procedure on the deposited film will result in improved layer quality of the photovoltaic active layer. The effect of the annealing procedure can, in the case of depositing the solution with a higher viscosity level, clearly be monitored by a colour change of the deposited layer. The red-shifted colour of the highly viscous solution disappears upon annealing of the deposited layer. This shows that, in accordance with embodiments of the present invention, indeed the procedure is applied when still a considerable amount of solvent is present in the as-deposited film. The colour change typically indicates an occurrence of an amorphous orientation of the polymer material in solution whereby the different polymer chains are no longer strongly interacting with each other. The full evaporation of the solvent afterwards in controlled conditions results in a solid film with improved layer quality of the photovoltaic active layer.

The possibility to restrict the annealing procedure to a short time interval makes it highly compatible with additional treatments of the photovoltaic layer to optimize the performance of the final photovoltaic device. However, dissolving the active layer materials in appropriate solvent or solvent mixtures, in combination with a deposition technique like linear casting or printing and

controlling its parameters, can thereby make some additional treatments obsolete, such as e.g. a temperature treatment after the film has completely dried out.

By controlling the evaporation, i.e. evaporation speed or time, of the solvent
5 from the deposited layer, a broadening of the radiation absorption of the photovoltaic layer in the longer wavelength range can be induced. This also improves the layer quality. A slow evaporation speed yields thereby a strong broadening in the longer wavelength range, whereas a fast evaporation of the solvent results in a photovoltaic active layer with reduced absorption in the
10 longer wavelength range. Besides state of the art techniques like, for example, controlling the ambient temperature or atmosphere, the evaporation of the solvent can also be controlled by dissolving the active layer materials in solvent or solvent mixtures with appropriate boiling points, i.e. preferably high boiling points, such as boiling points above 61, 80, 100, 101, 110 degrees
15 Celciusl, in combination with a deposition technique like linear casting or printing and controlling its deposition parameters like deposition speed and pressure. Contrary to spin-coating, in linear casting or printing techniques the evaporation of the solvent can be fully controlled by an appropriate choice of the solvent or solvent mixture in which the active layer materials are dissolved.
20 The evaporation speed can thereby be lowered when using higher boiling point solvents or solvent mixtures. In this way, the increase of the absorption of the photovoltaic active layer in the longer wavelength range is controlled by the use of appropriate solvent in combination with the linear casting or printing technique. The application of the aforementioned reflow step to improve the
25 film quality can still be advantageously combined with this method without deteriorating the final result (even making the final result even better) since the reflow step can be kept limited in time.

The application of linear casting techniques allows a good control of the evaporation speed, as evaporation speed is dependent on e.g. ambient
30 parameters which are better controllable with linear casting techniques than with spin-coating techniques. Linear casting techniques allow more process freedom, e.g. the temperature ranges suitable for spin-coating are smaller than for linear casting techniques. Furthermore, linear casting techniques allow

reducing the evaporation speed when compared to the classical spin-coating to produce the active layer of organic devices, e.g. containing regioregular conjugated polymers. This can result in a broadening of the absorption spectrum compared to rotation based casting techniques.

- 5 In the following example a comparison is made between films with a thickness of 150 nm, deposited by doctor blading, a linear casting technique, and same films deposited by spin coating, a rotation based technique. The deposition mixture contained a 1.5% (weight/volume) 1:2 weight ratio blend of the regioregular conjugated polymer P3HT and the molecule PCBM dissolved in
10 orthodichlorobenzene + 2.5% (volume %) tetrahydronaphtalene mixture, as used in solar cell devices. The spin-coated film was deposited at 1000 rpm for 60s. The doctor bladed film was deposited at a blade speed of 80 mm/s. The UltraViolet-Visual (UV-Vis) spectrum of the as-produced active layer films is shown in Fig. 2. It has been reported in literature that a link exists between the
15 UV-Vis absorption spectrum of this material system and the performance in organic solar cells. The film deposited by doctor blading shows the desired broader absorption band compared to the film deposited by spin coating.

The described technique:

- is not restricted to the P3HT or PCBM materials mentioned but can be
20 widely applicable to materials or material combinations that are readily to be solution processed. For instance materials which are mentioned in "Organic Solar Cells: An Overview", Harald Hoppe and Niyazi Serdar Sariciftci, Journal of Materials Research, Vol. 19, Nr 7, July 2004, pp. 1924-1945, Chapter II, "Materials", have suitable properties for being
25 applied in the methods according to the present invention. Examples of such suitable materials are:

- (a) molecular materials, e.g. ZnPc (zinc-phthalocyanine), MePtcdi (N, N'-dimethyl-perylene-3,4,9,10-dicarboximide), C₆₀, pentacene, oligomeric thiophenes, derivatized compounds of these molecular
30 materials,
- (b) hole-conducting donor type polymers, e.g. MDMO-PPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylene-vinylene), P3HT

(poly(3-hexylthiophene-2,5-diyl)), PFB (poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)),
(c) electron-conducting acceptor polymers, e.g. CN-MEH-PPV (poly-[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)-phenylene]),
5 F8TB (poly(9,9'-dioctylfluorene-co-benzothiadiazole)), a soluble derivative of C₆₀, namely PCBM (1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C₆₁).

All of these materials are solution processible due to their side-chain solubilization. The organic polymers can be, for example, polymers
10 having a conjugated repeating unit, in particular polymers in which neighboring repeating units are bonded in a conjugated manner, such as polythiophenes, polyphenylenes, polythiophenevinylenes, poly(3-alkyl)thiophene, polyfluorenes, or poly-p-phenylenevinylenes or their families, copolymers, derivatives, or mixtures thereof. More specifically,
15 the organic polymers can be, for example: polyfluorenes; poly-p-phenylenevinylenes, 2-, or 2, 5-substituted poly-p-phenylenevinylenes; polyspiro polymers; or their families, copolymers, derivatives, or mixtures thereof.

- The organic polymers can for example include a material capable of
20 charge transport. Charge transport materials include polymers or small molecules that can transport charge carriers. For example, organic materials such as polythiophene, derivatized polythiophene, oligomeric polythiophene, derivatized oligomeric polythiophene, pentacene, compositions including C₆₀, and compositions including derivatized C₆₀
25 may be used.

- The described method is not restricted to the THN solvent mentioned but can be widely applicable to many solvents or solvent mixtures.

- The described method is not restricted to the screen printing or doctor blading method mentioned but is relevant in many solution processes
30 like for example, roll-coating, dip-coating, web-coating, spray-coating or ink jet printing, gravure printing, flexographic printing, offset printing, where thin films are to be deposited with a minor surface roughness and a high quality of line resolution and edge definition.

- The described method is not restricted to the photovoltaic application mentioned but is relevant for many applications where thin films, i.e. films thinner than 1 micron, are to be deposited with a minor surface roughness and a high quality of line resolution and edge definition like in, for example, organic light-emitting diodes, photodetectors, transistors, lasers, memory elements.

CLAIMS

1. A method for producing a layer of organic material, the method comprising
 - a. providing a substrate;
 - b. providing, onto said substrate, under deposition conditions, a layer of
 - 5 a solution comprising said organic material dissolved in a solvent;
 - c. reflowing said layer, said reflowing being applied before said layer has been dried out completely and said reflowing further being limited in time such that said layer is not dried out completely during the reflowing; and
 - 10 d. thereafter controlling drying out of the layer so that drying is performed slower than it would be under deposition conditions
2. A method according to any of the previous claims, wherein said organic material is a conjugated polymer.
3. A method according to any of claims 1 to 2, wherein said organic material
- 15 is a regio-regular material.
4. A method according to any of claims 1 to 3, wherein said organic material is a poly(thiophene).
5. A method according to any of claims 1 to 4, wherein said organic material further comprises fullerenes and/or fullerene derivatives.
- 20 6. A method according to any of claims 1 to 5, wherein said organic material further comprises conjugated additives.
7. A method according to any of claims 1 to 6, wherein said organic material further comprises non-conjugated additives.
8. A method according to any of claims 1 to 7, wherein said solvent
- 25 comprises tetralin.
9. A method according to any of claims 1 to 8, wherein said solvent is a mixture of solvents.
10. A method according to any of claims 1 to 9, wherein providing a layer of solution comprises providing a solution with a viscosity high enough to
- 30 prevent bleed through of the solution in a screen printing process, and applying the solution onto the substrate.
11. A method according to any of claims 1 to 10, wherein providing a layer of solution comprises dissolving said organic material in said solvent, waiting

until said solution attains a viscosity high enough to prevent bleed through of the solution in a screen printing process, and applying said solution onto the substrate.

- 5 12. A method according to any of claims 1 to 11, wherein providing a solution comprises providing a solution with a ratio of weight of organic material per volume of solution (w/v) is in the range between 0.5% and 15%.
13. A method according to any of the previous claims, wherein providing a layer of said solution onto said substrate comprises providing said layer by means of a linear casting technique.
- 10 14. A method according to claim 13, wherein said linear casting technique is a doctor-blading technique or a roll-casting technique or a printing technique.
- 15 15. A method according to any of claims 1 to 14, wherein said reflowing comprises increasing a temperature up to a temperature lower than the boiling point of said solvent.
16. A method according to any of claims 1 to 15, wherein said reflowing has a duration between 0.1 and 60 seconds.
- 20 17. A method according to any of the previous claims, furthermore comprising, between the step of providing a layer of solution onto the substrate, and the step of reflowing the layer of solution, partially drying said layer of solution.
- 25 18. A method according to any of the previous claims for production of a solar cell, wherein providing a substrate comprises providing a substrate provided with first electrodes, the method furthermore comprising, after reflowing, providing second electrodes on top of said layer of organic material.
19. The use of a method according to any of the previous claims, for the production of an organic layer as part of a photovoltaic cell, a light-emitting diode, a photodetector, transistor, laser or memory element.

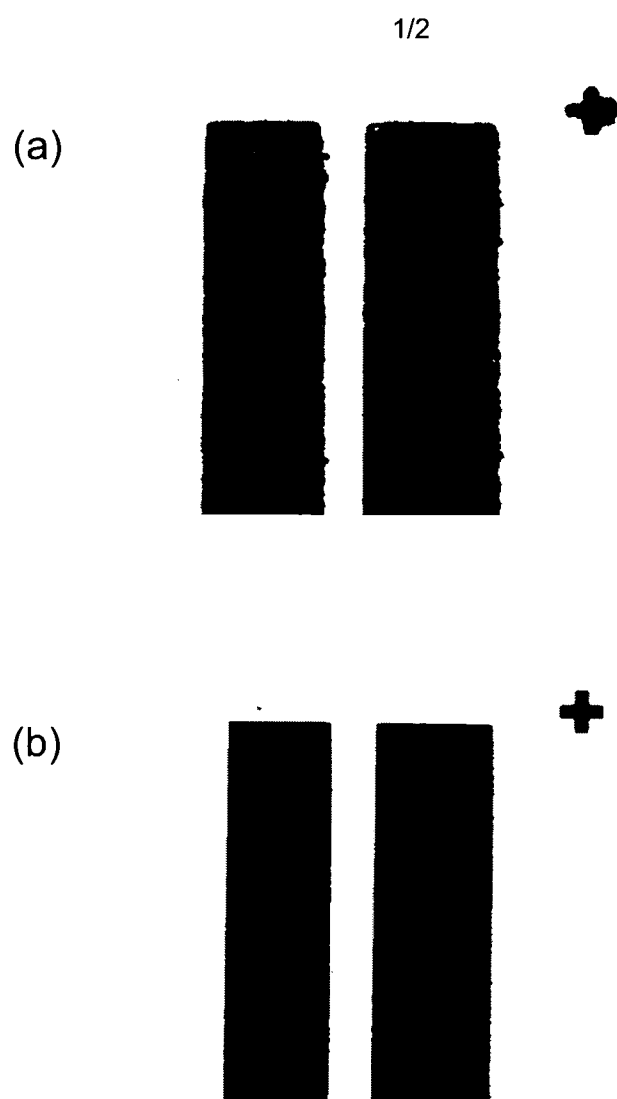
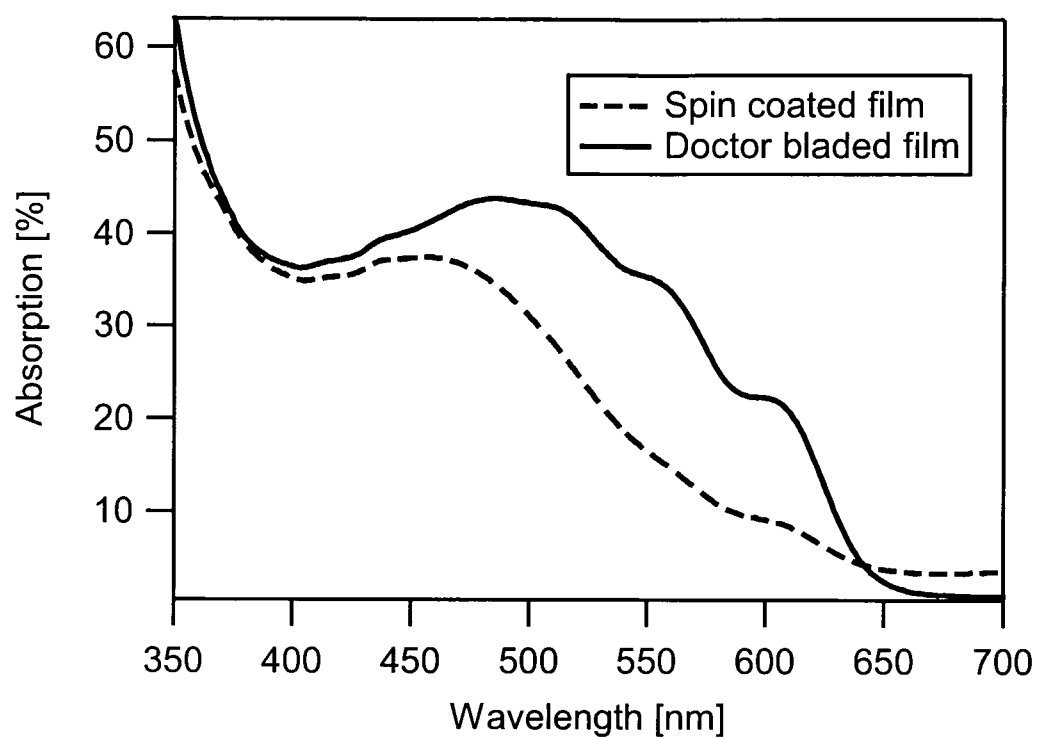


Fig. 1

2/2

**Fig. 2**

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/004768

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 2005/276910 A1 (GUPTA RAHUL [US]) 15 December 2005 (2005-12-15) cited in the application the whole document ----- -/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

13 February 2007

Date of mailing of the international search report

26/02/2007

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/004768

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No

PCT/EP2006/004768

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