



(51) International Patent Classification:

H01L 51/40 (2006.01) H01L 21/388 (2006.01)

(21) International Application Number:

PCT/NL2019/050791

(22) International Filing Date:

29 November 2019 (29.11.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2022110 30 November 2018 (30.11.2018) NL

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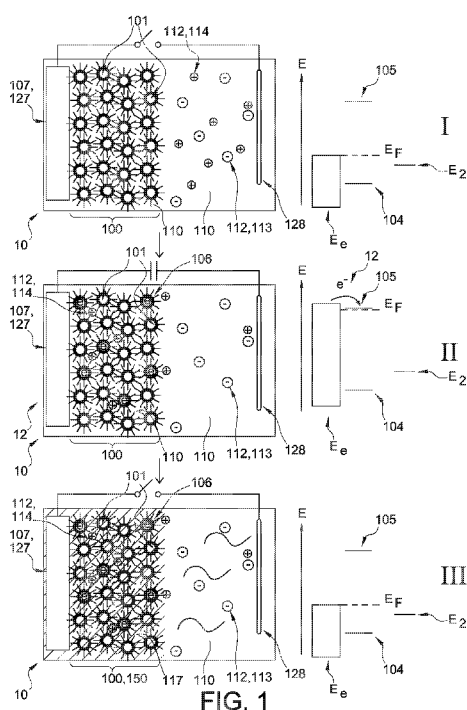
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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: ELECTROCHEMICAL DOPING OF SEMICONDUCTOR MATERIALS



(57) Abstract: The invention provides a method for providing a doped semiconductor layer, wherein the method comprises: (i) a charge injection stage comprising imposing a potential difference between a layer arranged on an electrically conductive substrate and a reference electrode, wherein the layer comprises a semiconductor material, and wherein the layer is in fluid contact with an electrolyte solution comprising ions, wherein the layer is porous to the electrolyte solution, thereby introducing ions into the layer; and (ii) an immobilization stage comprising immobilizing the ions in the layer; thereby providing the doped semiconductor layer.

Declarations under Rule 4.17:

- *as to the identity of the inventor (Rule 4.17(i))*
- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

Electrochemical doping of semiconductor materials

FIELD OF THE INVENTION

5 The invention relates to a method for providing a doped semiconductor layer. The invention further relates to a doped semiconductor layer. The invention further relates to the use of the doped semiconductor layer in a semiconductor device.

BACKGROUND OF THE INVENTION

10 Methods for doping semiconductor materials are known in the art. For example, US20060149002A1 describes a method for forming a conjugated polymer which is doped by a dopant including the steps of (a) adding a doping agent comprising a dopant moiety to a solution containing the conjugated polymer or a precursor thereof and, optionally, a second polymer, the dopant moiety being capable of bonding to the conjugated polymer,
15 precursor thereof or the second polymer; (b) allowing the dopant moiety to bond to the conjugated polymer, precursor thereof or the second polymer to perform doping of the conjugated polymer, wherein the amount of doping agent added in step (a) is less than the amount required to form a fully doped conjugated polymer.

 Yuen J, et al., "Electrochemical Doping in Electrolyte-Gated Polymer
20 Transistors", Journal of the American Chemical society, 2007 describes charge injection into a polymer film which is in contact with an electrolyte, causing ions to move from the electrolyte into the bulk of the polymer.

 WO2004017422 relates to a material for an intermediate layer of an organic photovoltaic component. It describes that the photovoltaic component has an improved
25 efficiency by the adaptation of a working function.

 FR2759495 describes a polymer semiconductor device comprising a rectifying function formed by a polymer film between a first and a second electrode, the polymer film constituting a host matrix for polar molecules, the polar molecules being electrically oriented in a direction perpendicular to the electrodes, the electric charges of the polar molecules
30 having the same sign being directed towards the same electrode.

SUMMARY OF THE INVENTION

Impurity doping, the intentional introduction of impurity atoms to semiconductor materials to control the charge carrier density, may be at the heart of the semiconductor industry. Over the last decades several new promising semiconductor materials may have emerged, including semiconductive polymers, fullerenes, semiconducting organic molecules, semiconducting metal organic frameworks and (colloidal) quantum dots. However, these semiconductor materials may have the caveat in common that their charge carrier density may not be easily tuned via methods of impurity doping that were developed for bulk inorganic semiconductors such as for silicon semiconductors and for other bulk ((semi-)crystalline) semiconductors such as Ge, GaAs, InP, and CdTe semiconductors. This may limit the application of these new promising semiconductor materials in semiconductor devices.

The electronic doping of aforementioned new promising materials may be a huge challenge. The ability to dope these materials on an industrial scale may be limited (organic semiconductors) or may even be absent (quantum dots, metal organic frameworks). The state of the art for organic semiconductors may be that they can be doped via molecular doping; the addition of redox molecules that donate electrons or electron holes to the organic semiconductor. Challenges with molecular doping may include a limited control over the doping density through complex interactions between the molecular dopants and the semiconductor, which may result in limited control over the concentration and/or the spatial distribution of the dopant molecules, as well as diffusion of the organic dopant molecules, which may result in unstable charge densities that prevent long term use in devices.

Prior art methods for the doping of semiconductor materials may be unsuitable for the doping of new promising semiconductor materials, may provide insufficient control over the doping process, may be practically incompatible with semiconductor applications, may require substantial process optimization due to different process condition requirements for different semiconductor materials, may be limited to specific dopants, and/or may provide unstably doped semiconductor materials.

Hence, it is an aspect of the invention to provide an alternative method for providing a doped semiconductor material, which preferably further at least partly obviates one or more of above-described drawbacks. The present invention may have as object to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Surprisingly, the inventors discovered that a reversibly doped semiconductor layer doped via electrochemical doping can be hardened to provide a (stably) doped semiconductor layer.

Electrochemical doping of organic semiconductors may be a means to actively temporarily switch the conductivity in an organic transistor. Typically, in electrochemical doping, a layer (also "film") may be deposited on a working electrode and charge may be injected into the layer from the electrode. To neutralize the injected charge, electrolyte ions of the opposite charge may diffuse into the layer and act as external dopants. The amount of injected charge and thus the placement of the Fermi level may be determined by the potential applied to the working electrode, for example with a potentiostat, and may thus be precisely controlled. However, when the charged layer is disconnected from the working electrode it has been repeatedly observed in the prior art that the injected charge disappears. This loss of charge carrier density may, for example, be due to electrochemical reactions with impurities or intrinsic electrochemical reactions with the material itself or, when used in devices, applied voltages may cause diffusion of ions that act as external dopants resulting in a change of the doping density.

Surprisingly, the inventors discovered that the injected charge may be stabilized by immobilizing the ions at the doped semiconductor material, while the injected electrons (or holes) may still move within the hardened semiconductor material.

Therefore, in a first aspect, the invention provides a method for providing a doped semiconductor layer, wherein the method comprises: - a charge injection stage comprising imposing a potential difference between (i) a layer arranged on an (electrically conductive) substrate and (ii) a reference electrode, wherein the layer comprises a semiconductor material, and wherein the layer is in fluid contact with an electrolyte solution comprising ions, wherein the layer is porous to the electrolyte solution, thereby introducing ions into the layer; and - an immobilization stage comprising immobilizing the ions in the layer; thereby providing the doped semiconductor layer.

The method according to the invention may open up new and enticing possibilities such as the development of improved and tunable properties, and the establishment of cheap, competitive and environmentally friendly processing conditions. The method may be broadly applicable for the electronic doping of semiconductor materials without the need to search for and optimize new molecular dopants for each semiconductor material.

The method according to the invention may provide a doped semiconductor layer having a desired spatial distribution of charge carrier density by successively and selectively immobilizing parts of the layer while imposing different potential differences (see further below). This may enable the design of new device geometries, such as lateral pn
5 junctions that could enable easy on chip integration of, for example, solution processable LEDs.

A semiconductor material (also “semiconductor”) is a material having an electrical conductivity that falls between a metal and an insulator. The electrical conductivity of a material may depend on the (number of) partially filled electron states near the Fermi
10 level of the material; the electrons occupying these electron states may move around relatively freely, thereby allowing electrical conductivity. Typically, a metal – a good electrical conductor – has many partially filled electron states near the Fermi level, an insulator has few partially filled electron states near the Fermi level, and a semiconductor falls in between, *i.e.*, for insulators and semiconductors the Fermi level falls in an energy range wherein no electron
15 states are available; a band gap. However, for a semiconductor this band gap is relatively small allowing, for example, thermal excitation of electrons from the valence band to the conduction band, resulting in partially filled electron states in the valence band and in the conduction band.

The semiconductor material may be arranged in a (thin) layer (also: “film”) on
20 an electrically conductive substrate, *i.e.*, a layer comprising a semiconductor material may be arranged on an electrically conductive substrate. The layer may substantially cover a surface of the electrically conductive substrate. In embodiments, the layer may have a thickness ≥ 20 nm, such as ≥ 50 nm, especially ≥ 100 nm, such as ≥ 200 nm, especially ≥ 500 nm, such as ≥ 1000 nm, especially ≥ 1500 nm. The layer is porous to the electrolyte solution. Hence, the
25 layer may comprise part of the electrolyte solution. In embodiments, the layer may further comprise a binder and/or cross-linking molecules.

The electrically conductive substrate may comprise or be functionally coupled to a working electrode, especially a working electrode arranged in an electrolytic cell. Hence, in embodiments, the layer may be arranged on a working electrode. The layer may be in fluid
30 contact with an electrolyte solution. In embodiments, the electrically conductive substrate may be used as working electrode.

The electrolyte solution comprises ions, especially ions having a size suitable for entering the layer, *i.e.*, the layer may be a porous layer comprising pores having a pore size S_p and the ions may have an ion size smaller than the pore size S_p .

The electrolyte solution may be in fluid contact with a reference electrode (or “counter electrode”). In embodiments, the working electrode and the electrolyte solution and the reference electrode may be arranged in an electrolytic cell, *i.e.*, an electrolytic cell may comprise the working electrode, the electrolyte solution and the reference electrode. In further embodiments, the electrolytic cell may be controlled by a potentiostat.

The charge injection stage comprises imposing a potential difference between the layer arranged on the electrically conductive substrate and the reference electrode, especially resulting in a charge injection in the layer, more especially a charge injection in the semiconductor material. In embodiments, the potential difference may be selected to provide a positive charge injection. The term “positive charge injection” refers to an electron leaving the valence band of the semiconductor material, resulting in a positive charge of the semiconductor material, and resulting in an electron hole in the valence band (and thereby in partially filled electron states in the valence band). In further embodiments, the potential difference may be selected to provide a negative charge injection. The term “negative charge injection” refers to an electron entering the conduction band of the semiconductor material, resulting in a negative charge of the semiconductor material, and resulting in partially filled electron states in the conduction band. The term “charge injection” may be used herein to refer both to “positive charge injection” and “negative charge injection”.

A semiconductor material having a positive charge injection resulting in electron holes in the valence band may be referred to as a P-type semiconductor.

Similarly, a semiconductor material having a negative charge injection resulting in electrons in the conduction band may be referred to as an N-type semiconductor.

It will be clear to the person skilled in the art that the potential difference required for a charge injection may depend on several factors, including, for example, the desired charge carrier density, the semiconductor material, the type of reference electrode used, the temperature, the composition of the electrolyte solution, the porosity of the semiconductor material, and duration (of imposing the potential difference). The Fermi level in the semiconductor layer corresponds to the applied potential difference added to the Fermi level of the reference electrode. The desired Fermi level depends in first instance on the desired charge carrier density in the semiconductor material (which differs for different

applications), as well as the conduction or valence band of the semiconductor material and the Fermi level of the reference electrode that is used. The person skilled in the art will be capable of selecting a potential difference and other parameters suitable for the desired charge injection. In embodiments, optical spectroscopy and/or electrical conductivity measurements
5 may be used to determine whether the desired charge carrier density is reached.

The conductivity of a semiconductor material may be modified via the introduction of a dopant into the semiconductor material. A dopant is an intentionally introduced impurity that modifies the electrical conductivity of the semiconductor material.

Herein, the term “dopant” may especially be used to refer to an ion stabilizing
10 the charge injected into the semiconductor material, *i.e.*, stabilizing the positive charge resulting from an electron hole in the valence band or stabilizing the negative charge resulting from an electron in the conduction band.

The term “ions” herein may refer to cations, anions, and to a mixture of cations and anions as appropriate. For example, it will be clear to the person skilled in the art that the
15 term “ions” in a phrase such as “ions stabilizing a positive charge injection” will refer to anions, and that the term “ions” in a phrase such as “ions stabilizing a negative charge injection” will refer to cations.

The charge injection stage may provide a (reversibly) doped semiconductor layer. The (reversibly) doped semiconductor layer comprises a semiconductor material and
20 ions, wherein the semiconductor material comprises an injected charge, and wherein the ions stabilize the injected charge. The stabilization of the charge may facilitate maintaining the electron or the electron hole in respectively the conduction band or the valence band. However, the (reversibly) doped semiconductor layer may not be stable as the ions are not immobilized, *i.e.*, the injected charge and the ions may be lost if the potential difference is no
25 longer imposed between the layer and the reference electrode, and particularly if electric fields are present, such as in a working semiconductor device selected from the group comprising an LED, a transistor and a solar cell, which may cause the ions to migrate away from their intended location.

Hence, the immobilization stage comprises immobilizing the ions in the layer.
30 The immobilization of the ions in the layer enables the ions to continue to stabilize the charge injection in the semiconductor material without the need for a potential difference being continuously applied between the layer and the reference electrode, *i.e.*, after the charge

injection stage. Hence, the immobilization stage may provide a (stably) doped semiconductor layer.

The doped semiconductor layer may have a more stable charge carrier density than doped semiconductor layers obtained via prior art methods for doping of non-bulk
5 semiconductors. The long term stability regarding the charge carrier density may be better than for alternative methods (i.e. molecular doping) facilitating the use in devices that operate for prolonged periods.

Hence, in embodiments, the method may provide a stably doped semiconductor layer. The term “stably” in “stably doped semiconductor layer” refers to the
10 charge carrier density remaining stable over time, especially under the application of electric fields. In preliminary examples, the Fermi level was shown to drop by less than 0.2V after 3 days at 21°C and no loss of charge density was observed at a reduced temperature of -75°C showing that further improvements are possible. Especially, under the application of an electric field of 1 MV/m no loss of charge density was observed in 1000s at -75°C.

The term “stage” used herein refers to a (time) period (also “phase”) of the method. The different stages may in embodiments (partially) overlap (in time). For example,
15 the charge injection stage may be initiated prior to the immobilization stage, but may continue until the end of the immobilization stage or even longer. It will be clear to the person skilled in the art how the stages may be beneficially arranged in time. For example, the charge
20 injection stage may last during substantially all of the immobilization stage, and an optional second charge injection stage (see further below) may especially be temporally arranged after the immobilization stage.

In specific embodiments, the method may comprise a charge injection stage and an immobilization stage, wherein the charge injection stage comprises imposing a
25 potential difference between a layer arranged on an electrically conductive substrate and a reference electrode, wherein the layer comprises a semiconductor material, and wherein the layer is in fluid contact with an electrolyte solution comprising ions, wherein the layer is porous to the electrolyte solution, thereby introducing ions into the layer; and wherein the immobilization stage comprises immobilizing the ions in the layer; thereby providing the
30 doped semiconductor layer. In further embodiments, the electrolyte solution may comprise a cross-linkable and/or polymerizable matrix forming material configured to harden when exposed to radiation comprising a first wavelength, wherein the immobilization stage comprises hardening of the matrix forming material via one or more of cross-linking and

polymerization, wherein the immobilization stage comprises providing radiation comprising the first wavelength to a first part of the layer. In further embodiments, the electrolyte solution may comprise a solvent having a solvent melting point T_{ms} , wherein the charge injection stage comprises imposing a temperature at or above the solvent melting point T_{ms} , and wherein the
5 immobilization stage comprises imposing a temperature below the solvent melting point T_{ms} . In further embodiments, the charge injection stage may comprise imposing a first pressure and the immobilization stage may comprise imposing a second pressure, wherein the first pressure is selected such that the electrolyte solution is at least partially liquid, and wherein the second pressure is selected such that the electrolyte solution solidifies.

10 In embodiments, the working electrode and the reference electrode may be composed of any conductive and stable material including e.g. gold, silver, platinum, or indium tin oxide or fluorine doped tin oxide, glassy carbon or commonly used reference electrodes such as silver/silver chloride, calomel, etc.

In embodiments, the immobilization stage may comprise hardening of the layer
15 (for immobilizing the ions in the layer). In further embodiments, the hardening of the layer may comprise the hardening of a matrix forming material (to provide a matrix material), especially via one or more of cross-linking and polymerization. In yet further embodiments, the hardening of the layer may comprise solidifying (of the layer), especially solidifying by cooling.

20 In embodiments, the electrolyte solution may comprise a cross-linkable and/or polymerizable matrix forming material. In such an embodiment, the immobilization stage may comprise hardening of the matrix forming material via one or more of cross-linking and polymerization, especially to provide a matrix material. Hence, the (liquid) electrolyte solution may comprise ions and a cross-linkable and/or polymerizable matrix forming
25 material. During the charge injection stage, (part of) the ions may enter the layer to stabilize the injected charge. Similarly, part of the ions that were in the layer may leave the layer (for example, anions may migrate to the reference electrode during a negative charge injection in the layer). During the immobilization stage, the electrolyte solution is hardened, thereby immobilizing the ions in the layer (and inhibiting other ions from entering the layer). The ions
30 may effectively become locked in place within the cross-linked and/or polymerized matrix material. In embodiments, the (cross-linked and/or polymerized) matrix material may comprise the ions, especially monomeric ions may have become part of the matrix material.

In embodiments, the electrolyte solution may comprise a cross-linkable and/or polymerizable matrix forming material. In further embodiments, the matrix forming material may comprise a cross-linkable material, and the immobilization stage may comprise cross-linking of the matrix material. In further embodiments, the matrix forming material may
5 comprise a polymerizable material, and the immobilization stage may comprise polymerization of the matrix material.

The matrix forming material may comprise a material cross-linkable and/or polymerizable via the addition of an initiator, such as a free radical. The matrix forming material may comprise a material cross-linkable and/or polymerizable via exposing the
10 material to specific conditions, such as heat and/or illumination.

In embodiments, the matrix forming material may be configured to harden when exposed to radiation, especially radiation comprising a first wavelength, and the immobilization stage may comprise providing radiation, especially radiation comprising the first wavelength, to (at least) a first part of the layer, especially to substantially the entire layer.
15 The term “harden” with regards to the matrix forming material may refer to “cross-linking” and/or “polymerizing”.

In further embodiments, the first wavelength may especially comprise a wavelength selected from the UV-spectrum, *i.e.*, a wavelength selected from the range of 10 – 380 nm, or up to deep blue such as up to 420 nm. In further embodiments, the first
20 wavelength may comprise a wavelength selected from the visible spectrum, *i.e.*, a wavelength selected from the range of 380 – 780 nm.

The first part of the layer may comprise substantially all of the layer, however, the layer may also be partially hardened, thereby facilitating partitioning the layer into parts with different types and/or concentrations of dopants, as well as different (levels of) charge
25 injections and/or different charge carrier densities, as well as undoped (intermediate) parts.

In further embodiments, the (electrically conductive) substrate may be translucent, especially transparent, allowing the radiation to be provided to the layer through the substrate, especially allowing the first wavelength to be provided to the layer through the substrate. In yet further embodiments, the electrically conductive substrate may comprise
30 indium tin oxide (ITO).

In further embodiments, the (electrically conductive) substrate may comprise an opaque material. In yet further embodiments, the (electrically conductive) substrate may

comprise an (opaque) metal, which may be beneficial due to the relatively low resistivity of metals.

In further embodiments, the method may comprise: (i) a second charge injection stage comprising imposing a second potential difference to the layer, especially resulting in a second charge injection in the layer, wherein the second potential difference is different from the potential difference (in sign and/or value), especially resulting in a second charge injection different from the charge injection, thereby introducing (second) ions into the layer; and (ii) a second immobilization stage comprising providing radiation comprising the first wavelength to a second part of the layer, wherein the second part is at least partially non-overlapping with the first part. Hence, the immobilization stage and the second immobilization stage may resemble a photolithographic method. In further embodiments, an optical mask may be used to selectively expose the first part (or the second part) to the radiation comprising the first wavelength. The method thus facilitates partitioning the layer into multiple parts having different charge densities and dopant concentrations and/or types. Hence, the method according to the invention may facilitate precisely controlling the charge carrier density (also: “charge density”) in (new) semiconductor materials and also facilitates patterning of the doping density via methods akin to photolithography.

The phrase “imposing a (second) potential difference to the layer” may especially refer to imposing a (second) potential difference between the layer and the reference electrode.

Hence, in embodiments, the second charge injection stage may comprise imposing a second potential difference between the layer and the reference electrode, especially resulting in a second charge injection in the layer, wherein the second potential difference is different from the potential difference (in sign and/or value), especially resulting in a second charge injection different from the charge injection, thereby introducing (second) ions into the layer.

In general, the first part and the second part may be arranged in the same plane (of the layer), especially, the first part and the second part may be arranged in a different plane (within the layer). For example, in embodiments, the layer may be exposed to radiation from different angles during the immobilization stage and the second immobilization stage.

The second charge injection stage especially occurs after the immobilization stage. In embodiments, the second charge injection stage may occur after the (first) injection stage and the (first) immobilization stage. In further embodiments, the method may comprise

three or more charge injection stages and respective immobilization stages. In such embodiment, there may especially be an immobilization stage arranged between successive charge injection stages, especially there may be an immobilization stage arranged at the end of each charge injection stage. Hence, in embodiments, the method may comprise a plurality
5 of stages arranged according to the pattern $(S_{inj}S_{immob})_n$, wherein S_{inj} indicates an charge injection stage, and wherein S_{immob} indicates an immobilization stage, wherein $S_{inj}S_{immob}$ indicates that the charge injection stage and the immobilization stage may partially overlap in time, and wherein $n \geq 1$ and is an integer.

In further embodiments, the second charge injection stage may comprise
10 (bringing) the layer in fluid contact with a second electrolyte solution. The second electrolyte solution may comprise second ions different from the ions in concentration and/or type. The second electrolyte solution may comprise a second matrix forming material, especially a second matrix forming material configured to harden when exposed to radiation comprising a second wavelength. Hence, the second immobilization stage may comprise providing
15 radiation comprising the second wavelength (instead of or in addition to the first wavelength) to a second part of the layer. In general, the electrolyte solution and the second electrolyte solution may be substantially similar, especially, the electrolyte solution may be the same *i.e.*, the electrolyte solution is not replaced after an immobilization stage and before the subsequent (such as second) charge injection stage.

20 In embodiments wherein the layer is brought into fluid contact with a second electrolyte solution after the immobilization stage, the second electrolyte solution may typically be selected such that the hardened (first) part of the layer may be substantially unaffected by the second electrolyte solution, *i.e.*, the ions may be substantially immobilized in the hardened part of the layer, and the second ions may practically not enter the hardened
25 part of the layer.

In further embodiments, the potential difference and the second potential difference may be of opposite sign. Especially, the potential difference and the second potential difference may be selected such that the injected charge carriers are of opposite sign, which may be at a potential difference and second potential difference of the same sign. The
30 doped semiconductor layer provided via such embodiment may thus, for example, comprise a first part (second part) having a positive charge injection and a second part (first part) having a negative charge injection, *i.e.*, the doped semiconductor layer may comprise a first part

(second part) comprising a p-type semiconductor and a second part (first part) comprising an n-type semiconductor.

Hence, in further embodiments, the method according to the invention provides a doped semiconductor layer comprising a pn junction. In particular, in embodiments
5 wherein the electrolyte solution comprises a material that may be hardened when exposed to radiation comprising a first wavelength, the pn junction may be provided with a high spatial resolution, facilitating providing stably doped semiconductor materials with a precisely determined pn junction arrangement. In further embodiments, the doped semiconductor layer may comprise a pn junction selected from the group comprising a lateral pn junction, an
10 interdigitated later pn junction, and a transverse pn junction.

In further embodiments, the ions may comprise ionic monomers configured to bind to the matrix forming material during hardening, especially monomers configured to covalently bind to the matrix forming material during hardening. Hence, the electrolyte solution, especially the matrix forming material, may comprise an ionic monomer. In further
15 embodiments, the ionic monomers may copolymerize with the matrix forming material (during hardening). In further embodiments, the ionic monomers may cross-link with the matrix forming material (during hardening).

In further embodiments, the matrix forming material may comprise one or more compounds selected from the group comprising di(ethylene) glycol dimethacrylate
20 (DEGMA), poly(ethylene glycol) dimethacrylate (PEGDMA), poly(ethylene glycol) diacrylate (PEGDA), and pentaerythritol tetraacrylate (PETA).

In further embodiments, the matrix forming material may comprise one or more compounds selected from the group comprising ethylene glycol dimethacrylate (EGMA), DEGMA, tetra(ethylene glycol) diacrylate (TEGA), and poly(ethylene glycol)
25 (PEG), such as PEG550, including poly(ethylene glycol) dimethacrylate PEG550MA. In further embodiments, the matrix forming material may comprise one or more compounds selected from the group comprising EGMA and DEGMA, especially DEGMA.

In further embodiments, the ionic monomer may comprise one or more compounds selected from the group comprising 4-vinylbenzenesulfonate, vinylsulfonate,
30 acrylate, 3-Sulfopropyl acrylate, 3-Sulfopropyl methacrylate. The person skilled in the art will select an ionic monomer suitable for binding to the matrix forming material during hardening.

In a specific embodiment, the matrix forming material may comprise 2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethyl 2-methylprop-2-enoate (also: “di(ethylene) glycol dimethacrylate” and “DEGMA”), and the ionic monomer may comprise 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium.

5 In further embodiments, the electrolyte solution may comprise a photo initiator, especially 4,4'-bis(diethylamino)benzophenone. The photo initiator may be configured to initiate hardening of the matrix forming material when exposed to radiation, especially radiation comprising the first wavelength. In further embodiments, the photo initiator may provide reactive species when exposed to the radiation, especially one or more
10 reactive species selected from the group comprising free radicals, cations and anions, more especially free radicals.

In embodiments, the electrolyte solution may comprise a solvent, especially a solvent selected for the solubility of one or more of the matrix forming material, an ionic monomer, and/or a photo initiator therein. Hence, in embodiments, the electrolyte solution
15 may comprise a solvent, wherein the solvent is selected to be suitable to provide a solution of the matrix forming material, the ionic monomer and the photo initiator. In further embodiments, the solvent may comprise a solvent selected from the group comprising N-methyl-2-pyrrolidone (NMP) and formamide (FA), especially FA. Formamide may be particularly suitable as a solvent as films with improved stability are obtained.

20 In embodiments, the volumetric ratio matrix forming material : solvent may be selected from the range of 5:1 to 1:1.

In embodiments, the electrolyte solution may comprise the ionic monomer in a concentration selected from the range of 0.001M - 1M.

In embodiments, the electrolyte solution may comprise the photo initiator in a
25 concentration selected from the range of 0.001- 4 mg/ml, especially from the range of 0.001 - 0.5 mg/ml, such as from the range of 0.005 - 0.3 mg/ml, more especially from the range of 0.005 - 0.1 mg/ml, such as from the range of 0.005 - 0.02.

In embodiments, the electrolyte solution may comprise a solvent having a solvent melting point T_{ms} , wherein the charge injection stage comprises imposing a (first)
30 temperature at or above the solvent melting point T_{ms} (to the layer), and wherein the immobilization stage comprises imposing a (second) temperature below the solvent melting point T_{ms} (to the layer). Hence, in embodiments, the electrolyte solution may be (at least partially) liquid during the charge injection stage, and the electrolyte solution may be cooled

down (or “frozen”) during the immobilization stage to solidify, especially to immobilize the ions.

In further embodiments, the solvent melting point $T_{ms} \geq 20$ °C, such as ≥ 25 °C, especially ≥ 40 °C, such as ≥ 50 °C, especially ≥ 75 °C, such as ≥ 100 °C.

5 Similarly, the charge injection stage may comprise imposing a first pressure (to the layer) and the immobilization stage may comprise a second pressure (to the layer), wherein the first pressure is selected such that the electrolyte solution is (at least partially) liquid, and wherein the second pressure is selected such that the electrolyte solution solidifies.

10 It will be clear to the person skilled in the art that the phase transition of a material may be dependent on both temperature and pressure, and that a material may exhibit hysteresis in its solid-liquid transition temperatures (and/or pressures). Hence, the charge injection stage may comprise imposing a first pressure and a first temperature (to the layer) and the immobilization stage may comprise imposing a second pressure and a second temperature (to the layer), wherein the combination of the first pressure and the first
15 temperature cause the electrolyte solution to be in an (at least partially) liquid state, and wherein the combination of the second pressure and the second temperature cause the electrolyte solution to solidify.

In further embodiments, the solvent may comprise a solvent selected from the group comprising ethylene carbonate, succinonitrile, fumaronitrile,
20 2,2,3,3-tetramethylsuccinonitrile, 1,4-dicyano-2-butene, and polyethylene glycol, especially a polyethylene glycol selected from the group comprising PEG600, PEG4000, PEG6000, PEG8000, PEG20000, and PEG35000, and dimethyl sulfone.

In further embodiments, the solvent may comprise a solvent selected from the group comprising succinonitrile, 3-hexenedinitrile, 1,2-dicyanobenzene, butyramide, iso-
25 butyramide, and cyanoacetoamide, especially a solvent selected from the group comprising butyramide, iso-butyramide, and cyanoacetoamide, more especially cyanoacetoamide.

In embodiments wherein the immobilization stage comprises imposing temperature below the solvent melting point T_{ms} , the solvent may especially be selected for one or more, especially all, of a high melting point, low/no charge extraction, electrochemical
30 stability, the generation of hydrogen bonds, and a melting rather than subliming behavior when heated.

In further embodiments, the solvent may comprise a eutectic solvent, wherein for which the melting point may be selected by changing the ratio of two solvent components.

In particular, the solvent may comprise a solvent selected from the group comprising biphenyl diphenyl ether eutectic, choline chloride + ethylene glycol, choline chloride + 1,2-propanediol, choline chloride + triethanolamine, choline chloride + trifluoroacetamide, choline chloride + glycerol.

5 In general, the pressure and/or temperature of the immobilization stage may reflect (or be based on) the intended application conditions of the doped semiconductor layer. Hence, if the doped semiconductor layer is intended for application at room temperature under atmospheric pressure, the immobilization stage may comprise imposing a similar temperature and pressure. In contrast, in embodiments, the charge injection stage may comprise imposing
10 a temperature different from room temperature, especially an elevated temperature, and/or a non-atmospheric pressure, especially a reduced pressure, to cause the electrolyte solution to be in a liquid state.

 In embodiments, the doped semiconductor layer may comprise a plurality of layers. Especially, after the immobilization step, the method may be repeated with a second
15 layer arranged on top of the (first) layer. Hence, in embodiments the invention also provides a multi-layer stack, wherein two or more layers comprise doped semiconductor parts, e.g. pn layers.

 Hence, in embodiments, the method may further comprise: - a second layer application stage comprising arranging a second layer on the layer, especially after the
20 immobilization stage; and - a second layer charge injection stage, especially following the second layer application stage, comprising imposing a second layer potential difference to the second layer, especially resulting in a second layer charge injection in the second layer, thereby introducing second layer ions into the second layer; and - a second layer immobilization stage comprising immobilizing the second layer ions in the second layer,
25 especially by hardening (at least) a first part of the second layer. In particular, the second layer charge injection stage may comprise imposing a second layer potential difference between the second layer and the reference electrode.

 In further embodiments, the method may comprise further layer application stages and corresponding charge injection stages and immobilization stages.

30 In further embodiments, the second layer potential difference may be different from the potential difference. Especially, the potential difference and the second potential difference may be selected such that the injected charge carriers are of opposite sign, which may be at a potential difference and second potential difference of the same sign. Hence, the

second layer charge injection may be different from the charge injection, especially of opposite sign. In further embodiments, the potential difference and the second layer potential difference may (at least) be of opposite sign.

In further embodiments, the method may comprise both (i) partitioning a layer
5 into a first part and a second part via a (first) charge injection stage and a second charge injection stage, and (ii) providing a second layer via a second layer application stage (and a second layer charge injection stage and a second layer immobilization stage). In yet further embodiments, the second layer may be partitioned into a first part and a second part via a second layer charge injection stage and a second layer second charge injection stage. It will
10 be clear to the person skilled in the art how the partitioning within a layer and along layers may be temporally arranged to provide a doped semiconductor layer having a desired three-dimensional arrangement of dopants (and charge (carrier) densities).

Hence, in embodiments, aforementioned pattern $(S_{inj}S_{immob})_n$ may be repeated
k times with intermittent layer application stages, wherein n may have different values for
15 different layers. For example, for $k=3$, the (first) layer may be provided via pattern $(S_{inj}S_{immob})_3$, the second layer may be provided via pattern $(S_{inj}S_{immob})_5$, and the third layer may be provided via pattern $(S_{inj}S_{immob})_3$. Especially, in embodiments, n may also have the same value for different layers, such as for sets of two or more (adjacent) (stacked) layers.

The embodiments involving a matrix forming material that may be hardened,
20 especially via exposure to radiation, may be particularly suitable for partitioning both within a layer and for providing multiple layers. However, the embodiments involving immobilizing via changes in temperatures and/or pressures may also be used to provide such partitioning by using multiple different electrolyte solutions.

In embodiments, (after the charge injection stage but) before the
25 immobilization stage the electrolyte solution outside the layer is removed. For instance, in an electrolytic cell the electrolyte solution may be removed, followed by the immobilization. Alternatively, (after the charge injection stage but before the immobilization stage) the electrically conductive substrate with layer may be removed from the electrolyte solution followed by the immobilization. Alternatively, especially when the electrically conductive
30 substrate with layer is configured in a horizontal configuration (especially with the layer on top), (after the charge injection stage but before the immobilization stage) the position of the layer and the liquid level of the electrolyte solution may be chosen such that the liquid level of the electrolyte solution is essentially as high as the layer (or its top layer). Having achieved

this configuration, the immobilization stage may be executed. The latter embodiment may be useful as one or more of the following may be obtained: (i) the electrolyte liquid may stay in contact with an edge of the layer, (ii) the electrolyte liquid may stay as film over the layer, (iii) the time between removal of (at least part of the liquid) over the layer and the
5 immobilization stage may be short, and (iv) the potential difference may be maintained until close to (in time) the immobilization stage or even during the immobilization stage.

In embodiments, the immobilization stage may also (inevitably) comprise hardening (part of) the electrolyte solution external from the layer. In further embodiments, the hardened electrolyte solution external from the layer may be (partially) removed, for
10 example, via cutting and/or etching. In further embodiments, the doped semiconductor layer may be provided with hardened electrolyte solution external from the layer, *i.e.*, with part of the continuous phase external from the layer, and be used as such.

In further embodiments, a distance d_1 between the electrically conductive substrate and the reference electrode may be $\leq 1000\text{ }\mu\text{m}$, such as $\leq 500\text{ }\mu\text{m}$, especially ≤ 100
15 μm , such as $\leq 50\text{ }\mu\text{m}$, especially $\leq 30\text{ }\mu\text{m}$, such as $\leq 10\text{ }\mu\text{m}$, especially with the layer configured between the electrically conductive substrate and the reference electrode. Such embodiments may be particularly suitable for providing the doped semiconductor layer with hardened electrolyte solution external from the layer.

Hence, in embodiments, the method according to the invention may also
20 provide a doped semiconductor layer with a pn junction within a layer and/or with a pn junction between a layer and an adjacent layer.

The definitions and embodiments described herein for a charge injection stage and/or an immobilization stage may also apply respectively – insofar appropriate – to other charge injection stages and other immobilization stages and *vice versa*. Hence, in general the
25 embodiments for the charge injection stage may further apply for the second charge injection stage, the third charge injection stage, the second layer charge injection stage, the second layer second charge injection stage, the third layer charge injection stage, and so forth, unless indicated otherwise or clear from the context.

Solvent impurities may extract the injected charges from the
30 conduction/valence band of a (doped) semiconductor material. For example, molecular oxygen, a common impurity, can be reduced to its radical anion superoxide by electrons in the conduction band of a semiconductor material.

Hence, in embodiments, the method may comprise executing the charge injection stage and the immobilization stage in a controlled atmosphere. In further embodiments, the controlled atmosphere may have an O₂ concentration ≤ 1000 ppm, such as ≤ 1 ppm, especially ≤ 0.1 ppm, such as ≤ 0.01 ppm. In further embodiments, the controlled atmosphere may have an H₂O concentration ≤ 1000 ppm, such as ≤ 1 ppm, especially ≤ 0.1 ppm, such as ≤ 0.01 ppm.

In further embodiments, the method may comprise executing the charge injection stage and the immobilization stage in a nitrogen filled glovebox providing the controlled atmosphere.

In further embodiments, the method may comprise pre-treating one or more materials to remove O₂ and/or H₂O, especially by degassing, such as vacuum degassing. In further embodiments, the method may comprise pre-treating (at least part of) the electrolyte solution to remove O₂ and/or H₂O, especially by vacuum degassing. In further embodiments, the method may comprise pre-treating one or more of the solvent, the matrix forming material, the ionic monomer, and the photo initiator, especially the solvent and/or the matrix forming material, to remove O₂ and/or H₂O, especially by degassing, such as vacuum degassing.

The method according to the invention may be particularly suitable for a semiconductor material that (i) is electrochemically stable, i.e. does not decompose at the applied potential difference, and (ii) offers a pathway for electrolyte ions to diffuse close to the injected charge for charge stabilization, i.e. a material that is (nano)porous. Hence, in embodiments, the layer, especially the semiconductor material, may comprise pores having a pore size S_p enabling the diffusion of ions, i.e., a pore size $S_p >$ the ion size of the respective ions, such as a pore size $S_p >$ the cation size of the respective cations and/or a pore size $S_p >$ the anion size of the respective anions. In further embodiments, the pores may (typically) have a (median) pore radius larger than the radius of the ions, especially a pore radius ≥ 0.1 nm, such as ≥ 0.5 nm, especially ≥ 1.0 nm.

In embodiments, the semiconductor material may be a material selected from the group comprising semiconductive polymers, fullerenes, semiconductor nanomaterials such as quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic frameworks, semiconductive graphene, and 2D layered semiconductors such as transition metal dichalcogenides, especially from the group comprising semiconductive polymers, fullerenes and semiconductive graphene. In further embodiments, the semiconductor material may comprise a solution-synthesized semiconductor material. In

further embodiments, the semiconductor material may comprise a semiconductor material with nanometer scale porosity, such as a semiconductor material comprising pores (typically) having a (median) pore radius larger than the radius of the ions, especially a pore radius ≥ 0.1 nm, such as ≥ 0.5 nm, especially ≥ 1.0 nm.

5 In embodiments, the semiconductor material may comprise a nanocrystal, especially a quantum dot (QD). In further embodiments, the QD may especially be selected from the group comprising ZnO QD, PbS QD, CdSe QD, CdSe/CdS QD.

 In embodiments, the ions may comprise one or more ions selected from the group comprising Li^+ , ClO_4^- , 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium, 4-
10 vinylbenzenesulfonate, vinylsulfonate, acrylate, 3-Sulfopropyl acrylate, 3-Sulfopropyl methacrylate, especially one or more ions selected from the group comprising 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium, 4-vinylbenzenesulfonate, vinylsulfonate, acrylate, 3-Sulfopropyl acrylate, 3-Sulfopropyl methacrylate.

 In a second aspect, the invention further provides a doped semiconductor layer,
15 wherein the doped semiconductor layer comprises a semiconductor material selected from the group comprising semiconductive polymers, fullerenes, semiconductor nanomaterials such as quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic frameworks, semiconductive graphene, and 2D layered semiconductors such as transition metal dichalcogenides, especially from the group comprising semiconductive polymers,
20 fullerenes and semiconductive graphene, wherein the doped semiconductor layer comprises a continuous phase wherein the semiconductor material is embedded, wherein the continuous phase comprises one or more of (i) a cross-linked and/or polymerized matrix material, and (ii) a material having a solvent melting point $T_{ms} \geq 40$ °C, wherein the continuous phase further comprises one or more ions.

25 In embodiments, the doped semiconductor layer may be provided by the method according to the invention.

 In embodiments, the continuous phase may comprise a matrix material obtainable from a matrix forming material, especially from a matrix forming material that was hardened during an immobilization stage.

30 In further embodiments, the continuous phase may comprise a solidified solvent, especially a solidified solvent obtained during an immobilization stage.

 In a further aspect the invention provides a semiconductor device comprising the doped semiconductor layer according to the invention. In embodiments, the

semiconductor device may comprise a device selected from the group comprising a light-emitting diode, a laser diode, a solar cell, and a photodetector.

The embodiments described herein are not limited to a single aspect of the invention. For example, an embodiment describing a matrix forming material in relation to the immobilization stage may further apply to the doped semiconductor layer; it will be clear to the person skilled in the art that if a matrix forming material may be used during the method to provide the stably doped semiconductor material that the stably doped semiconductor material may comprise the matrix material formable by the matrix forming material.

The doped semiconductor layer may be part of or may be applied in semiconductor devices such as (LED) displays, (LED) lighting systems, (flexible) solar cells, transistors, camera's, lasers, photodetectors, and in new unforeseen applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying schematic drawings in which corresponding reference symbols indicate corresponding parts, and in which:

Fig. 1 schematically depicts an embodiment of the method according to the invention.

Fig. 2 schematically depicts another embodiment of the method according to the invention providing a doped semiconductor layer comprising a pn junction.

Fig. 3 schematically depicts an embodiment of a doped semiconductor layer provided with the method according to the invention using interdigitated electrodes.

Fig. 4A-H are graphs depicting measurements obtained using doped semiconductor layers examples obtained via the method according to the invention.

The schematic drawings are not necessarily to scale.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Fig. 1 schematically depicts the method 10 for providing a doped semiconductor layer 150. Fig. 1-I schematically depicts a layer 100 arranged on an electrically conductive substrate 107. In the depicted embodiment, the electrically conductive substrate 107 comprises the working electrode 127 of an electrolytic cell. The electrolytic cell further comprises a reference electrode 128. In the depicted embodiment, the layer 100 comprises a semiconductor material 101 selected from the group comprising quantum dots. In further

embodiments, the semiconductor material 101 may be selected from the group comprising semiconductive polymers, fullerenes, semiconductor nanomaterials such as quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic frameworks, semiconductive graphene, and 2D layered semiconductors such as transition metal dichalcogenides. The layer 100, especially the semiconductor material 101, is in fluid contact with an electrolyte solution 110 comprising ions 112. The layer 100, especially the semiconductor material, is porous to (at least part of) the electrolyte solution 110, allowing (at least part of) the electrolyte solution 110 to enter the layer 100 between the semiconductor material 101. In further embodiments, the electrolyte solution may comprise a compound larger than the pore size S_p of the layer. For example, part of the ions 112, such as part of or all of the anions 113 (or cations 114), may be larger than the pore size S_p of the layer 100. The electrolyte solution 110 may further be in fluid contact with a reference electrode 128.

In Fig. 1-I the potential difference applied between the layer 100 and the reference electrode 128 results in the Fermi level E_F to remain between the valence band 104 and the conduction band 105 of the semiconductor material 101. Hence, no charge is injected into the semiconductor material. Reference E_2 indicates the Fermi level of the reference electrode.

Fig. 1-II schematically depicts an embodiment of the charge injection stage 12. A negative potential difference is imposed between the layer 100 and the reference electrode 128 such that the Fermi level E_F becomes sufficiently high to inject charge (electrons e^-) into the conduction band 105 of the semiconductor material 101. Hence, a charge injection 106 may occur in the layer, especially in the semiconductor material 101. As the charge injection 106 is negative (due to the injection of charge (electrons) into the conduction band 105), cations 114 may diffuse into the layer 100 to stabilize the injected charge. Hence, the layer 100 may be doped with ions 112.

In further embodiments, a positive potential difference may be imposed between the layer 100 and the reference electrode 128 such that the Fermi level E_F becomes sufficiently low to inject charge (electron holes) into the valence band 104 of the semiconductor material 101.

If the imposing of negative potential difference as depicted in Fig. 1A-II is ceased, the injected charge and the ions 112 may again leave the layer 100.

Hence, the method 10 further comprises an immobilization stage comprising immobilizing the ions 112 in the layer 100.

In the depicted embodiment, the electrolyte solution 110 may comprise a cross-linkable and/or polymerizable matrix forming material, and the immobilization stage comprises hardening of the matrix forming material via one or more of cross-linking and polymerization. Hence, the immobilization stage may comprise immobilizing part of the electrolyte solution, such as the electrolyte solution 110 in and directly surrounding the layer. The immobilization stage may comprise hardening the matrix forming material to a continuous phase 117, especially to a matrix material.

Fig. 1-III schematically depicts the layer 100 after the immobilization stage. The continuous phase 117 may prevent the ions 112 stabilizing the charge injection 106 from diffusing away from the semiconductor material 101. Hence, even if the imposed potential difference is returned to the level of Fig. 1-I, the charge injection 106 may remain in the layer, especially in the semiconductor material 101. Hence, the method 10 may provide a doped semiconductor layer.

In embodiments, the ions 112 may comprise ionic monomers configured to bind to the matrix forming material during hardening. Hence, the immobilization stage may comprise hardening the matrix forming materials and the ionic monomers, such that the ionic monomers become (covalently) bound to the continuous phase 117, which may provide particularly good immobilization of the ions 112 in the layer 100.

During (and after) the method 10 for providing the stably doped semiconductor material 150, solvent impurities may extract the injected charges from the conduction band 104 / valence band 105 of a (doped) semiconductor material 101. For example, molecular oxygen, a common impurity, can be reduced to its radical anion superoxide by electrons in the conduction band of a semiconductor material 101. Hence, in embodiments, the method 10 may comprise executing the charge injection stage and the immobilization stage in a controlled atmosphere having an H₂O concentration ≤ 1000 ppm and an O₂ concentration ≤ 1000 ppm. In further embodiments, the method 10 may comprise executing the charge injection stage and the immobilization stage in a nitrogen filled glovebox providing the controlled atmosphere.

Fig. 2 schematically depicts an embodiment of the doped semiconductor layer 150 comprising a pn junction and provided by an embodiment of the method 10 according to the invention. In the embodiment of the method 10, the layer 100 may be arranged on a first electrically conductive substrate 107, 107a comprising a working electrode 127 and on a second electrically conductive substrate 107, 107b comprising a reference electrode 128. The

layer may comprise a first semiconductor material 101, 101a (arranged on the first electrically conductive substrate 107, 107a) and a second semiconductor material 101, 101b (arranged on the second electrically conductive substrate), wherein the first semiconductor material 101, 101a and the second semiconductor material 101, 101b are independently selected from the group comprising semiconductive polymers, fullerenes, semiconductor nanomaterials such as quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic frameworks, semiconductive graphene, and 2D layered semiconductors such as transition metal dichalcogenides. In further embodiments, the first semiconductor material 101, 101a, and the second semiconductor material 101, 101b may comprise the same semiconductor material 101. In the depicted embodiment, the first semiconductor material 101, 101a comprises an n-type (doped and negatively charged) semiconductor material 102, whereas the second semiconductor material 101, 101b comprises a p-type (doped and positively charged) semiconductor material 103. The injected charge in the first semiconductor material 101, 101a comprises electron holes h^+ . The injected charge in the second semiconductor material 101, 101b comprises electrons e^- .

In the depicted embodiment, the layer 100 spans between the working electrode 127 and the reference electrode 128. Hence, the depicted embodiment may be particularly suitable for embodiments of the immobilization stage comprising imposing substantially the same conditions to the entire layer. Hence, in further embodiment, the electrolyte solution 110 may comprise a solvent having a solvent melting point T_{ms} , wherein the charge injection stage 12 comprises imposing a temperature at or above the solvent melting point T_{ms} , and wherein the immobilization stage comprises imposing a temperature below the solvent melting point T_{ms} , especially wherein the solvent melting point $T_{ms} \geq 40$ °C. The hardening of the solvent provides the continuous phase 117. In further embodiments, the solvent may comprise a solvent selected from the group comprising ethylene carbonate, succinonitrile, fumaronitrile, 2,2,3,3 tetramethylsuccinonitrile, 1,4-dicyano-2-butene, polyethylene glycol, and dimethyl sulfone.

In further embodiments, the doped semiconductor layer 150 may comprise two or more layers provided by an embodiment of the method 10 comprising two or more charge injection stages 12 and two or more immobilization stages. Hence, in further embodiments, the method 10 further comprises: - a second layer application stage comprising arranging a second layer on the layer 100; and - a second layer charge injection stage comprising imposing a second layer potential difference to the second layer, thereby introducing second layer ions

into the second layer; and - a second layer immobilization stage comprising immobilizing the second layer ions in the second layer. In further embodiments, the second layer may be in physical contact with the reference electrode 128 (as in Fig. 2), however, in general, the second layer may be physically separated from the reference electrode by 128 the electrolyte solution 110.

Hence, in further embodiments, the first continuous phase 117, 117a may be provided by the charge injection stage and the immobilization stage, whereas the second continuous phase 117, 117b may be provided by the second layer charge injection stage and the second immobilization stage.

In further embodiments, the potential difference and the second layer potential difference may be of opposite sign.

Fig. 2 schematically depicts a doped semiconductor layer 150 comprising a pn junction within the layer 100. The doped semiconductor layer 150 may especially be provided by an embodiment of the method 10 wherein the layer 100 is partitioned into two or more parts. Especially, in embodiments, the electrolyte solution 110 may comprise a cross-linkable and/or polymerizable matrix forming material, and the immobilization stage comprises hardening of the matrix forming material via one or more of cross-linking and polymerization. In further embodiments, the matrix forming material may be configured to harden when exposed to radiation, especially radiation comprising a first wavelength, wherein the immobilization stage comprises providing radiation, especially comprising the first wavelength, to (at least) a first part of the layer. Hence, part of the layer may selectively be immobilized by exposing the part of the layer to radiation comprising the first wavelength, especially by exposing the part of the layer to radiation using a (photo)mask. By successively and selectively immobilizing parts of the layer, a doped semiconductor layer with a desired spatial distribution of charge (carrier) density may be obtained. In further embodiments, the method 10 may comprise: - a second charge injection stage comprising imposing a second potential difference to the layer, wherein the second potential difference is different from the potential difference, thereby introducing (second) ions into the layer; and - a second immobilization stage comprising providing radiation comprising the first wavelength to a second part of the layer, wherein the second part is at least partially non-overlapping with the first part. Especially, the potential difference and the second potential difference may be of opposite sign. The matrix forming material configured to harden when exposed to radiation may facilitate providing a layer 100 with a desired spatial distribution of charge carrier density

and dopants (ions), especially wherein sharp transitions exist between n-type semiconductor material and p-type semiconductor material, or especially wherein transitions exist between parts having a different concentration of the same dopants (and charge (carrier) density).

In further embodiments, the method 10 may comprise both partitioning of the layer 100 in a first part and a second part, as well as arranging a second layer on top of the layer 100. The doped semiconductor layer 150 obtained from such an embodiment may comprise a desired 3D spatial distribution of both charge (carrier) density and (different) dopants. In further embodiments, the doped semiconductor layer 150 may comprise a plurality of different semiconductor materials (especially in different layers). In further embodiments, the method 10 may comprise the use of different electrolyte solutions, such as electrolyte solutions differing, for example, in ions, solvents, and/or matrix forming materials.

Fig. 3 schematically depicts an embodiment of a doped semiconductor layer 150 provided with the method 10 according to the invention. The layer 100 was arranged on interdigitated electrodes, *i.e.*, the layer was arranged on a first electrically conductive substrate 107, 107a comprising a working electrode 127 and on a second electrically conductive substrate 107, 107b comprising a reference electrode 128, wherein the working electrode 127 and the reference electrode 128 are interdigitated. The working electrode 127 and the reference electrode 128 are not in direct physical contact. The layer 150 comprises a first continuous part 117, 117a (the hashed 'beams') comprising an n-type semiconductor material 101, 102, and a second continuous part 117, 117b comprising a p-type semiconductor material 101, 103. In particular, the layer comprises an arrangement of beams alternatingly comprising n-type and p-type semiconductor materials. For visualization purposes only, parts of the (rightmost) beams are removed to visualize the structure of the working electrode 127 and the reference electrode 128 underneath the layer 150. In further embodiments, the doped semiconductor layer 150 of Fig. 3 may be applied in a (sensitive) photodiode.

Fig. 1-III, Fig. 2, and Fig. 3 schematically depict a doped semiconductor layer 150, especially obtainable by the method according to the invention. The doped semiconductor layer 150 comprises a semiconductor material 101 selected from the group comprising semiconductive polymers, fullerenes, semiconductor nanomaterials such as quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic frameworks, semiconductive graphene, and 2D layered semiconductors such as transition metal dichalcogenides. The doped semiconductor layer 150 comprises a continuous phase 117 wherein the semiconductor material 101 is embedded. The continuous phase 117 further

comprises one or more ions 112 (to stabilize the charge injection). In embodiments, the continuous phase 117 comprises one or more of (i) a cross-linked and/or polymerized matrix material, and (ii) a material having a solvent melting point $T_{ms} \geq 40$ °C.

Fig. 4A-C depict experimental measurements of examples of electrochemically doped semiconductor layers provided by the method according to the invention. The method for providing the doped semiconductor layer as well as the subsequent electrochemical measurements were performed in a nitrogen-filled glovebox.

Fig. 4A - example 1: immobilization of ions through cooling at different temperatures. ZnO quantum dots (also: "QDs") were drop-casted in air and annealed for 1 hour at 60 °C to provide the layer 100 on an electrically conductive substrate 107 comprising a working electrode 127. The electrically conductive substrate 107 (with the layer 100) was immersed in a 0.1 M LiClO₄ electrolyte solution comprising succinonitrile as the electrolyte solvent. The solution further contained an Ag pseudo reference electrode (RE) and a Pt sheet as a counter electrode (CE). A potential difference of -1.36 V was applied between the layer 100 and the reference electrode 128 at temperatures where charge injection can occur, here 60°C. While continuously applying this potential the temperature was reduced. Next, Fermi-level stability measurements were performed at different temperatures (the potential is normalized, such that the applied potential is 1 and the initial open circuit voltage V_{oc} is 0) and the experimental measurements are depicted in Fig. 4A. The electrochemical measurements were performed in a nitrogen filled glovebox with H₂O and O₂ levels ≤ 0.1 ppm. Fig 4.A depicts the normalized potential (V) against time in seconds at 60 °C (T_1), 50 °C (T_2), 40 °C (T_3), 20 °C (T_4), 0°C (indiscernible in the graph from 20 °C) and -77 °C (T_5). For measurements performed at temperatures above the melting point of succinonitrile (57 °C), electrons are still in the conduction band of the QDs after 10 mins, but a significant drop in potential is observed. By lowering the temperature, the potential increases (becomes less negative) more gradually, showing that electrons leave the conduction band of the ZnO QDs more slowly. Strikingly, at temperatures below the melting point of pure succinonitrile, electrons do not stay permanently in the conduction band. It is not until -77 °C that the injected electrons are entirely stable for at least 10 minutes. Still, at 20 °C it takes around 145 minutes for the potential to reach the value of -1.17 V vs. ferrocene.

In the Fermi-level stability measurements, the electrons may leave the conduction band spontaneously, but it is also possible to apply a potential close to the original V_{oc} after charging, to see how long it takes to force the electrons out of the conduction band

of the ZnO QDs. This may show the stability of the injected electrons and counter ions under the application of an external electric field. In an experimental measurement, a potential of -1.36 V was applied to the ZnO QDs when the solvent was liquid, then the temperature was lowered and at the desired temperature the potential was changed to -0.36 V and the current was recorded. At 60 °C (when succinonitrile is liquid) it takes around 1 second to discharge the doped semiconductor layer, while at -30 °C it takes about 1000s. At -75 °C the electrolyte cations are immobilized by the frozen solvent and there was no noticeable decay in the charge carrier density of the doped semiconductor layer after several days.

Fig. 4B – example 2: immobilization of ions at the same temperature in different electrolyte solutions comprising different solvents. Doped semiconductor layers were obtained as described in example 1, except that the electrolyte solution comprised different solvents. Fig. 4B depicts Fermi-level stability measurements for ZnO QD layers with LiClO₄ in acetonitrile (C₁), ethylene carbonate (C₂), dimethyl sulfone (C₃), succinonitrile (C₄) and PEG 6000 (C₅). The compounds may be known to have the following melting points: acetonitrile: -45 °C, ethylene carbonate: 37 °C, succinonitrile 57 °C, PEG 6000: 56-63 °C (depending on chain length), and dimethyl sulfone: 109 °C. The measurements were performed on an ITO (indium tin oxide) electrode at room temperature. After 170 minutes, the potential of the ZnO QD layer in PEG 6000 has changed from -1.30 V to -1.273 V while it only takes 11 seconds for a ZnO QD layer to reach this potential in acetonitrile. Therefore, the measured electron stability is three orders of magnitude higher in PEG 6000 compared to acetonitrile. It may be observed that PEG 6000 has a lower melting point than dimethyl sulfone (56-63 °C vs. 109 °C) but shows better electron stability at the same temperature. Without being bound by theory, the inventors hypothesize that the better stability in PEG 6000 may be caused by its high viscosity, resulting in slower diffusion of impurities, or by a lower impurity concentration.

Fig. 4C – example 3: immobilization of different ions in a matrix forming material. ZnO QD layers were prepared by drop-casting on indium tin oxide (ITO) coated glass substrates and subsequent annealing at 60 °C for 1 hour in open-air. The electrochemical measurements were performed using a three-electrode system. The QD layer arranged on a working electrode was immersed in an electrolyte solution. The electrolyte solution contained a 5:3 ratio of matrix forming material to solvent, wherein the matrix forming material comprised di(ethylene) glycol dimethacrylate (also: “DEGMA”), and wherein the solvent comprised acetonitrile. A Pt wire electrode was used as counter electrode and an Ag wire was

used as pseudo reference. A potential difference of -1.0 V was imposed between the working electrode and the reference electrode. Measurements took place with a potentiostat configured inside a nitrogen-filled glovebox to minimize the exposure to impurities such as O₂ and H₂O. Three different sets of ions are used for example 3: a first set of ions comprising Li⁺ and ClO₄⁻, (ii) a second set of ions comprising tetrabutylammonium⁺ and hexafluorophosphate⁻, and (iii) a third set of ions comprising 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium⁺ (also: "ATMA") and I⁻. In particular, ATMA is an ionic monomer suitable to (covalently) bind DEGMA during hardening in the immobilization stage.

Line M₁ in Fig. 4C depicts the electron stability (in V) of the layer over time (in seconds) with the third set of ions (comprising 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium⁺ and I⁻), without the layer having been exposed to an immobilization stage (M₁).

M₂-M₄ depict the electron stability (in V) of the layer over time (in seconds) with the three different sets of ions, wherein the layer was exposed to radiation comprising a wavelength of 400 nm suitable for the polymerization and cross-linking of DEGMA: line M₂: the first set of ions (Li⁺ and ClO₄⁻), line M₃: the second set of ions (comprising tetrabutylammonium⁺ and hexafluorophosphate⁻), line M₄: the third set of ions (comprising 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium⁺ and I⁻). Clearly, the immobilization stage improves the electron stability of the layer 100 (M₄ vs. M₁). Without being bound by theory, the results depicted in Fig. 4C further suggest that (i) larger ions may result in a better electron stability (M₃ vs. M₂), and (ii) an ionic monomer suitable for (covalently) binding the matrix forming material during hardening may result in a better electron stability.

Hence, in embodiments, the matrix forming material may comprise 2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethyl 2-methylprop-2-enoate, and the ionic monomer may comprise 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium.

Fig. 4D-H – example 4: open circuit measurements with doped semiconductor materials comprising different semiconductor materials. Fig. 4D-H depict measurements obtained with the method as described for Fig. 4B with different semiconductor materials: CdSe quantum dots (Fig. 4D), CdSe/CdS quantum dots (Fig. 4E), the organic polymer (system) P3DT (Fig. 4F), the fullerene (system) PCBM (Fig. 4G) (in acetonitrile (C1), succinonitrile (C4) and PEG 6000 (C5)), and the fullerene (system) C60 (Fig. 4H) (in succinonitrile (C4) and PEG 6000 (C5)).

Fig. 5A-D schematically depict experimental measurements of examples of electrochemically doped semiconductor layers provided by the method according to the

invention. The method for providing the doped semiconductor layer as well as the subsequent electrochemical measurements were performed in a nitrogen-filled glovebox.

Fig. 5A – example 5: open circuit voltage measurements with doped semiconductor layers provided from the four different matrix forming materials DEGMA, EGMA, TEGA and PEG550MA. Each of the matrix forming materials was mixed with a 0.1M solution of ATMA-Cl in formamide in a 5:3 ratio of matrix forming material to formamide and with 0.1 mg/ml of photo initiator and with ZnO nanocrystals and was polymerized for 90 minutes. The lines correspond to linear fit of the measurements for DEGMA (L₁, n=2), EGMA (L₂, n=1), TEGA (L₃, n=4), and PEG550MA (L₄, n=9). The measurements were started at -0.9 V vs a silver-wire pseudo-reference electrode, which has a potential of -4.79 V vs vacuum. The open-circuit potential before electrochemical doping was 0 V vs Ag for all four experiments.

As is clear from fig. 5A, the doped semiconductor layers are stable for hours after doping, especially for the doped semiconductor layers provided from EGMA and DEGMA, especially DEGMA.

Fig. 5B – example 6: conductance (S) versus time in days measurements (L₅) of an embodiment of a doped semiconductor layer, wherein the semiconductor material comprises PbS nanocrystals. The electrolyte solution contains [2-(Acryloyloxy)ethyl]trimethylammonium chloride as polymerizable salt, Di(ethylene glycol)dimethacrylate as matrix forming material, 4,4'-bis(diethylamino)benzophenone as photoinitiator and formamide as solvent. Fig. 5B shows that the doped semiconductor layer is essentially stable for three weeks. The results are similar to those obtained for ZnO nanocrystals and demonstrate that the method of the invention is general and is applicable to a wide range of semiconductor materials.

Fig. 5C – example 7: stability measurements with different potential values selected for the electrochemical charge injection. The selected potential values for the electrochemical charge injection are about 0.9 V (L₆), 0.7 V (L₇), 0.5 V (L₈). The depicted results correspond to ZnO nanocrystals semiconductor material, formamide as solvent, DEGMA as matrix forming material, and 4,4'-bis(diethylamino)benzophenone as photo initiator. Both formamide and DEGMA were vacuum degassed for 3 hours under rigorous stirring before use and were stored in a glove box. The ZnO nanocrystal film was immersed in an electrochemical cell containing 0.1 M ATMA-Cl electrolyte solution in a solvent mixture of FA:DEGMA (40% v/v) together with a Ag wire as pseudoreference electrode and

Pt wire as counter electrode. Hence, embodiments of the method of the invention may provide stably doped semiconductor layers with the ability to tune the doping density.

Fig. 5D – example 8: conductance measurements (L_9) for a ZnO nanocrystal film in 0.1 M LiClO₄ cyanoacetoamide at room temperature. The doped semiconductor layer was electrochemically doped at a temperature above the solvent melting point T_{ms} of cyanoacetoamide (~120 °C) and was immobilized by providing a temperature below the solvent melting point T_{ms} of cyanoacetoamide. For about the first 20 hours no decrease in the conductance was observed. The term “plurality” refers to two or more. Furthermore, the terms “a plurality of” and “a number of” may be used interchangeably.

The terms “substantially” or “essentially” herein, and similar terms, will be understood by the person skilled in the art. The terms “substantially” or “essentially” may also include embodiments with “entirely”, “completely”, “all”, etc. Hence, in embodiments the adjective substantially or essentially may also be removed. Where applicable, the term “substantially” or the term “essentially” may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. Moreover, the terms “about” and “approximately” may also relate to 90% or higher, such as 95% or higher, especially 99% or higher, even more especially 99.5% or higher, including 100%. For numerical values it is to be understood that the terms “substantially”, “essentially”, “about”, and “approximately” may also relate to the range of 90% - 110%, such as 95%-105%, especially 99%-101% of the values(s) it refers to.

The term “comprise” includes also embodiments wherein the term “comprises” means “consists of”.

The term “and/or” especially relates to one or more of the items mentioned before and after “and/or”. For instance, a phrase “item 1 and/or item 2” and similar phrases may relate to one or more of item 1 and item 2. The term “comprising” may in an embodiment refer to “consisting of” but may in another embodiment also refer to “containing at least the defined species and optionally one or more other species”.

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 capable of operation in other sequences than described or illustrated herein.

The devices, apparatus, or systems may herein amongst others be described during operation. As will be clear to the person skilled in the art, the invention is not limited to methods of operation, or devices, apparatus, or systems in operation.

It should be noted that the above-mentioned embodiments illustrate rather than
5 limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims.

In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim.

Use of the verb "to comprise" and its conjugations does not exclude the
10 presence of elements or steps other than those stated in a claim. Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", "include", "including", "contain", "containing" and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

15 The article "a" or "an" preceding an element does not exclude the presence of a plurality of such elements.

The invention may be implemented by means of hardware comprising several distinct elements, and by means of a suitably programmed computer. In a device claim, or an apparatus claim, or a system claim, enumerating several means, several of these means may
20 be embodied by one and the same item of hardware. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage.

The invention also provides a control system that may control the device, apparatus, or system, or that may execute the herein described method or process. Yet further,
25 the invention also provides a computer program product, when running on a computer which is functionally coupled to or comprised by the device, apparatus, or system, controls one or more controllable elements of such device, apparatus, or system.

The invention further applies to a device, apparatus, or system comprising one or more of the characterizing features described in the description and/or shown in the
30 attached drawings. The invention further pertains to a method or process comprising one or more of the characterizing features described in the description and/or shown in the attached drawings. Moreover, if a method or an embodiment of the method is described being executed in a device, apparatus, or system, it will be understood that the device, apparatus, or system

is suitable for or configured for (executing) the method or the embodiment of the method respectively.

The various aspects discussed in this patent can be combined in order to provide additional advantages. Further, the person skilled in the art will understand that
5 embodiments can be combined, and that also more than two embodiments can be combined.
Furthermore, some of the features can form the basis for one or more divisional applications.

CLAIMS:

- 5 1. A method (10) for providing a doped semiconductor layer (150), wherein the method (10) comprises:
- a charge injection stage (12) comprising imposing a potential difference between a layer (100) arranged on an electrically conductive substrate (107) and a reference electrode (128), wherein the layer (100) comprises a semiconductor material (101), and
 - 10 wherein the layer (100) is in fluid contact with an electrolyte solution (110) comprising ions (112), wherein the layer (100) is porous to the electrolyte solution (110), thereby introducing ions (112) into the layer (100); and
 - an immobilization stage comprising immobilizing the ions (112) in the layer (100); thereby providing the doped semiconductor layer (150);
- 15 wherein:
- the electrolyte solution (110) comprises a cross-linkable and/or polymerizable matrix forming material configured to harden when exposed to radiation comprising a first wavelength, wherein the immobilization stage comprises hardening of the matrix forming material via one or more
 - 20 of cross-linking and polymerization. wherein the immobilization stage comprises providing radiation comprising the first wavelength to a first part of the layer (100); or
 - the electrolyte solution comprises a solvent having a solvent melting point T_{ms} , wherein the charge injection stage comprises imposing a temperature at or above the solvent melting point T_{ms} , and wherein the immobilization stage comprises imposing a temperature below the solvent melting point T_{ms} ; or
 - 25 - wherein the charge injection stage comprises imposing a first pressure and the immobilization stage comprises imposing a second pressure, wherein
 - 30 the first pressure is selected such that the electrolyte solution is at least partially liquid, and wherein the second pressure is selected such that the electrolyte solution solidifies.

2. The method (10) according to claim 1, wherein the electrolyte solution (110) comprises the cross-linkable and/or polymerizable matrix forming material, wherein the immobilization stage comprises hardening of the matrix forming material via one or more of cross-linking and polymerization, and wherein the matrix forming material is configured to
5 harden when exposed to radiation comprising a first wavelength, wherein the immobilization stage comprises providing radiation comprising the first wavelength to a first part of the layer (100).
3. The method (10) according to claim 3, wherein the method comprises:
10 - a second charge injection stage comprising imposing a second potential difference between the layer (100) and the reference electrode (128), wherein the second potential difference is different from the potential difference, thereby introducing (second) ions into the layer (100); and
- a second immobilization stage comprising providing radiation comprising the
15 first wavelength to a second part of the layer (100), wherein the second part is at least partially non-overlapping with the first part.
4. The method (10) according to claim 3, wherein the potential difference and the second potential difference are of opposite sign.
20
5. The method (10) according to any one of the preceding claims 2-4, wherein the ions (112) comprise ionic monomers configured to bind to the matrix forming material during hardening.
- 25 6. The method (10) according to claim 5, wherein the matrix forming material comprises 2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethyl 2-methylprop-2-enoate, and wherein the ionic monomer comprises 2-(acryloyloxy)-N,N,N-trimethylethan-1-ammonium.
7. The method (10) according to any one of the preceding claims, wherein the
30 method (10) further comprises:
- a second layer application stage comprising arranging a second layer on the layer (100); and

- a second layer charge injection stage comprising imposing a second layer potential difference between the second layer and the reference electrode (128), thereby introducing second layer ions into the second layer; and
- a second layer immobilization stage comprising immobilizing the second layer ions in the second layer.

8. The method (10) according to claim 7, wherein the potential difference and the second layer potential difference are of opposite sign.

9. The method (10) according to any one of the preceding claims 1-8, wherein the electrolyte solution (110) further comprises a photo initiator, wherein the photo initiator comprises 4,4'-bis(diethylamino)benzophenone.

10. The method (10) according to any one of the preceding claims, the method (10) comprising executing the charge injection stage (12) and the immobilization stage in a controlled atmosphere having an H₂O concentration ≤ 1000 ppm and an O₂ concentration ≤ 1000 ppm.

11. The method (10) according to any one of the preceding claims, wherein the semiconductor material (101) is selected from the group comprising semiconductive polymers, fullerenes, semiconductor nanomaterials such as quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic frameworks, semiconductive graphene, and 2D layered semiconductors such as transition metal dichalcogenides.

12. The method (10) according to any one of the preceding claims, wherein the electrolyte solution (110) comprises a solvent having a solvent melting point T_{ms} , wherein the charge injection stage (12) comprises imposing a temperature at or above the solvent melting point T_{ms} , and wherein the immobilization stage comprises imposing a temperature below the solvent melting point T_{ms} , wherein the solvent melting point $T_{ms} \geq 40$ °C.

13. The method (10) according to claim 12, wherein the solvent comprises a solvent selected from the group comprising ethylene carbonate, succinonitrile, fumaronitrile,

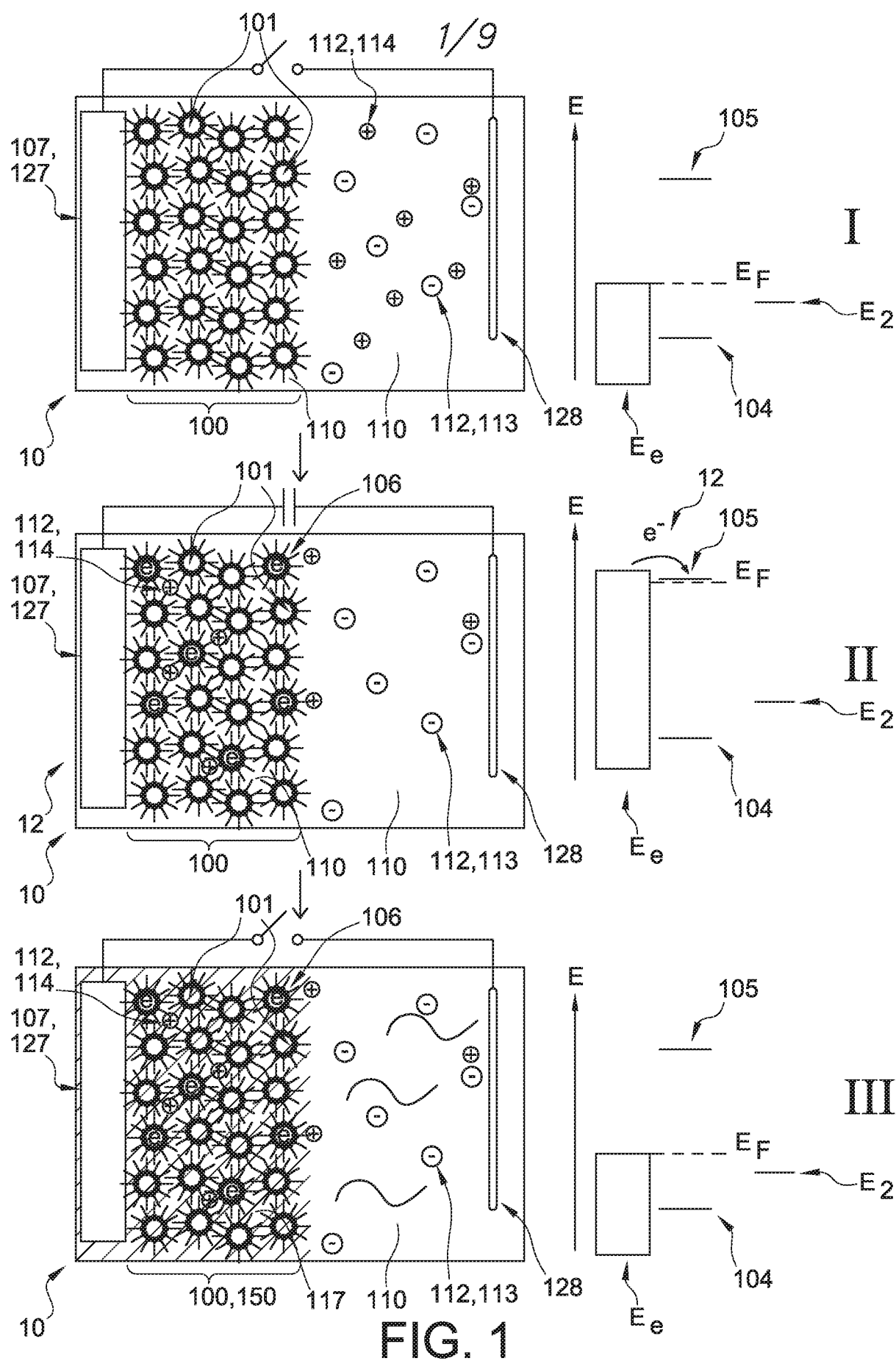
2,2,3,3-tetramethylsuccinonitrile, 1,4-dicyano-2-butene, polyethylene glycol, and dimethyl sulfone.

14. A doped semiconductor layer (150), wherein the doped semiconductor layer
5 (150) comprises a semiconductor material (101) selected from the group comprising
semiconductive polymers, semiconductive fullerenes, semiconductor nanomaterials such as
quantum dots, semiconductive nanowires and nanoplatelets, semiconducting metal organic
frameworks, semiconductive graphene, and 2D layered semiconductors such as transition
10 metal dichalcogenides, wherein the doped semiconductor layer (150) comprises a continuous
phase (117) wherein the semiconductor material (101) is embedded, wherein the continuous
phase (117) comprises one or more of (i) a cross-linked and/or polymerized matrix material,
and (ii) a material having a solvent melting point $T_{ms} \geq 40$ °C, wherein the continuous phase
further comprises one or more ions (112).

15 15. The doped semiconductor layer (150) according to claim 14, obtainable by the
method (10) according to any one of the preceding claims 1-13.

16. The doped semiconductor layer (150) according to any one of the preceding
claims 14-15, wherein the continuous phase (117) comprises cross-linked and/or polymerized
20 matrix material.

17. A semiconductor device comprising the doped semiconductor layer (150)
according to any one of the preceding claims 14-16.



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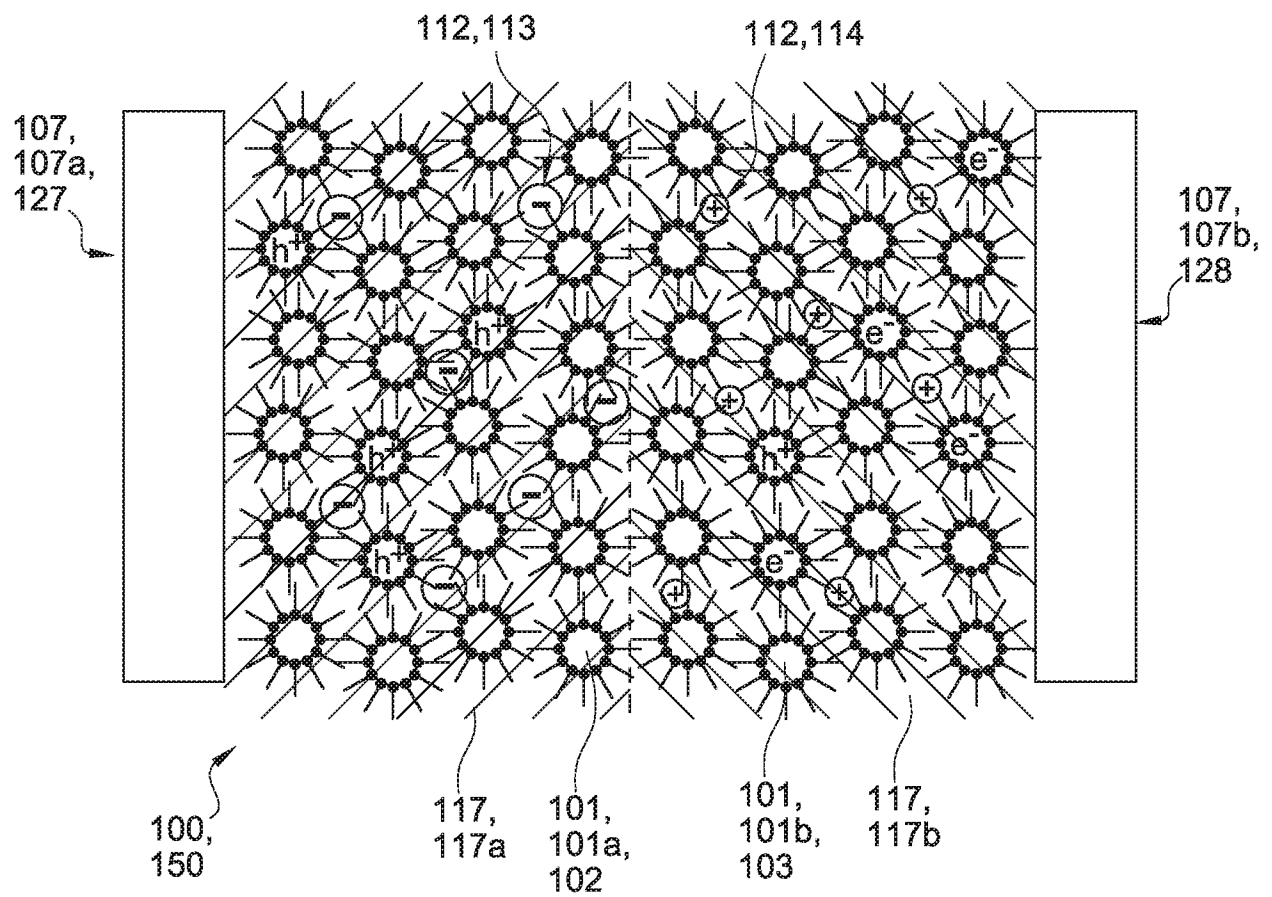


FIG. 2

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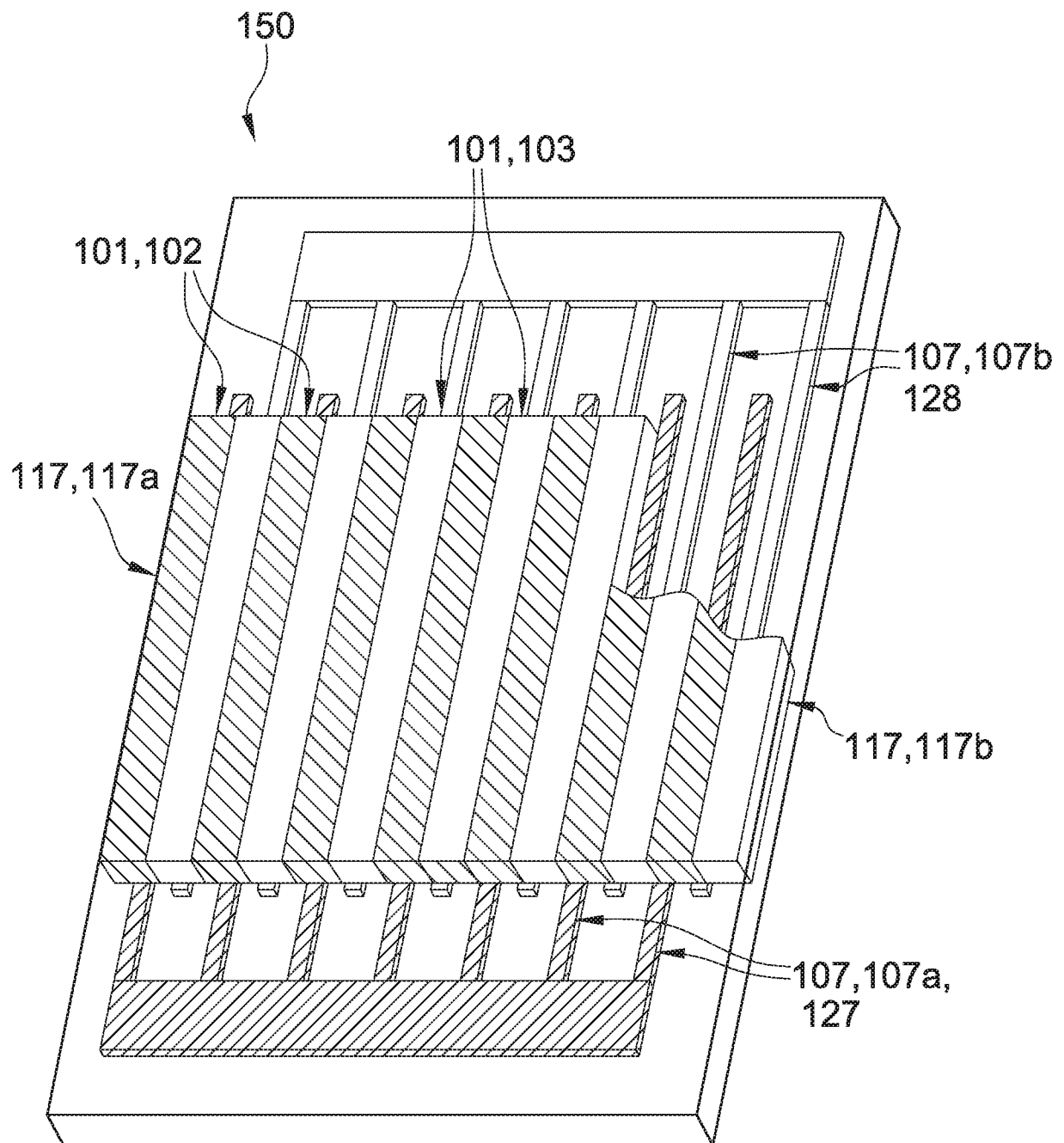


FIG. 3

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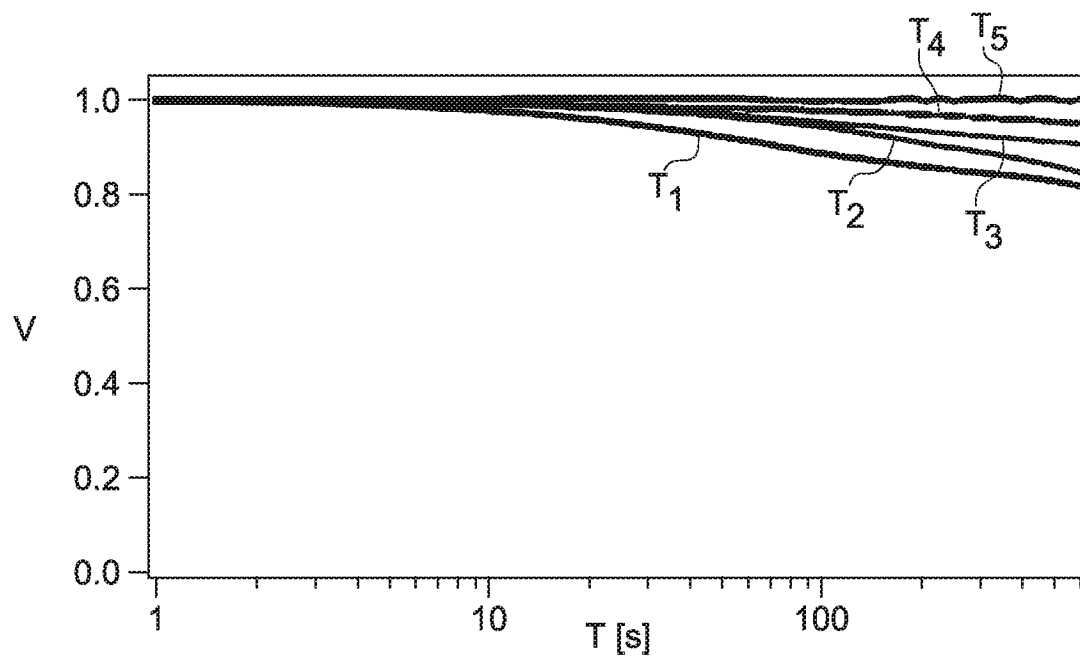


FIG. 4A

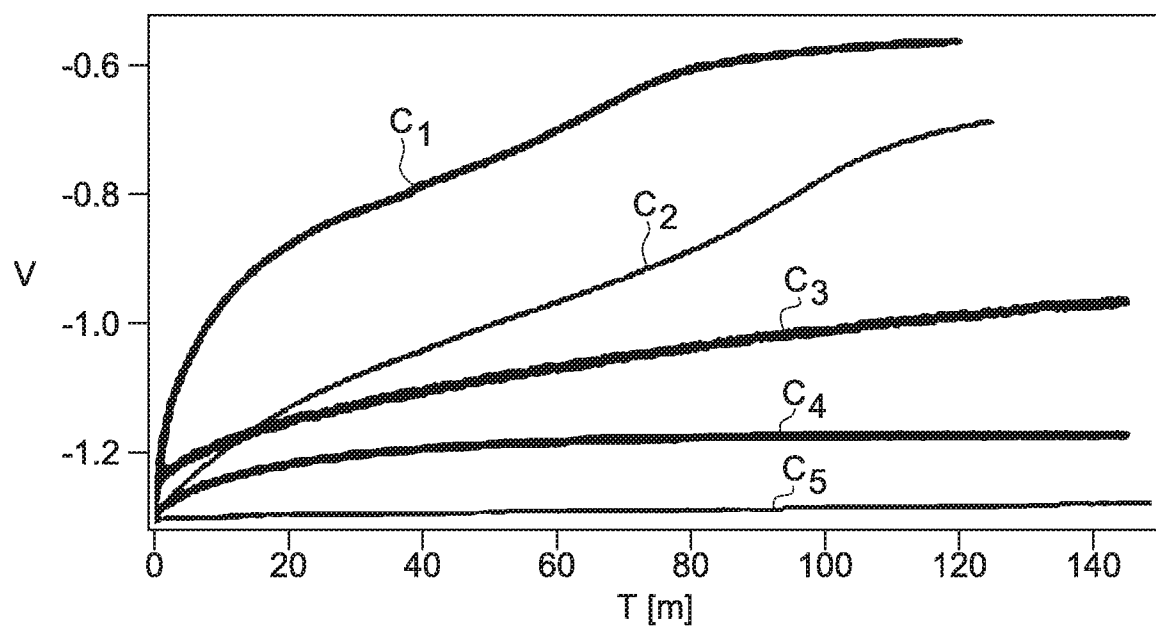


FIG. 4B

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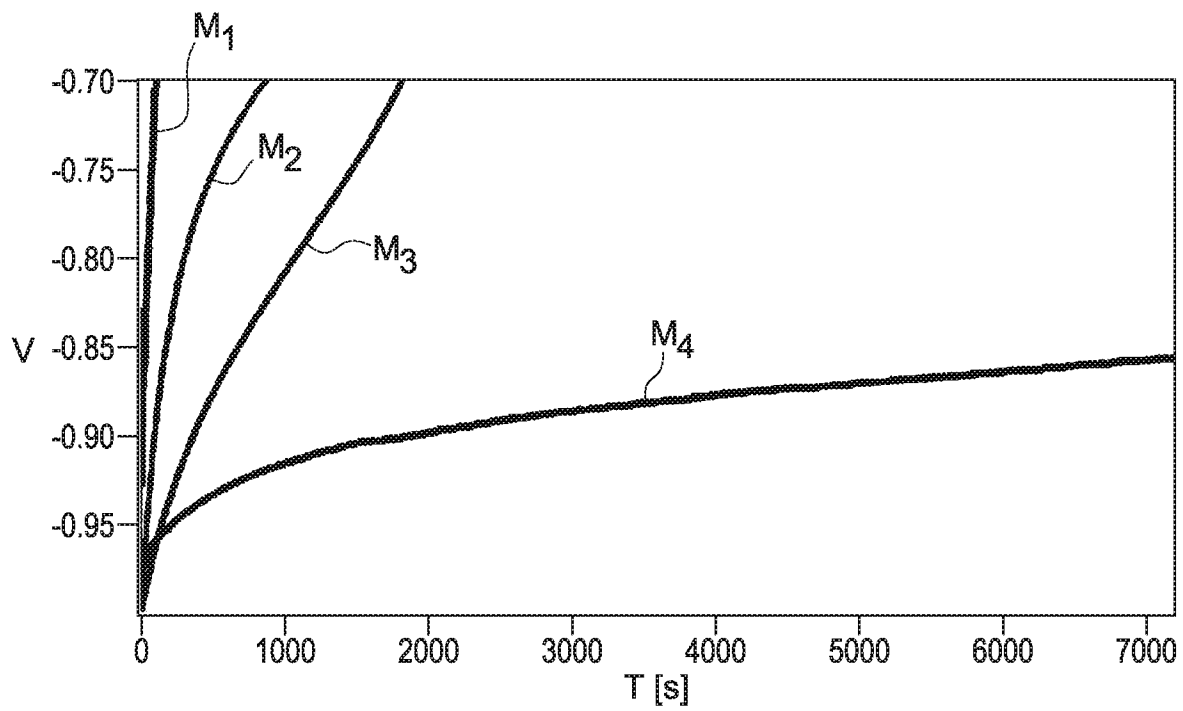


FIG. 4C

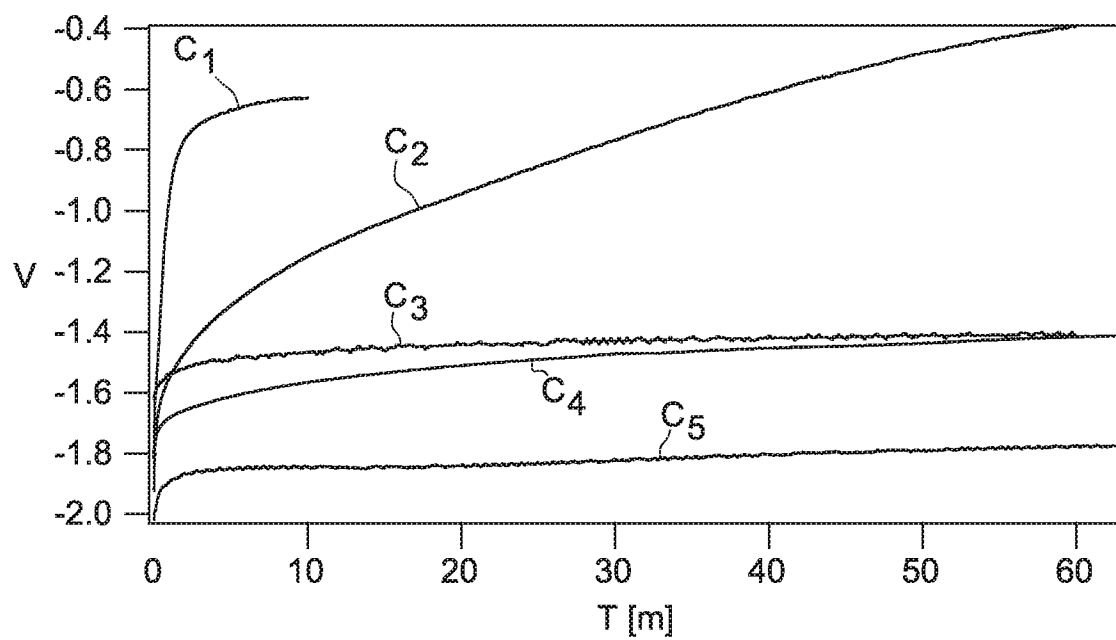


FIG. 4D

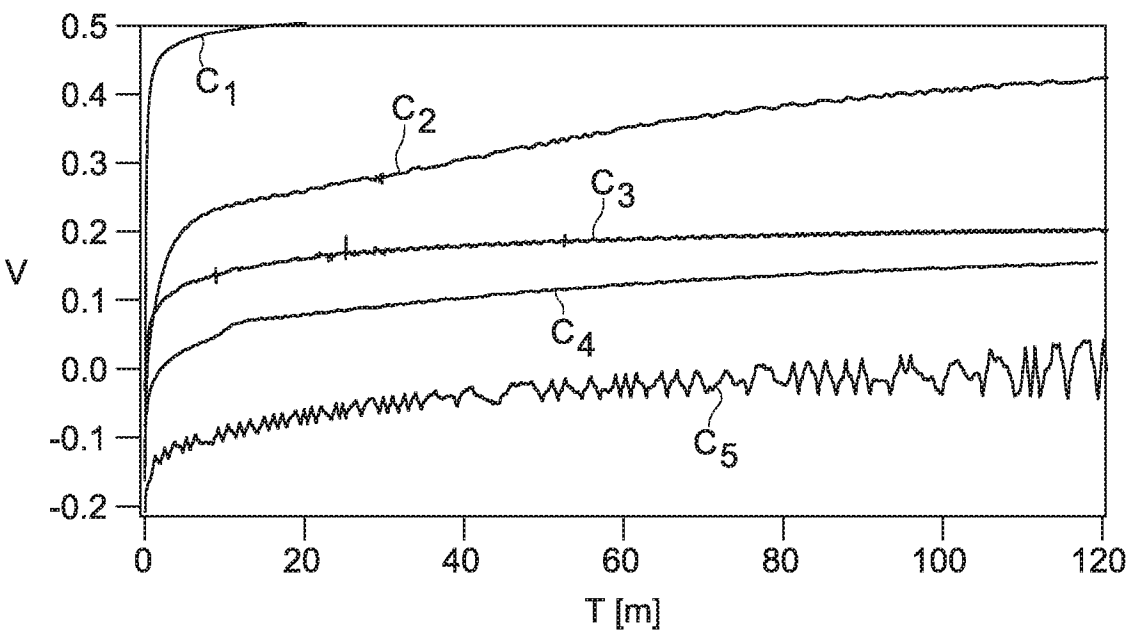


FIG. 4E

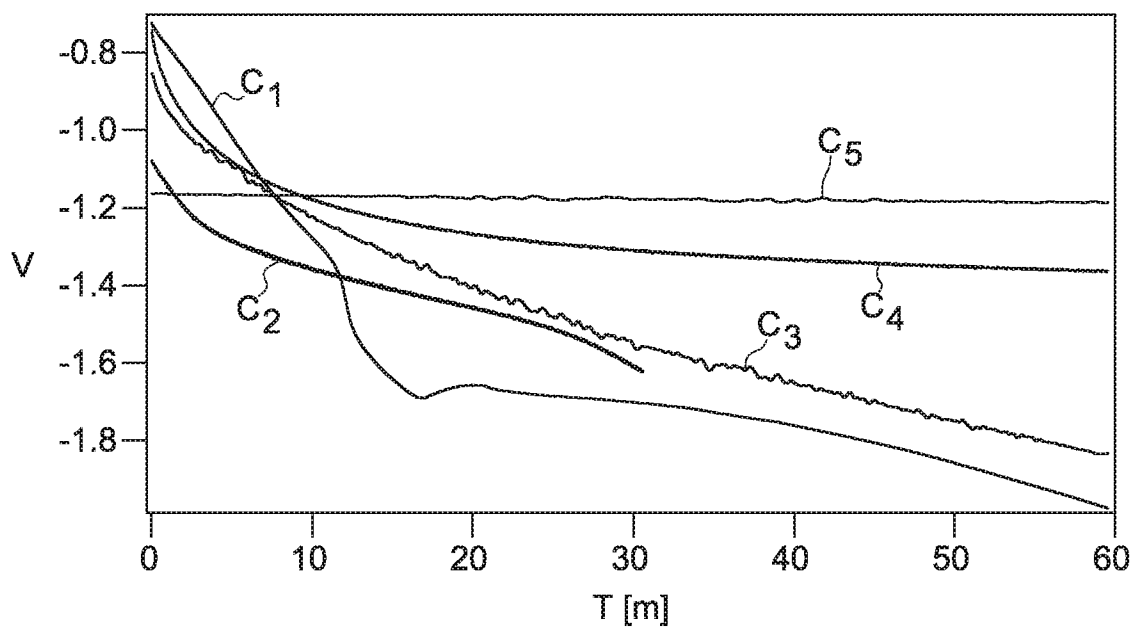


FIG. 4F

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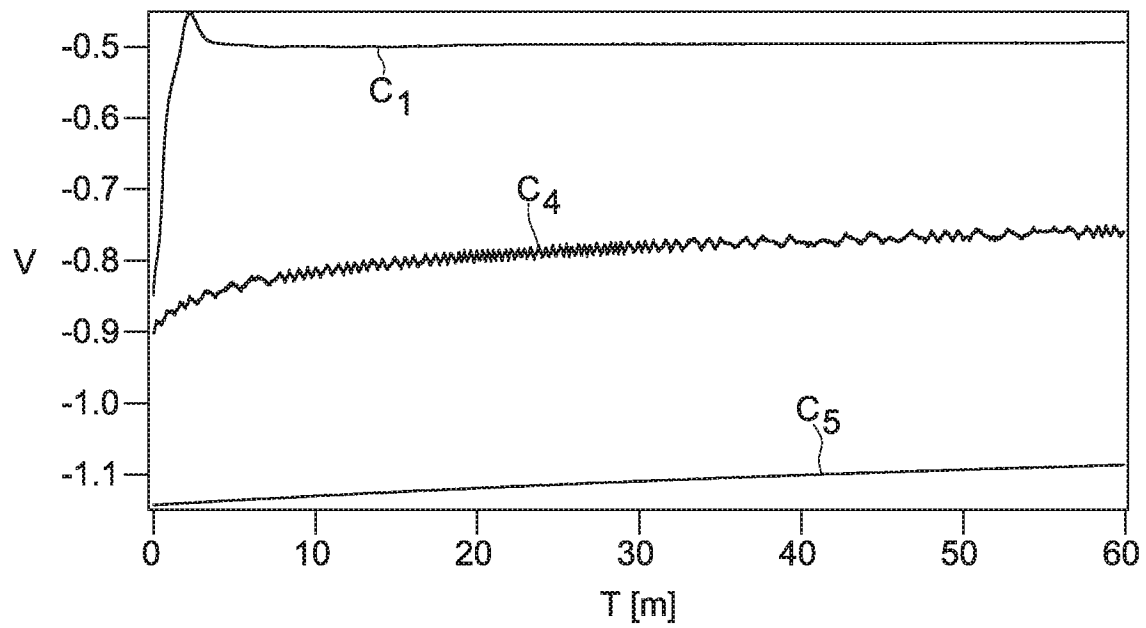


FIG. 4G

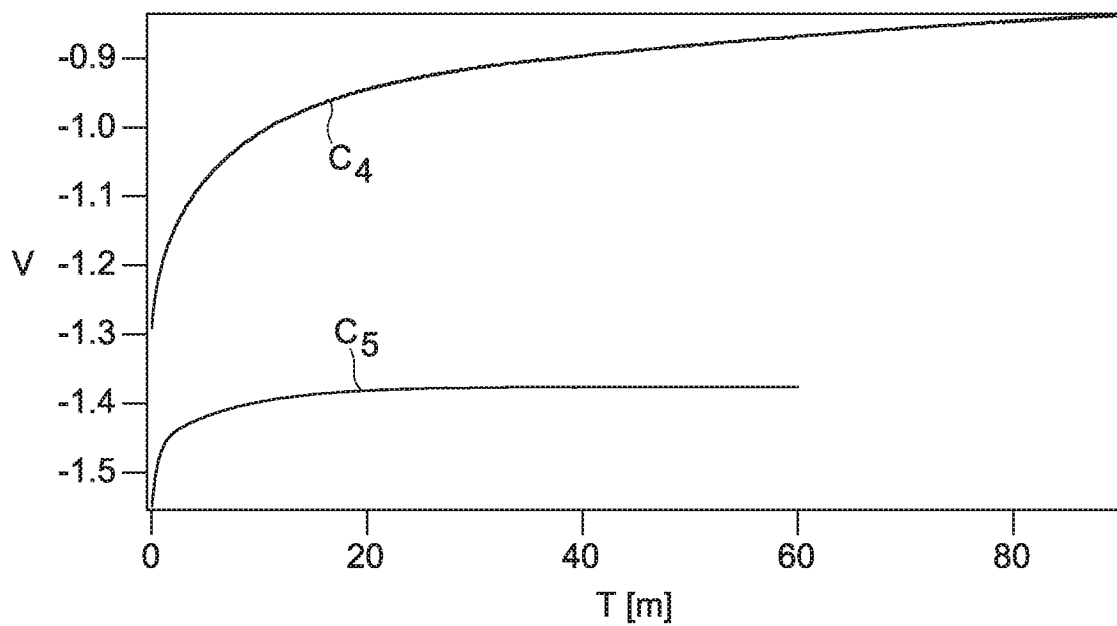


FIG. 4H

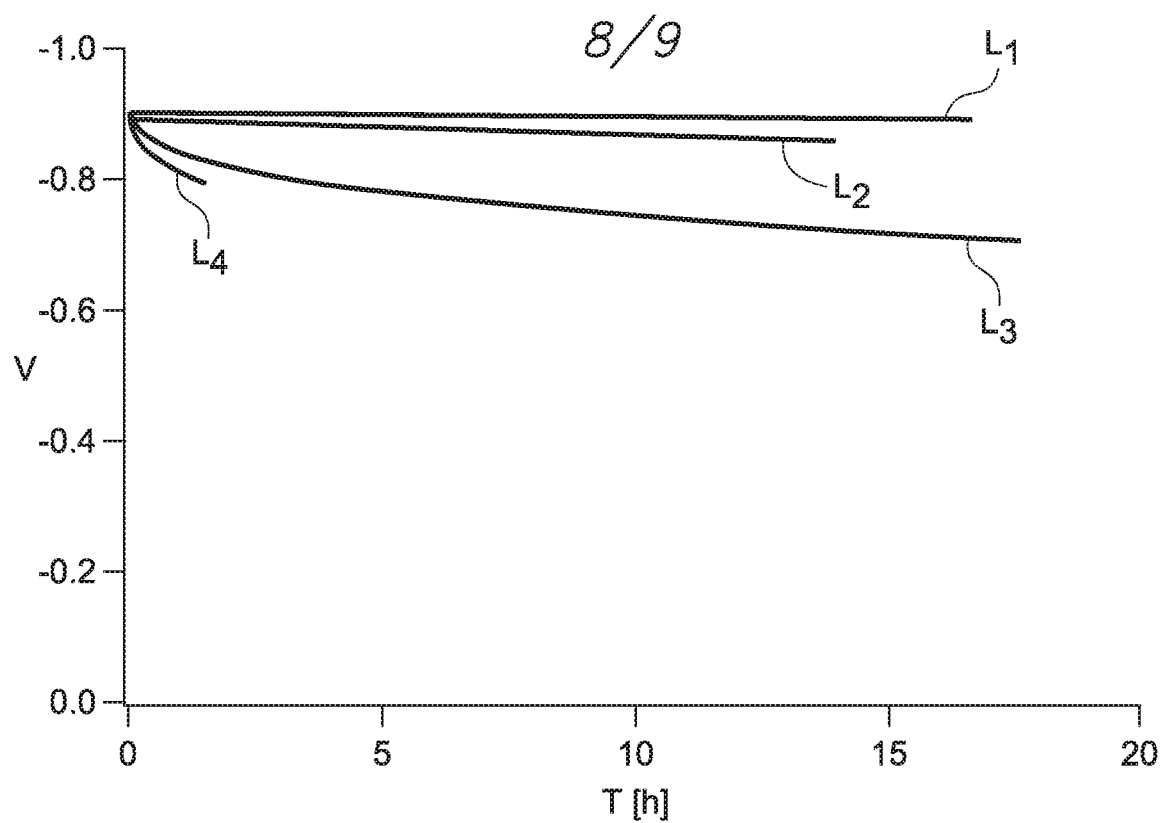


FIG. 5A

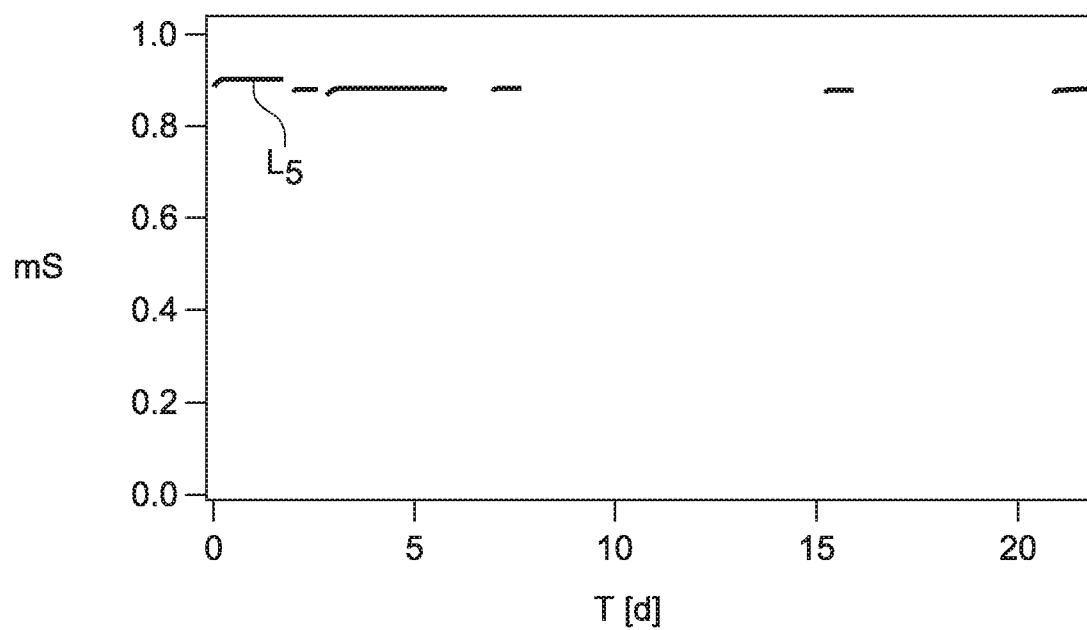


FIG. 5B

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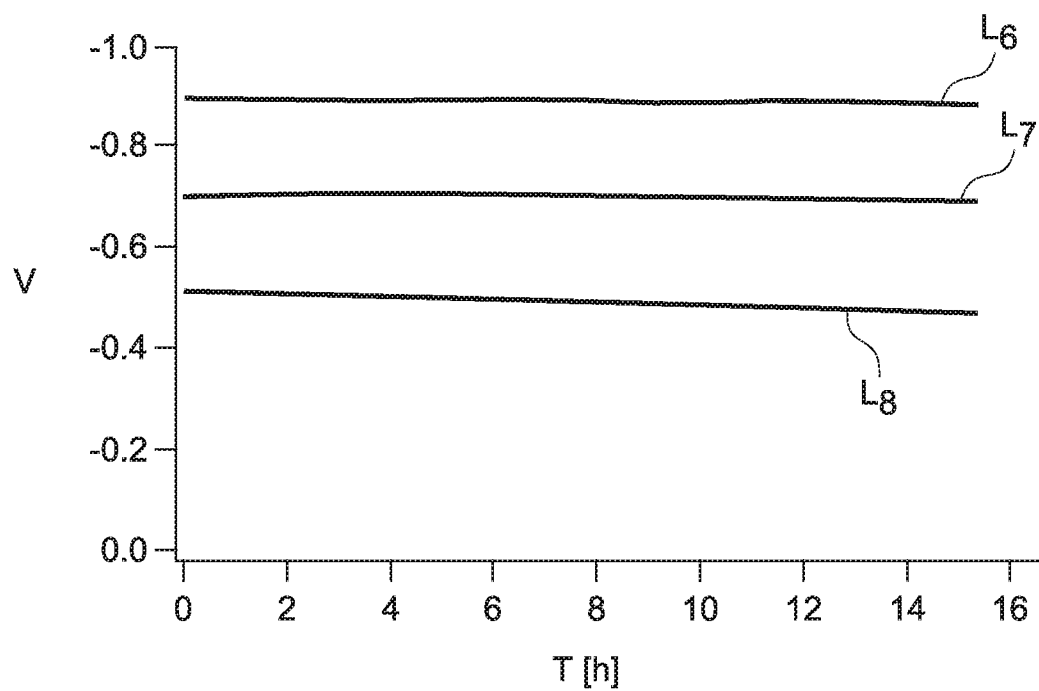


FIG. 5C

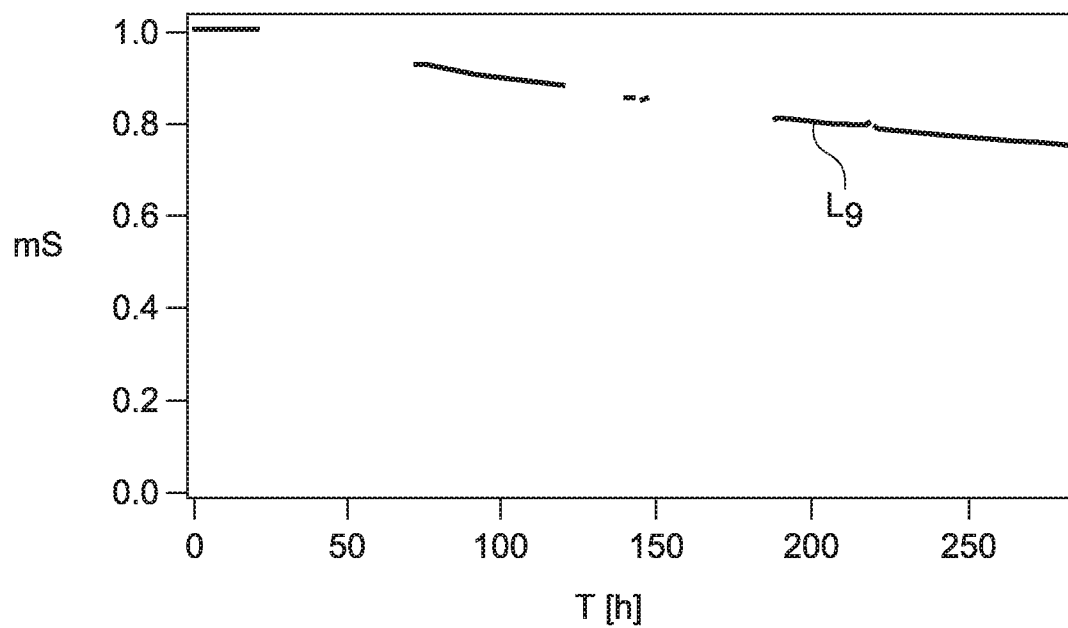


FIG. 5D

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2019/050791

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L51/40 H01L21/388
ADD.

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 practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUNGHO NAM ET AL: "Improved Performance of Polymer:Polymer Solar Cells by Doping Electron-Accepting Polymers with an Organosulfonic Acid", ADVANCED FUNCTIONAL MATERIALS, WILEY - VCH VERLAG GMBH & CO. KGAA, DE, vol. 21, no. 23, 6 December 2011 (2011-12-06), pages 4527-4534, XP001571421, ISSN: 1616-301X, DOI: 10.1002/ADFM.201101215 [retrieved on 2011-09-22]	14-17
A	page 4527 - page 4533; figure 1 ----- -/--	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

27 February 2020

Date of mailing of the international search report

10/03/2020

Name and mailing address of the ISA/

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Authorized officer

Königstein, C

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2019/050791

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/017422 A2 (SIEMENS AG [DE]; MEERHOLZ KLAUS [DE]; BRABEC CHRISTOPH [DE]) 26 February 2004 (2004-02-26) page 3, line 5 - page 8, line 5; claims 1-6; figures 1-3 -----	1-17
A	JONATHAN D. YUEN, ET AL.: "Electrochemical Doping in Electrolyte-Gated Polymer Transistors", J. AM. CHEM. SOC., vol. 129, 30 October 2007 (2007-10-30), pages 14367-14371, XP002793542, page 14367 - page 14371 -----	1-17
A	FR 2 759 495 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 14 August 1998 (1998-08-14) abstract; claims 1-17; figures 4-6 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2019/050791

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004017422 A2	26-02-2004	DE 10235012 A1 WO 2004017422 A2	04-03-2004 26-02-2004
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