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(54) **Method for manufacturing an electronic device by electrodeposition from an ionic liquid**

(57) Method for manufacturing an electronic device, the method comprising

- providing an electronic intermediate product, said intermediate product having an electronic conducting layer and
- forming an metallic or metalloid layer on an outer surface the electronic conducting layer by electrodeposition using a plating liquid comprising an ionic liquid and metal ions or metalloid ions, wherein

during electrodeposition the electronic conducting layer of the intermediate product on which electrodeposition takes place is connected to an electrical power source and the electronic conducting layer on which electrodeposition takes place provides a cathode for the elec-

trodeposition, and wherein the metallic or metalloid layer is formed gradually in the plane parallel to the surface of the electronic conducting layer on which electrodeposition takes place, which gradual forming comprises starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively remote from the connection to the power source.

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Description

[0001] The invention relates to a method for manufacturing an electronic device, wherein a metallic or metalloid layer is deposited by electrodeposition on an electronic conducting layer. Further, the invention related to an electronic device.

[0002] For electronic devices, in particular organic electronic devices, protection against oxygen and/or water (moisture) is very important. Usually organic devices are protected by encapsulation using a metal or glass sheet as a substrate (on which the functional layers are applied) and a metal or glass lid. However, disadvantages of such design include limitations, in particular with respect to the geometry (as the minimum thickness will be relatively high) and limited flexibility of the device, whereas for actuators and/or opto-electronic devices a low thickness and/or a high flexibility can be desirable. For protection against oxygen and/or water, the device may be sealed with a protective cap that is substantially impermeable to oxygen and/or water. Such cap adds to the volume of the device. Further, it is a challenge to adhere the cap sufficiently well, as adhesives suitable for gluing the cap may be permeable to water and /or oxygen. In particular, with respect to optoelectronics, reduced transparency may be a drawback of using classical encapsulation.

[0003] It has been proposed to provide an article, in particular an opto-electronic device, with a thin film barrier coating of an inorganic material in order to provide protection against oxygen and/or water, whilst maintaining flexibility.

[0004] For instance inorganic barrier coatings, such as a silicon carbide, silicon nitride or silicon oxide coating, can be applied in a sufficiently thin layer, to allow the device to remain sufficiently flexible. However, layers of such barrier material generally have defects in the layer structure, known as pinholes. These pinholes may give rise to increased permeability for oxygen and/or water, the presence of which may have a deteriorating effect on the functioning of the material covered by the coating. In particular, pinholes are an important cause of the occurrence of black spots in the device, leading to poorer quality of the device, e.g. reduced light intensity in case of a LED, or loss of image resolution in case the device is a device to display an image. Reducing pinholes is in particular a challenge for organic (opto-) electronic devices.

[0005] WO 2008/127110 relates to a method for manufacturing an article comprising a barrier layer, in particular an oxygen and/or water barrier layer, the method wherein a metallic or metalloid layer is electrodeposited on a substrate comprising an organic electro-active material, using a plating liquid comprising an ionic liquid. Such method is effective in considerably reducing pinholes.

[0006] The inventors have found that a metallic or metalloid layer electrodeposited from an ionic liquid on an electronic device substrate may have a non-uniform thickness. In particular they found a higher thickness near the connection to the power source for the electrodeposition (usually at or near an edge of the substrate) than remote from the connection to the power source. The inventors realised that this is undesired because such inhomogeneity in thickness is detrimental to the functioning of the electronic device, even to the extent that it will not function at all, at least in some circumstances. In particular, it is contemplated that this may be due to mechanical stress in the inhomogeneous layer. Further, for opto-electronic devices, the electroluminescent properties may be adversely affected by a inhomogeneity in thickness. In particular, the intensity of light generated in the centre of an electroluminescent layer may be less than close to the sides of the layer

[0007] It is an object of the present invention to provide a novel method which can serve as an alternative to known methodology for the manufacture of an electronic device, in particular a method that addresses one or more of the above mentioned disadvantages of known methodology.

[0008] It is further an object to provide a novel electronic device, in particular a novel organic electronic device, which is improved in one or more of the aspects addressed above.

[0009] One or more further objects will be apparent from the remainder of the description.

[0010] The inventors have found that one or more of the objects are met by depositing the metallic or metalloid layer on a substrate for an electronic device in a specific way, namely gradually (sequentially in time) rather than by subjecting the whole area that is to be provided with the layer at once. Accordingly, the invention relates to a method for manufacturing an electronic device, the method comprising

- providing an electronic intermediate product, said intermediate product having a an electronic conducting layer and
- forming an metallic or metalloid layer on an outer surface the electronic conducting layer by electrodeposition using a plating liquid comprising an ionic liquid and metal ions or metalloid ions, wherein

during electrodeposition the electronic conducting layer of the intermediate product on which electrodeposition takes place is connected to an electrical power source and the electronic conducting layer on which electrodeposition takes place provides a cathode for the electrodeposition, and wherein the metallic or metalloid layer is formed gradually in the plane parallel to the surface of the electronic conducting layer on which electrodeposition takes place , which gradual forming comprises starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electronic

[0011] conducting layer on which electrodeposition takes place relatively remote from the connection to the power source.

[0012] In particular, the invention relates to a method for manufacturing an electronic device, the method comprising

- providing an electronic intermediate product, said intermediate product having a first electronic conducting layer (for providing a first electrode of the electronic device, in particular an anode), a second electronic conducting layer (for providing a second electrode of the electronic device, in particular a cathode), and an electro-active material at least partially situated between said electronic conducting layers; and
- forming an metallic or metalloid layer on at least part of an outer surface of at least one of the electronic conducting layers by electrodeposition using a plating liquid comprising an ionic liquid and metal ions or metalloid ions, wherein

during electrodeposition the electronic conducting layer of the intermediate product on which electrodeposition takes place is connected to an electrical power source and the electronic conducting layer on which electrodeposition takes place provides a cathode for the electrodeposition, and wherein the metallic or metalloid layer is formed gradually in the plane parallel to the surface of the electronic conducting layer on which electrodeposition takes place, which gradual forming comprises starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively remote from the connection to the power source.

[0013] The electronic conducting layer on which electrodeposition takes place may hereafter be referred to as the 'electrodeposition-cathode'. As will be understood by the skilled person, in the final electronic device the electronic conducting layer that has served as electrodeposition-cathode may either serve as a cathode (as is usually the case if the device is an LED) or as a cathode (as is usually the case if the device is a photovoltaic cell).

[0014] Further, the invention relates to an electronic device obtainable by a method according to the invention.

[0015] By starting the electrodeposition on a part of the surface of the electrodeposition-cathode relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electrodeposition-cathode layer relatively remote from the connection to the power source it is possible to provide a deposited layer, in particular a barrier layer against water and/or oxygen with a highly uniform layer thickness.

[0016] A method of the invention is in particular suitable for electrodepositing a metallic or metalloid layer that (optionally after subjecting the layer to oxidation) has adequate barrier function against a gas or a liquid, in particular water (liquid or vaporous) or oxygen, i.e. the electrodeposited layer may in particular serve as a barrier layer.

[0017] Further, it is an advantage of an embodiment of the invention that the process time for electrodepositing a layer having a specified minimal thickness (also in parts remote from the connection to the power source, such as in the middle of the substrate if the power source is provided at the edges) is decreased. In particular, it is envisaged that the deposition rate of the layer may be increased by up to about 10 times, i.e. a target thickness may be reached up to about 10 times faster.

[0018] In particular, the invention allows a deposition rate of the metal or metalloid to be deposited of at least 0.1 μm layer thickness per min, in particular of at least 0.5 μm layer thickness per min, more in particular of at least 1.0 μm layer thickness per min. For instance, in a specific embodiment, a 10 μm thick (aluminium) layer is deposited within 10 min. A method according to the invention is particularly suitable to make a flexible electronic device, in particular a flexible organic (opto-)electronic device. A device is in particular considered flexible if it can be rolled onto a roll having a diameter of 20 cm or less, in particular a roll of 10-20 cm. It is possible to carry out a method according to the invention as a roll-to-roll process or as a sheet-to-sheet process. On a roll or sheet a plurality of intermediate products for providing a plurality of electronic device are usually present. A sheet may comprise a plurality of (intermediate products for) electronic devices, e.g. as illustrated in Figure 3. Herein all devices are electrically connected to the power source. This can be accomplished in a manner known *per se*.

[0019] In particular for an (opto-)electronic organic device the invention is particularly suitable to provide a device with a low occurrence of black spots, in particular compared to a device wherein the metallic or metalloid layer has been deposited by vapour deposition. The tendency for black spot formation (over time) can for instance be carried out by evaluating the number of black spots immediately after manufacture, storing the device at ambient atmosphere (20°C and 50% Relative Humidity) for a specified amount of time, e.g. 1 day, 1 week or 1 month, and evaluating the number of black spots again. Evaluation can be performed visually, with the naked eye or under a light microscope or a scanning electron microscope. Each black spot corresponds usually to a crystal defect in the electrode layer. If the device is a LED, a black spot can be visualised by letting the LED emit light, upon which black spots will show up as parts not emitting light. In particular, the present invention is suitable to provide an organic (opto-)electronic device comprising an metallic, metalloid, metal oxide or metalloid oxide layer (on the first or second electronic conducting layer) with a highly homogenous and/or smooth surface. In particular, the said layer may be essentially free of crystal defects in the surface. A method according to the invention is further advantageous in that heat development in the layer that is being

electrodeposited is well controllable in accordance with the invention. In particular it is contemplated that the current through the layer that is deposited is reduced compared to a known method of electrodeposition. Thus, the electrodeposition can take place without the risk detrimentally affecting the properties of the layer to an unacceptable extent, also at a relatively high deposition rate, in particular since the risk of 'burning off' of the layer is reduced.

[0020] A method according to the invention may suitably be carried out at about atmospheric pressure.

[0021] The electrodeposition in accordance with the invention allows a quality check of the layer on which the electrodeposition takes place at an early stage of the process, i.e. it can be established at an early stage whether this layer has satisfactory conducting properties. This advantage applies in particular to roll to roll and sheet to sheet processes.

[0022] The invention is in particular advantageous for electro-depositing a metallic or metalloid layer (for use as a barrier layer, optionally after subjecting the layer to an oxidation treatment) on a relatively thin electrode (cathode or anode), such as an electrode having a thickness of 1 μm or less, in particular of 1-500 nm, more in particular of 10-250 nm, or 50-150 nm. The electrodeposition-cathode may have been provided in a manner known *per se*, e.g. by electrodeposition, electroless deposition, chemical vapour deposition or physical vapour deposition.

[0023] A metallic or metalloid layer that has been electrodeposited on a thin electrode by conventional means, may in particular show considerable inhomogeneity in thickness. This is thought to be due to the relatively high voltage drop over the thin electrode layer. The inventors realised that this can be a reason for a much higher deposition rate at and near the connection(s) of the electrode (cathode) to the power source than remote from the connection, when using a conventional method, thereby causing the inhomogeneity in thickness of the electrodeposited layer.

[0024] The term "or" as used herein means "and/or" unless specified other wise.

[0025] The term "a" or "an" as used herein means "at least one" unless specified other wise.

[0026] When referring to a moiety (e.g. a compound, an ion, an additive etc.) in singular, the plural is meant to be included. Thus, when referring to a specific moiety, e.g. "ion", this means "at least one" of that moiety, e.g. "at least one ion", unless specified otherwise.

[0027] The term 'barrier layer' is used herein for a layer protecting the article from a detrimental effect that may be caused by a gas or liquid to which the article may be exposed, in particular a detrimental effect that would decrease the life-time expectancy of the article. Typically, a barrier layer has a low permeability or is (essentially) impermeable to such gas and/or liquid. In particular, the barrier layer may be a barrier layer against oxygen or water (moisture). With an effective barrier against a specific substance (such as water or oxygen) is in particular meant a barrier with a permeability of 1 $\text{mg}/\text{m}^2\cdot\text{day}$ or less, of 0.1 $\text{mg}/\text{m}^2\cdot\text{day}$ or less, or of 1 $\mu\text{g}/\text{m}^2\cdot\text{day}$ or less. The permeability may be determined as described in US 2006/147346. Thus, a barrier layer in particular is a layer by which life-time expectancy of the article is increased. In a specific embodiment, such detrimental effect is an effect leading to the (excessive) formation and/or growth of black spots in a LED or another optical electronic device (as may be determined with a light microscope or at least in some circumstances with the naked eye).

[0028] The term "electroactive" is used herein for an electrically (semi-) conductive material which is (1) capable of converting a non-electric form of energy into electric energy or *vice versa*, (2) capable of absorbing or emitting light, or (3) capable of changing colour, reflectivity or transmittance.

[0029] Generally, an electroactive material is capable of acting as a (semi-)conductor for electrical energy. In particular an electroactive material in a device of the invention is capable of converting electromagnetic radiation (such as UV, visible light or IR) into electrical energy or converting electrical energy into electromagnetic radiation.

[0030] The term 'ionic liquid' is used for a liquid formed of a salt that is liquid under the process conditions, such as a melt of a salt. An ionic liquid is liquid (above its melting point) in the absence of a solvent, such as water. Thus, an ionic liquid can be free of liquid solvent, and can thus be nonaqueous, which is an advantage since water may adversely affect the electrodeposition or deposited layer of at least some metals or metalloids, for instance aluminium. In general, an ionic liquid used in a method of the invention, has a melting point below 200°C, preferably of 100°C or less, in particular of 50°C or less. It is in particular preferred that the ionic liquid is liquid at about 20 °C or at about 25°C. Such liquid may be referred to as a room temperature liquid salt.

[0031] The design and materials of the intermediate product may be based on electronic devices known *per se*, e.g. as described in WO 2008/127110, in WO 2010/093237 or the prior art cited therein, of which the contents are incorporated herein by reference.

[0032] Figure 4 schematically shows an intermediate product for an LED according to the invention. The electric connection (via 'A' and 'V') between anode and cathode needs not be present during electrodeposition.

[0033] Figure 1 schematically shows an (organic) electronic device obtainable in a method according to the invention. Electronic devices, as used herein are devices, usually comprising, a first electrode 2, a second electrode 5, and one or more electro-active layers 3, usually situated between the electrodes. Item 6 represents a connector for the second electrode 5. The electroactive material may be photo-active, capable of converting electrical energy into mechanical energy and/or capable of converting mechanical energy into electrical energy.

[0034] The electrodes and electro-active layer comprising the electro-active compound, and an electrode are usually applied on a carrier-substrate 1. The barrier layer 0 (the electrodeposited metallic or metalloid layer) is usually at least

applied to cover electrode 5, and in a preferred embodiment the assembly of electrodes 2, 5 and electro-active compound 3, such that these are essentially sealed (encapsulated) between the substrate and the barrier layer. Preferably, a barrier layer is also provided between the carrier-substrate 1 (e.g. a glass or polymeric plate, a polymeric sheet, a polymeric foil) and the assembly of electrodes and electro-active compound, i.e. between carrier substrate 1 and electrode 2.

[0035] One or more other layers may be present, such as an (organic) conducting layer (also referred to a buffer layer), between an electrode, in particular cathode, and electro-active material. An example thereof is optional layer 4 in Figure 1. The position of this layer as shown in the Figure is exemplary; e.g. in an OLED it is usually provided between the active layer 3 and the anode. Suitable conducting layers are for instance, poly(ethylene dioxythiophene) doped with poly(sodium styrenesulphonate) (PEDOT), polyaniline (PANI) or poly(styrenesulphonate) (PSS), or a combination thereof such as PEDOT+PSS.

[0036] One or more further functional layers for the electronic device, such as one or more planarisation layers, etc., may be applied. The layers may be carried out in a manner known *per se*, e.g. as described in US 2002/0113548, WO 2005/001945, WO 2005/015173, WO 03/026011, WO03/022581 or

[0037] WO 02/082561, with the proviso that at least one of the electrodes, is applied by electro-deposition in accordance with the present invention.

[0038] The electrodes (anode, cathode) of the intermediate product (and the resultant device) are generally made of a metallic material or a conductive oxide.

[0039] As a material for the electronic conducting layer on which the metallic layer is to be electrodeposited, aluminium is particularly suitable, especially in case the metal to be electrodeposited is also aluminium, silver or molybdenum. The electro-active material may in principle be any electro-active material suitable for use in a electronic device. In principle it may be an inorganic semi-conducting material. It is contemplated though that the present invention is particularly advantageous for manufacturing an organic electronic device.

[0040] As used herein, the term 'organic electronic device' is used for an electronic device comprising an organic electro-active material. Various kinds of organic electro-active compounds are known in the art. An organic electro-active compound may be polymeric or non-polymeric.

[0041] In an embodiment, the electro-active material is a polymer selected from the group of polyarylene compounds, poly(paraphenylene vinylene) compounds, polyfluorene compounds, polyacetylene compounds, polythiophene compounds, polypyrroles, polyanilines, including derivatives of said polymers (in particular alkyl, aryl and alkoxy derivatives), copolymers of said polymers and said polymers which have been derivatised with a dye.

[0042] In a photovoltaic cell, such polymers have been found very suitable as electron-donating compound. The photoactive layer may comprise a fullerene and/or a fullerene derivative, preferably [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), as electron-accepting compound.

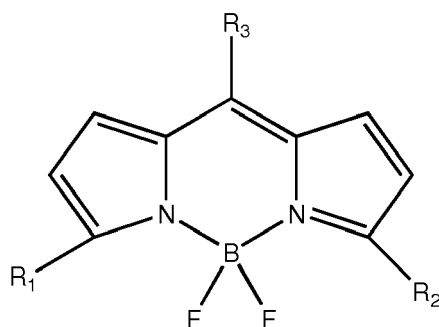
[0043] In an embodiment, the electroactive material comprises a material selected from the group of non-polymeric materials, mixtures and stacks of polymers and non-polymeric compounds, and quantum-dot embedded organic materials.

[0044] In the case of an organic light emitting diode (OLED), the electro-active material comprises an electroluminescent compound. An organic light emitting diode is herein understood to mean a light emitting diode whose photoactive layer consists at least substantially of at least one (semi)conductive electroluminescent organic compound or composition. A polymeric light emitting diode (hereinafter called PLED) is herein understood to mean a light emitting diode whose photoactive layer consists at least substantially of at least one (semi)conductive electroluminescent organic polymer (including polymer mixtures) or at least one (semi)conductive organic polymer (including polymer mixtures) and at least one other organic compound (for instance a single compound), which is electroluminescent.

[0045] Preferred electroluminescent compounds are polyarylenes, more preferably poly(paraphenylene vinylene) compounds (PPV compounds), polyacetylenes, polyanilines, polythiophenes, polyfluorenes, polyvinylcarbazoles, polyphenylene compounds polyfluorene compounds polypyrroles, polyanilines, including derivatives of these polymers (in particular alkyl, aryl and alkoxy derivatives), copolymers of these polymers and mixtures thereof.

[0046] Besides a polymer (which term as used herein includes "oligomer") a non-polymeric electroluminescent compound may be used, such as a non-polymeric electroluminescent dye. Examples of such compounds are monomers and other non-polymerized molecules with conjugated bonds. Often, such compounds have a relatively low molecular weight compared with polymers.

[0047] With regard to the non-polymeric dyes, *inter alia*, a compound according to Formula 1 may be used.



Formula 1

wherein each R_1 , R_2 , R_3 and R_4 are preferably each selected independently from the group of:

- H
- branched and unbranched alkyl groups of the formula $-C_aH_{2a+1}$,
- branched and unbranched alkoxy groups of the formula $-O-C_aH_{2a+1}$,
- aryl groups (optionally substituted with one or more alkyl groups and/or one or more alkoxy alkyl groups, preferably of the formula $-C_aH_{2a+1}$, and $-O-C_aH_{2a+1}$, respectively, as described above), preferably aryl groups having 6 to 12 carbon atoms in the ring structure
- $C\equiv N$

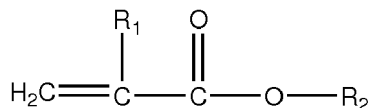
Herein "a" is preferably chosen in the range of from 1 to 20 and more preferably in the range of 2-10.

In a preferred embodiment, the OLED has at least two maxima. Light of a wavelength on or near one maximum can then serve, for instance, as a reference signal, and light of a wavelength at another maximum can then serve as detection signal. An OLED with more than one maximum can be provided for in that the OLED contains at least one electroluminescent active layer which comprises at least two different electroluminescent functionalities. Thus, for instance, the photoactive layer can contain a mixture of two different electroluminescent compounds. Examples include mixtures of the polymers mentioned herein, mixtures of the polymers mentioned herein with other electroluminescent compounds, for instance single conjugated compounds, and copolymers with different electroluminescent segments. Suitable examples thereof are described in WO 2005/001945, of which the contents with respect to the suitable electroluminescent compounds are incorporated herein by reference, in particular the part from page 10 line 10 to page 14, line 17.

In an embodiment, the electronic device is an actuator for converting between electrical and mechanical energy. Suitable examples thereof are e.g. described in European patent application 06076435.4 and in European patent application 06075808.3. The actuator may in particular comprise at least one polymer selected from the group of polyvinyl chlorides, polysaccharides, aromatic urethanes, aromatic urethane acrylates, (alkyl)acrylates, (alkyl)methacrylates, acrylonitrile polymers, polysaccharide derivatives (such as starch acetate, cellulose (tri)acetate), polyethers, polyvinylpyrrolidone, polyethyloxazoline and polyvinylidene fluoride.

In an embodiment, the actuator comprises an electro-active polymer which comprises aromatic moieties in the chain and flexible moieties in the chain, the polymer further comprising side groups bound to the chain, which side groups are selected from the group consisting of polar side groups and side groups comprising an aromatic moiety. Said flexible moieties of the polymer may in particular be selected from the group of (cyclo)aliphatic ether moieties, (cyclo)aliphatic ester moieties, (cyclo)aliphatic thioether moieties and (cyclo)aliphatic thioester moieties. Said aromatic moieties in the chain and—when present—in the side groups may in particular be selected from unsubstituted and substituted aromatic moieties having 6-20 carbon atoms; and/or the side groups may comprise a moiety selected from the group consisting of $-OH$, $-CN$, $-NH_2$, $-NO_2$, aryloxy, phenyl, halogens, $-COOH$, NHR , NRR , $-(CO)(NH_2)$, $-(CO)(NHR)$ and $-(CO)(NRR)$, wherein each R is the same or a different C1-C6 substituted or unsubstituted alkyl group.

In an embodiment, the actuator comprises an electro-active polyurethane-(meth)acrylate copolymer comprising aromatic urethane units and (alkyl)acrylate units, wherein preferably at least part of (alkyl)acrylate units are based on a monomer represented by formula II



Formula II

wherein

R_1 is hydrogen, an optionally substituted alkyl (in particular methyl) or a polar moiety;

R_2 is a polar moiety, an aromatic moiety (in particular a moiety comprising a phenyl), an optionally substituted alkyl or hydrogen;

provided that at least one of R_1 and R_2 is a polar moiety or an aromatic moiety; and/or wherein preferably at least part of the aromatic moieties in the chain are selected from the group of toluenediisocyanates and methylene diphenyl isocyanate.

[0053] As mentioned above, the plating liquid used in a method according to the invention comprises an ionic liquid. Salts that form an ionic liquid are known in the art. For instance, US-A 4,764,440 discloses a composition comprising a mixture of a metal halide and a hydrocarbyl-saturated onium salt, wherein at least one of the hydrocarbyl groups is an aromatic hydrocarbyl group. The contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference.

[0054] US-A 5,731,101 discloses an ionic liquid composition comprising a mixture of a metal halide and an alkyl-containing amine hydrohalide salt of the formula $\text{R}_3 \text{N.HX}$, where at least one R is alkyl and X is halogen, which amine hydrohalide salt contains either one or two alkyl groups therein. The contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference.

[0055] US-A 5,892,124 discloses liquid salts of the general formula Q^+A^- , wherein Q^+ represents quaternary ammonium or phosphonium, and A^- represents various anions including tetrachloroaluminate and trichlorozincate. The contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference.

[0056] In particular suitable is an ionic liquid selected from the ionic liquids described in WO 02/26381, of which the contents of this publication with respect to the description of suitable ionic liquids, in particular as specified in the claims thereof is incorporated herein by reference. Such ionic compound can be formed by the reaction of at least one amine salt of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ (I) with at least one hydrated salt, which is a chloride, nitrate, sulphate or acetate of Li, Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Bi, La or Ce; wherein R^1 , R^2 and R^3 are each independently a C_1 to C_5 alkyl or a C_6 to C_{10} cycloalkyl group, or wherein R^2 and R^3 taken together represent a C_4 to C_{10} alkylene group, thereby forming with the N atom of formula I a 5 to 11 membered heterocyclic ring, and wherein R^4 is hydrogen, or phenyl, or a C_1 to C_{12} alkyl or cycloalkyl group, optionally substituted with at least one group selected from OH, Cl, Br, F, I, phenyl, NH_2 , CN, NO_2 , COOR^5 , CHO, COR^5 and OR^5 , wherein R^5 is a C_1 to C_{10} alkyl or cycloalkyl group, and X^- is an anion forming a complex with the said hydrated salt, for instance a halogen ion, such as Cl^- or Br^- .

[0057] In an embodiment, the ionic liquid comprises a salt of the following cations and/or anions:

- cations selected from the group of monosubstituted imidazolium compounds, disubstituted imidazolium compounds, trissubstituted imidazolium compounds, pyridinium compounds, pyrrolidinium compounds, phosphonium compounds, ammonium compounds, guanidinium compounds and isouronium compounds, including combinations thereof. The substituents may in particular be selected from the substituents described above, when referring to $\text{R}^1\text{-R}^5$ in the amine salt of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ (I).
- anions selected from the group of chloride, bromide, iodide, nitrate, nitrite, fluoride, phosphate, imide, amide, borate, tosylate, tetrafluoroborate, hexafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, methylsulfate, bis(pentafluoroethyl)phosphinate, thiocyanate, octylsulfate, hexylsulfate, butylsulfate, ethylsulfate, dicyanamide, hexafluoroantimonate, bis-(pentafluoroethyl)phosphinate, bis-(trifluoromethyl)imide, trifluoroacetate, bis-trifluorsulfonimide, triflate and dicyanamide, including combinations thereof.

[0058] The plating liquid may comprise a solvent, solvents being materials other than the liquid salt which are liquid under the conditions at which the method is carried out. In particular, the solvent may be chosen from inorganic solvents other than water and organic solvents, such as benzene or an alcohol.

[0059] The solvent concentration will usually be less than 25 wt. %, based on total liquid salt, in particular 20 wt. % or less, more in particular 15 wt. % or less. Preferably, the solvent concentration is up to 2 wt. % based on total liquid salt, more preferably less than 1 wt. %.

[0060] In general it is preferred that the plating liquid is essentially free of water and/or other solvents. A plating liquid

is in particular considered to be essentially free of a solvent if the concentration of that solvent is less than 0.5 wt. %, based on total liquid salt, more in particular less than 0.1 wt. % of a solvent, or less than 0.01 wt. %. In particular, it is contemplated that the (essential) absence of water during the plating may be beneficial to the life-time of the article, especially in case an aluminium, barium or lithium layer is electrodeposited from the ionic liquid.

[0061] A maximum desired water level (in view of efficiency and/or effectivity) depends on the metal to be deposited. In case the standard potential is higher than the standard potential of water to hydrogen (e.g. Ag, Au, Cu), then the water concentration is preferably 0.1 wt. % or less. In particular, in case the standard potential is equal to or less than the standard potential of water to hydrogen (e.g. Al, Ba, Li) then a water content of less than 10 ppm, in particular of 1 ppm or less is desired.

[0062] The ions to be deposited may be all ions of the same metal or metalloid. It is also possible to deposit ions from different metals/metalloids. In particular, ions to be deposited may be selected from metals or metalloids which form a dense oxide. In particular the oxide should have a low permeability to oxygen and/or water, such that it protects the metal covered by the oxide layer against corrosion. Metals of which the oxide forms a dense layer are also known in the art as valve metals.

[0063] A metallic layer as used herein is an layer comprising one or more metals, thus the term includes layers of a metallic alloy. In particular a layer is considered metallic if it shows metallic electrical conductance.

[0064] Metalloids are elements that are generally not considered real metals, but that do show more or less metallic behaviour in one or more specific aspects. In particular, metalloids are capable of conducting electricity, to the extent that they are semiconductors rather than metallic conductors. In particular, Boron (B), Silicon (Si), Germanium (Ge), Arsenic (As), Antimony (Sb), Tellurium (Te) and Polonium (Po) are examples of metalloids.

[0065] A metalloid layer as used herein is a layer comprising one or more metalloids, thus the term includes layers comprising a metalloid alloy. In particular a layer is considered a metalloid layer if it shows metalloid electrical conductance (i.e. showing semi-conductive properties, such as a semi-metal).

[0066] Preferably one or more ions selected from the group of aluminium, silicon, tantalum, titanium, chromium, bismuth, zirconium, hafnium, tungsten, niobium and zinc, may be reduced and deposited in accordance with the invention. Layers of any of these metals/metalloids are in particular suitable to form a moisture and/or oxygen barrier layer, optionally after at least partial oxidation.

[0067] The counter ions of the metal ions or metalloid ions used for deposition may be the same or different from the cations of the ionic liquid. In particular the counter ions may be chosen from the group of chloride, bromide, iodide, nitrate, nitrite, fluoride, phosphate, imide, amide, borate, tosylate, tetrafluoroborate, hexafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, methylsulfate, bis(pentafluoroethyl)phosphinate, thiocyanate, octylsulfate, hexylsulfate, butylsulfate, ethylsulfate, dicyanamide, hexafluoroantimonate, bis-(pentafluoroethyl)phosphinate, bis-(trifluoromethyl) imide, trifluoroacetate, bis-trifluorsulfonimide, triflate and dicyanamide, including combinations thereof.

[0068] In an embodiment of the invention, a layer of an alloy is formed by using co-deposition. This may be achieved by using a single plating liquid comprising more than one type of ions to be deposited on the substrate, to allow co-deposition to take place in a single electro-deposition process.

[0069] In an embodiment, the different ions to be deposited are dissolved in separate plating liquids, with which the substrate is sequentially contacted under plating conditions. This allows the formation of different layers on top of each other.

[0070] The total concentration of the salt comprising the ions for forming the electrode preferably is at least 0.1 mol%, more preferably at least 1 mol%, even more preferably at least 5 mol%, or at least 10 mol%. A relatively high concentration is in particular advantageous in order to allow a high deposition speed.

[0071] The upper limit is in particular determined by the maximum allowable concentration in order to maintain the plating liquid in a liquid state (the saturation level). A relatively high concentration usually advantageous for a high deposition rate. Also a large amount of ions can usually be reduced and deposited before depletion of the liquid may become noticeable. Also the presence of the ions to be deposited in a relatively high concentration may be advantageous for improved liquidity (reduced viscosity, reduced melting temperature of the liquid), and/or improved electrical conductance of the liquid.

[0072] The total concentration of the salt of the metal/metalloid ions for forming the layer by electro-deposition preferably is up to 70 mol %, more preferably up to 65 mol %, in particular up to 60 mol%. For practical reasons, e.g. reaching saturation in the liquid, a lower concentration may be chosen, e.g. up to 40 mol %, up to 20 mol %, up to 10 mol %, or 5 mol % or less.

[0073] In an advantageous embodiment, a "sacrificial electrode" is used as a counter electrode (anode). At least the surface of such an electrode comprises the same metal or metalloid as the metal or metalloid that is to be deposited. While the metal or metalloid is deposited on the substrate during electro-deposition, metal/metalloid at a surface of the sacrificial electrode will be oxidised and dissolve in the plating liquid. Thus, the composition of the plating liquid can be maintained at about the same concentration for a prolonged time, or at least depletion of the liquid with metal/metalloid ions can be postponed. Such electrode may for instance be a plate, foil or thread of the metal/metalloid to be deposited, e.g. an aluminium counter electrode can be used when depositing aluminium on a substrate from aluminium ions.

containing ionic liquid electrolyte. Further, a net or basket of an inert metal or other inert material (i.e. a material that does not oxidise or otherwise react under the electrodeposition conditions) may be used wherein pieces of the metal to be deposited are provided

[0074] In an advantageous embodiment, at least part of the electrodeposition is carried out while the surface on which the metal or metalloid layer is formed, or a part thereof is exposed to electromagnetic radiation. The wavelength of the electromagnetic radiation is typically of a high enough energy to overcome the band gap of the material on which the metal or metalloid is deposited (such as the organic semiconductive material). Hereby the deposition is aided and a smaller electric potential is required to achieve deposition. Hereby the risk of adversely affecting a property of the organic electro-active material is reduced. Further, it is envisaged by the inventors that such irradiation is in particular useful to provide a more homogenous deposition and/or a more dense deposition (within the deposition formed on the irradiated surface). Furthermore, it is contemplated that such irradiation may help to reduce the occurrence of pinholes.

[0075] As mentioned above, the metallic or metalloid layer is deposited gradually, by first starting electrodeposition on a part of the surface of the electrodeposition-cathode relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electrodeposition-cathode layer relatively remote from the connection to the power source.

[0076] In practice, the part of the electrodeposition-cathode connected to the power source usually is a peripheral section of the electrodeposition-cathode (closer to a side of the electrodeposition-cathode than the centre thereof). In particular, the connection with the power source can be at one or more sides of the electrodeposition-cathode.

[0077] Usually, electrodeposition on the part of the surface relatively close to the connection on which electrodeposition has started before electrodeposition on a corresponding relatively remote part of the surface, is stopped before electrodeposition on the part of the surface relatively remote from the connection is stopped, in order to obtain a good uniformity in layer thickness of the electrodeposited layer. With 'a corresponding relatively remote part' is generally meant a relatively remote part adjacent to the part of the surface relatively close to the connection on which electrodeposition has started earlier. A remote part generally lies in the same line perpendicular to the direction of movement of the intermediate product as the part of the surface relatively close to the connection to which the remote part corresponds.

[0078] In an advantageous method, the electrodeposition-cathode is connected to the power source at two essentially opposite peripheral sections of the electrodeposition-cathode and the relatively remote part is situated between said opposite peripheral sections.

[0079] In a preferred embodiment, the gradual electrodeposition is accomplished in a rather simple manner, namely using a mask. The mask, or at least its surface that is in contact with the ionic liquid is generally non-conductive. Examples of suitable materials are non-conductive plastics, ceramics and glass materials.

[0080] The mask is positioned between the counter electrode (anode) for the electrodeposition process and the intermediate product in such a way that it shields part of the surface of the electrodeposition-cathode from electrodeposition of ions from the ionic liquid on the electrodeposition-cathode. The shielding causes at least a significant drop in current flow from the counter electrode to the surface of the intermediate product that is shielded by the mask. Thereby, deposition of metal or metalloid is (temporarily) prevented or at least considerably reduced on the part of the surface that is shielded. The mask has one or more openings allowing the electrodeposition on the part of the electrode not shielded by the mask.

[0081] By moving the intermediate product relative to the mask (generally parallel thereto), whereby the part(s) of the surface previously shielded become unshielded and parts previously deposited become shielded, it is possible to electrodeposit a metallic or metalloid layer with a highly uniform thickness.

[0082] Figures 2A to 2C schematically illustrate a preferred embodiment, wherein the mask has two baffles, together forming an essentially V-shaped opening. Herein, conceptually, various peripheral parts of the surface of product 11 and parts of the surface more remote from the sides of the product 11 are indicated. These parts are shown as 11a-f. As will be understood by the skilled person, 11a-f do not necessarily represent physically distinguishable parts of the product, they are primarily shown to illustrate the position of these parts relative to each other and are used in support of the following description of the Figure, which illustrates an advantageous method according to the invention. Regarding the gap between the two baffles, this can be chosen within wide limits. In the Figures 2A-2C a relatively wide gap is shown, wherein the protruding end-point k of the left baffle does not extend into the area defined by the triangle m, n, 1 in the right baffle. In practice, it may be preferred that the gap is smaller than schematically shown in the Figure, and the protruding end-point k of the left baffle may extend into area defined by the triangle m, n, 1. Baffles 10a and 10b, defining the mask, are positioned between the counter electrode (not shown) and the intermediate product 11. Baffles and intermediate product are all placed in the plating liquid. For this embodiment, or for an embodiment wherein the baffles form an essentially U-shaped opening, connections of the power source (not shown) to intermediate product will generally be along sides 12. The direction arrow shows the movement of the product relative to the mask. Herein below, the verb 'to move' will be used to describe movement of the product relative to the mask. Thus, it is used to describe embodiments wherein in fact the mask is moved and to describe embodiments wherein the product is moved. In practice, it will usually be practical to move the product on which the layer is electrodeposited, especially in a continuous process, such as a roll-to-roll process. As illustrated in Figure 2A, the intermediate product 11 is moved into the opening 13.

[0083] First peripheral parts of the surface of product 11 (parts at or close to sides 12, illustratively marked 11a') at or near the front 14 reach the opening. In the current flow between the product 11 (of which a surface facing the counter electrode acts as electrodeposition-cathode) and the counter electrode metal or metalloid is electrodeposited from the ionic liquid onto the surface of the product 11 acting as the electrodeposition-cathode. The more central parts 11b of product 11 in the same perpendicular line as parts 11a are still shielded by baffle 10a, and no (substantial) deposition takes place yet on those parts of the surface.

[0084] In Figure 2B, the intermediate product 11 has moved to the extent that parts of the surface 11a, close to the connections to the power source near the front end 14 of the product 11, are shielded again, now by baffle 10b, but the corresponding parts 11b of the surface remote from the connections are now in the opening, and thus metal/metalloid is deposited on those parts. At and close to the rear end 15 of the product, the parts 11e of the surface of product 11 close to the connections to the power source are already in the opening, whereby electrodeposition can take place, whereas their corresponding parts 11f of the surface remote from the connection points are still shielded. In the parts 11c and 11d, remote from the front 14 and the rear 15 electrodeposition can take place over the full width (the dimension perpendicular to the direction of movement of the product 11)

[0085] In Figure 2C, the parts of the surface relatively close to the connections to the power source are all fully shielded again (parts 11a, 11c, 11d). Only parts 11f relatively remote from the connections to the power source and relatively close to the rear 15 are not shielded, yet. The electrodeposition will be finished, once the product 11 has moved fully underneath baffle 10b.

[0086] The electrodeposition is generally carried out at a potential equal to or larger than the reduction potential of the ion to be deposited. Suitable potentials for forming a layer of a specific metal or metalloid are generally known in the art. The electrodeposition may be carried out under potentiostatic conditions or under galvanostatic conditions. Potentiostatic conditions are advantageous for a well-controlled deposition wherein a uniform layer thickness is obtained, in particular in an embodiment wherein the intermediate product is a sheet or the like. Galvanostatic conditions are particularly suitable for a roll to roll or sheet to sheet process.

[0087] Thus, surprisingly, it is possible to obtain an electronic device, in particular an organic electronic device, with a metallic/metalloid layer that can serve as a barrier against water, oxygen or the like, using a mask with an opening having a constant size, without having to regulate the size of the opening based on monitored parameters such as deposition rate, current, or the like. In accordance with the invention it is thus possible to deposit a layer with a highly uniform thickness, whereby a subsequent treatment to increase uniformity of the thickness can generally be omitted.

[0088] Accordingly, the invention allows the manufacture of an electronic device on which a metallic/metalloid layer is electrodeposited, wherein essentially all parts of the surface of the electrodeposition-cathode on which the metallic or metalloid layer is deposited are subjected to electrodeposition for essentially the same duration.

[0089] In particular in case the electrodeposition-cathode is connected to the power source at only one side of the product, an essentially I-shaped mask (parallelogram-shaped mask) may be used.

[0090] The electrodeposition in accordance with the invention may be carried out to provide a metallic or metalloid layer with satisfactory properties within a wide thickness range. A desired thickness e.g. may be determined based on considerations such as the desired barrier properties, transparency

[0091] (which may or may not be desired), flexibility of the article (which may or may not be desired), etc.

[0092] The thickness may in particular be at least 1 nm, at least 10 nm, at least 100 nm, at least 1 μm , at least 10 μm or at least 100 μm . The thickness may in particular be up to 1 mm, up to 400 μm , up to 100 μm , up to 10 μm , up to 1 μm up to 100 nm or up to 10 nm.

[0093] After forming the layer, the device may be subjected to one or more post-treatment steps. For instance, excess ionic liquid may be removed. One or more further steps, such as the provision of one or more other functional layers, which may be employed are, e.g. described in the prior art identified herein.

[0094] In a specific embodiment, the deposited metal or metalloid is at least partially oxidised after the electrodeposition, to form a metal oxide or metalloid oxide barrier layer. Suitable oxidation techniques include thermal oxidation and chemical oxidation, in particular electrochemical oxidation.

[0095] (Electro)chemical oxidation may for instance be accomplished by oxidation in an aqueous liquid (usually comprising more than 50 wt. % water, based on total liquids, and an electrolyte to impart conductivity to the liquid. The skilled person will know how to choose suitable conditions, such as a suitable pH, temperature and reagents, depending upon the metal or metalloid to be oxidised. For instance, for aluminium a pH at or near neutral pH (neutral pH \pm 1 pH) is considered particularly suitable. Preferably, the oxidation is carried out in the presence of a pH modulator, in particular a (weak) acid or base, more in particular an acid and a base forming a pH-buffer.

[0096] Thermal oxidation may be accomplished by heating the layer in the presence of oxygen or a gas comprising oxygen, e.g. air.

[0097] The invention is further directed to an electronic device, in particular an organic electronic device. Suitable designs for electronic devices are generally known in the art, and may in particular have a design as described herein above or in the prior art mentioned in the present description, such as the above mentioned prior art or WO 2010/093237.

[0098] The electronic device may in particular be selected from opto-electronic devices and actuators, preferably from organic opto-electronic devices and organic actuators. Preferred opto-electronic devices are (organic) LEDS and (organic) photovoltaic cells. The photovoltaic cell may in particular be a solar cell.

[0099] The electronic device (obtainable) according to the invention generally comprises an anode, a cathode, an electro-active material at least partially situated between said anode and said cathode, and a metallic or metalloid layer. The metallic or metalloid layer is adjacent to the cathode on an outer surface of the electronic device (relative to the cathode).

[0100] Preferably, the metallic or metalloid layer has a permeability to water of 1 mg/m².day or less, of 0.1 mg /m².day or less, or of 1 µg/m².day or less.

[0101] Preferably, the metallic or metalloid layer has a permeability to oxygen of 1 mg/m².day or less, of 0.1 mg /m².day or less, or of 1 µg/m².day or less.

Claims

1. Method for manufacturing an electronic device, the method comprising

- providing an electronic intermediate product, said intermediate product having a an electronic conducting layer and

- forming an metallic or metalloid layer on an outer surface the electronic conducting layer by electrodeposition using a plating liquid comprising an ionic liquid and metal ions or metalloid ions, wherein during electrodeposition the electronic conducting layer of the intermediate product on which electrodeposition takes place is connected to an electrical power source and the electronic conducting layer on which electrodeposition takes place provides a cathode for the electrodeposition, and wherein

the metallic or metalloid layer is formed gradually in the plane parallel to the surface of the electronic conducting layer on which electrodeposition takes place , which gradual forming comprises starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively remote from the connection to the power source.

2. Method according to claim 1, the method comprising

- providing an electronic intermediate product, said intermediate product having a first electronic conducting layer, a second electronic conducting layer, and an electro-active material at least partially situated between said electronic conducting layers and

- forming an metallic or metalloid layer on at least part of an outer surface of at least one of the electronic conducting layers by electrodeposition using a plating liquid comprising an ionic liquid and metal ions or metalloid ions,

wherein

during electrodeposition the electronic conducting layer of the intermediate product on which electrodeposition takes place is connected to an electrical power source and the electronic conducting layer on which electrodeposition takes place provides a cathode for the electrodeposition, and wherein

the metallic or metalloid layer is formed gradually in the plane parallel to the surface of the electronic conducting layer on which electrodeposition takes place , which gradual forming comprises starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively close to the connection to the power source before starting the electrodeposition on a part of the surface of the electronic conducting layer on which electrodeposition takes place relatively remote from the connection to the power source.

3. Method according to claim 1 or 2, wherein electrodeposition on the part of the surface relatively close to the connection is stopped before electrodeposition on the part of the surface relatively remote from the connection is stopped.

4. Method according to claim 1, 2 or 3, wherein the part of the electronic conducting layer on which electrodeposition takes place connected to the power source is a peripheral section of said layer.

5. Method according to claim 4, wherein the electronic conducting layer on which electrodeposition takes place is connected to the power source at two essentially opposite peripheral sections of the electronic conducting layer on

which electrodeposition takes place and the relatively remote part is situated between said opposite peripheral sections.

- 5 6. Method according to any of the preceding claims, wherein the gradually forming of the metallic or metalloid layer is accomplished using a mask, the mask shielding part of the surface of the electronic conducting layer on which electrodeposition takes place of the intermediate product from electrodeposition of ions from the ionic liquid on the electronic conducting layer on which electrodeposition takes place and which mask has one or more openings allowing the electrodeposition on the part of the layer not shielded by the mask, in which method the surface the intermediate product is moved relative to the mask.
- 10 7. Method according to claim 6, wherein the mask comprises an essentially 'V'-shaped, an essentially 'U'-shaped opening or an essentially '/'-shaped opening.
- 15 8. Method according to any of the preceding claims, wherein essentially all parts of the surface of the electronic conducting layer on which the metallic or metalloid layer is deposited are subjected to electrodeposition for essentially the same duration.
- 20 9. Method according to any of the preceding claims, wherein the metal ions comprise aluminium ions and a layer comprising aluminium is formed by electrodeposition.
- 25 10. Method according to any of the preceding claims, wherein the metallic or metalloid layer is subjected to an oxidation step after deposition.
11. Method according to any of the preceding claims, wherein the metallic or metalloid layer is formed in a roll-to-roll process or in a sheet-to-sheet process.
12. Method according to any of the preceding claims, wherein the electroactive material is an organic electroactive material
- 30 13. Method according to any of the preceding claims, wherein the electrodeposition is carried at a deposition rate of at least 0.1 μm layer thickness per min, in particular of at least 0.5 μm layer thickness per min, more in particular of at least 1.0 μm layer thickness per min.
- 35 14. Electronic device obtainable by a method according to any of the preceding claims.
15. Electronic device according to claim 14, wherein the metallic or metalloid layer, or the oxidised metallic layer or oxidised metalloid layer has a water permeability is less than 10^{-3} g water/ m^2/day , preferably less than 10^{-5} g water/ m^2/day .

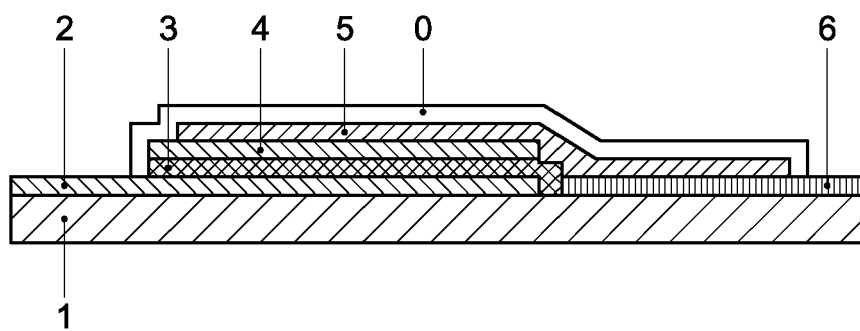


Fig. 1

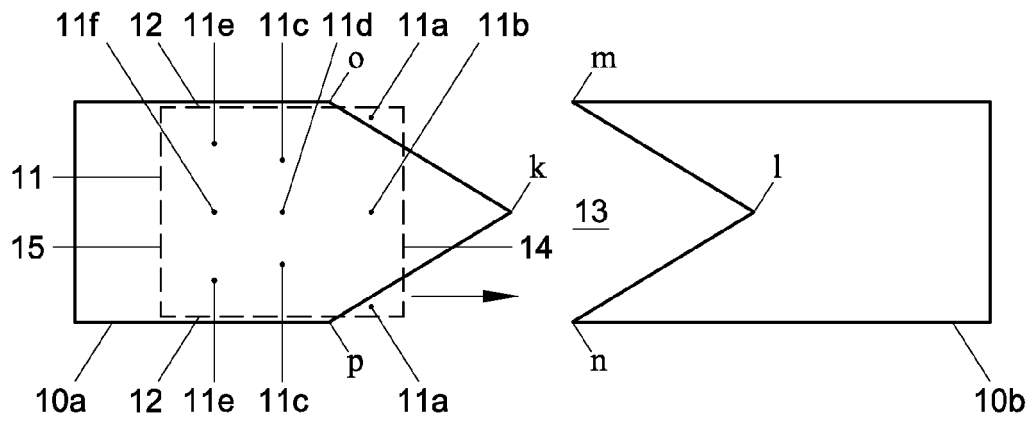


Fig. 2a

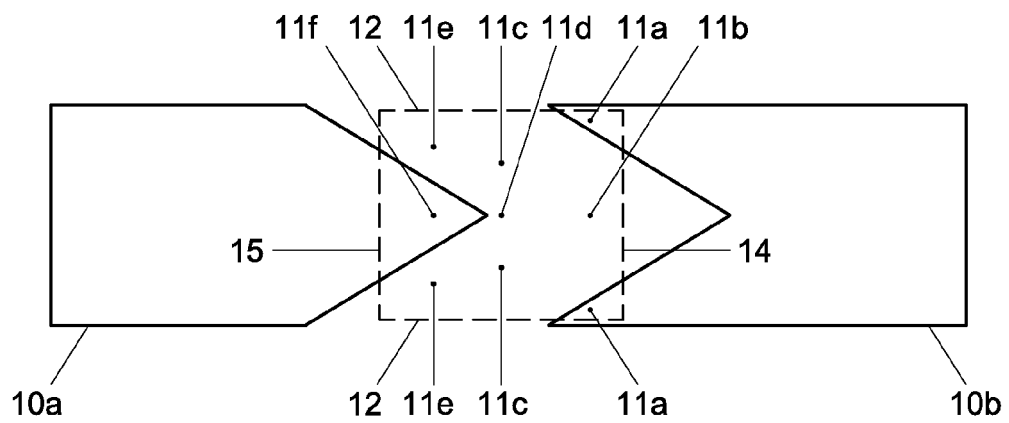


Fig. 2b

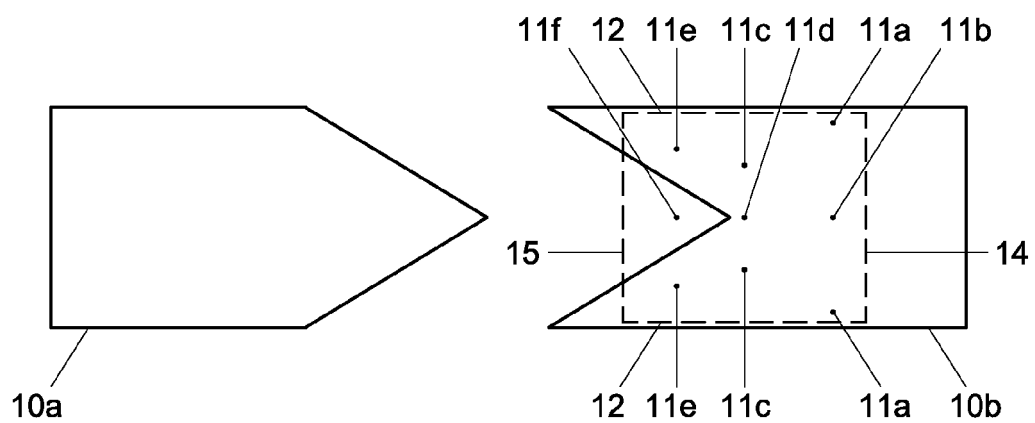


Fig. 2c

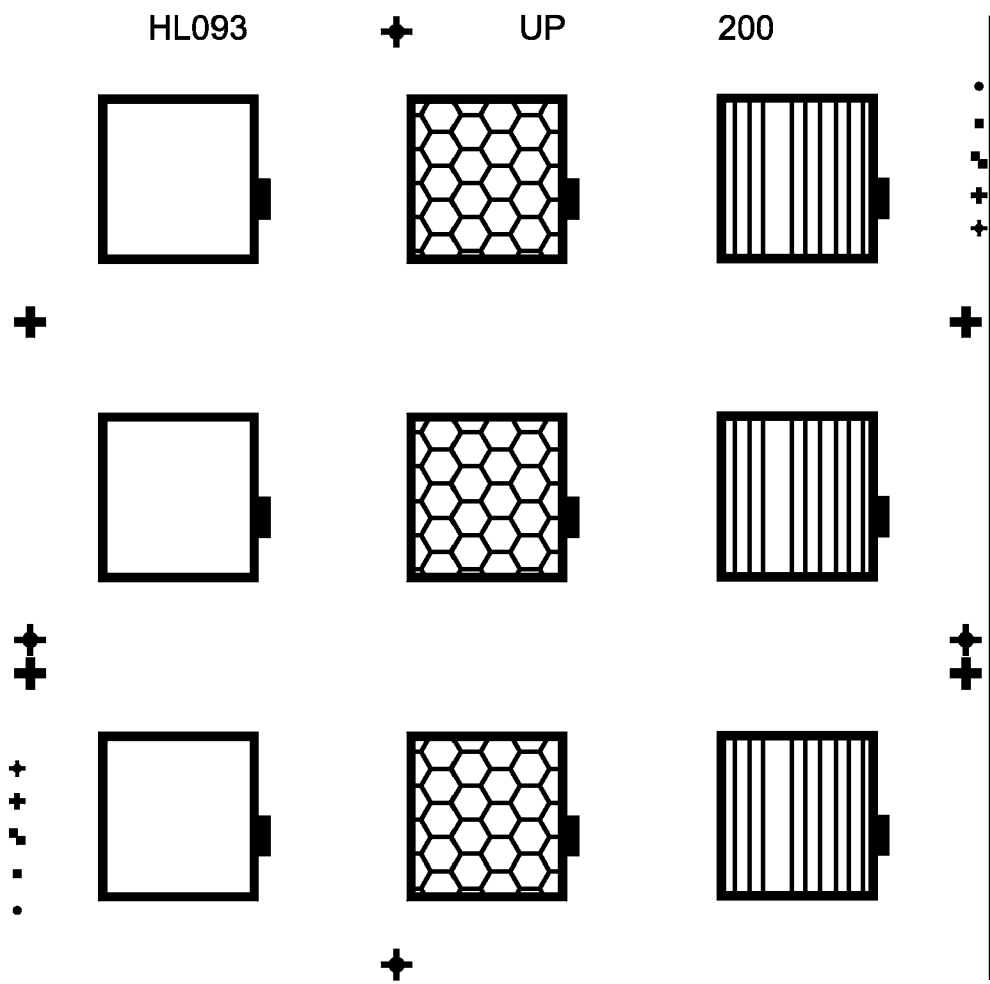


Fig. 3

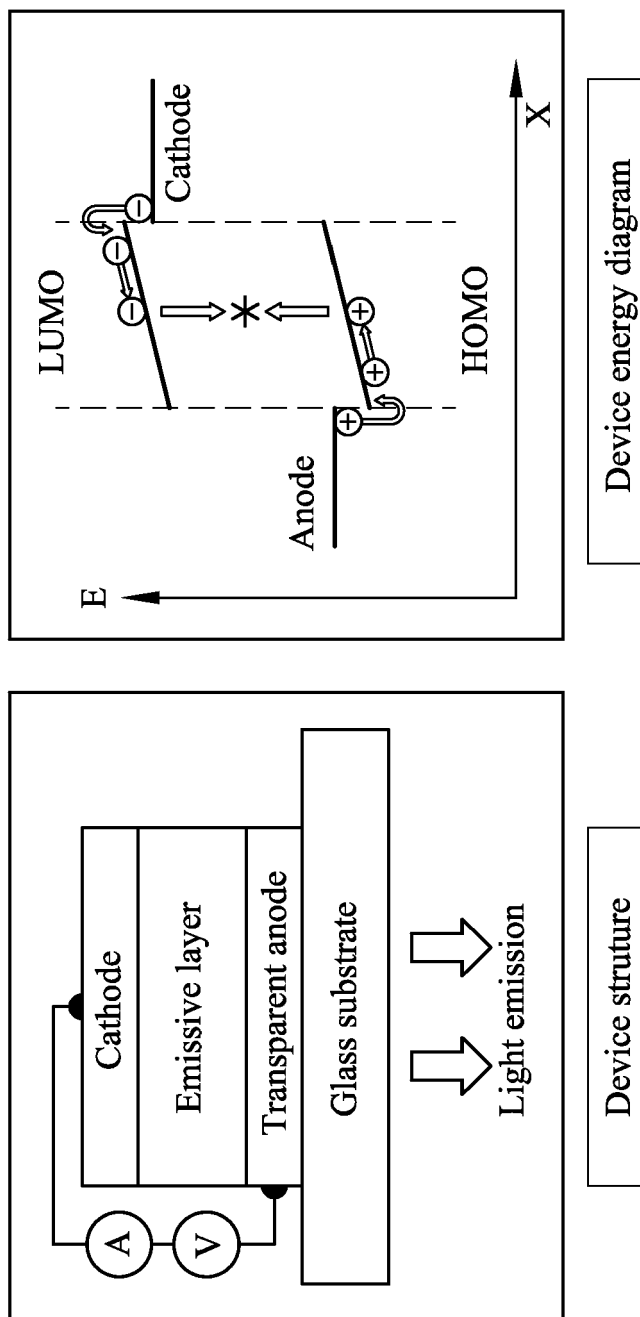


Fig. 4



EUROPEAN SEARCH REPORT

Application Number
EP 11 15 1257

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Place of search		Date of completion of the search	Examiner
The Hague		31 August 2011	Suárez Ramón, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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