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- **Bolton, Sean William**
Durham TS21 3FG (GB)
- **Miremont, Christophe Olivier**
South Queensferry, EH30 9HR (GB)
- **Snell, Thomas**
Durham TS21 3FG (GB)

(71) Applicant: **Polyphotonix Limited**
Sedgefield County, Durham TS21 3FG (GB)

(74) Representative: **Vinsome, Rex Martin**
Urquhart-Dykes & Lord LLP
Cale Cross House
Pilgrim Street 156
Newcastle-upon-Tyne, Tyne and Wear NE1 6SU (GB)

(72) Inventors:
• **Allott, Richard Mark**
Durham TS21 3FG (GB)

(54) **Method of manufacturing precursor material for forming light emitting region of electroluminescent device**

(57) A method of manufacturing a precursor material for use in forming a light emitting region of an electroluminescent device is disclosed. The method comprises providing a mixture of a matrix material and an electroluminescent material, wherein at least part of the matrix

material is in a molten state and the mixture includes an organic semiconductor material and an ionic material for providing positive ions and negative ions for contributing to electrochemical doping of the organic semiconductor material.

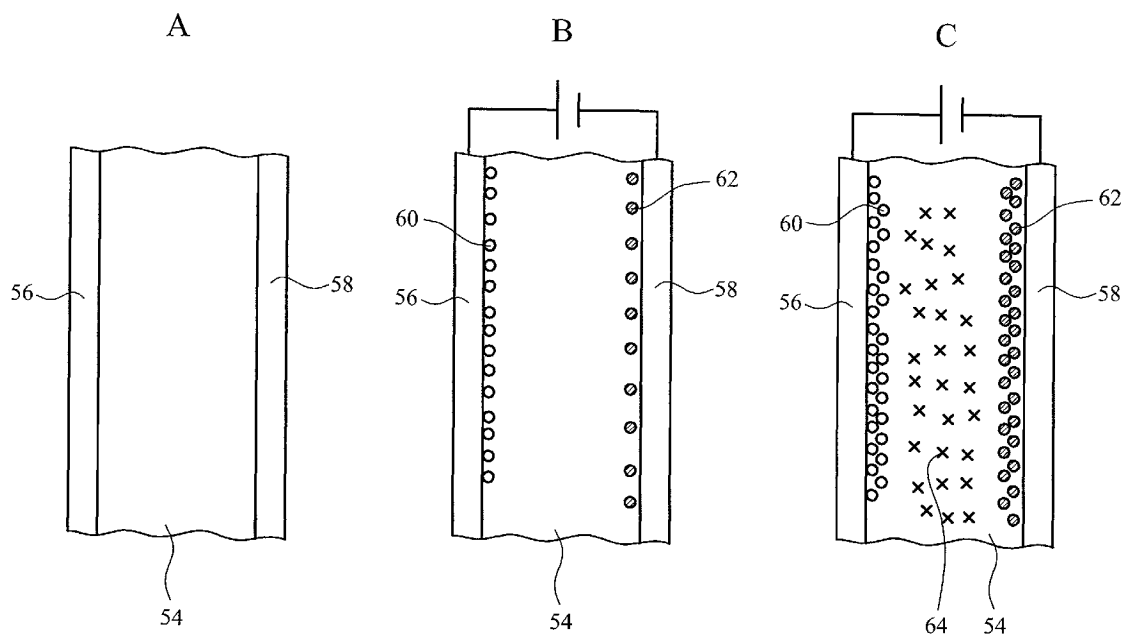


FIG. 4

Description

[0001] The present invention relates to a method of manufacturing a precursor material for use in forming a light emitting region of an electroluminescent device, and relates particularly, but not exclusively, to a method of making a precursor material for use in forming a light emitting region of an organic light emitting diode (OLED). The invention also relates to a method of manufacturing an electroluminescent device from the precursor material.

[0002] OLEDs are generally manufactured by forming a series of stacked thin functional layers. An example of a process for forming an OLED is disclosed in EP 1391944, in which a light emitting layer is formed by spraying a solution of an electroluminescent organic semiconductor material onto a substrate. However, this arrangement suffers from the drawback that it is not possible to use the process of EP 1391944 without a substrate, the manufacturing process is complicated and expensive because of the requirement for a substrate, and the requirement of a substrate limits the range of function shapes in which light emitting devices can be made. In addition, the use of thin layers of pure material makes the manufacturing process expensive since the material must be prepared in very clean conditions, and the use of thin films means that light emitting devices manufactured according to the process of EP 1391944 are prone to failure because of impurities.

[0003] Preferred embodiments of the present invention seek to overcome one or more of the above disadvantages of the prior art.

[0004] According to an aspect of the present invention, there is provided a method of manufacturing a precursor material for use in forming a light emitting region of an electroluminescent device, the method comprising providing a mixture of at least one matrix material and at least one electroluminescent material, wherein at least part of at least one said matrix material is in a molten state and the mixture includes at least one organic semiconductor material and at least one ionic material for providing positive ions and negative ions for contributing to electrochemical doping of at least one said organic semiconductor material.

[0005] The present invention is based on the surprising discovery that by providing a mixture of at least one matrix material and at least one electroluminescent material, wherein at least part of at least one said matrix material is in a molten state and the mixture includes at least one organic semiconductor material and at least one ionic material for providing positive ions and negative ions for contributing to electrochemical doping of at least one said organic semiconductor material, this provides the advantage of enabling a light emitting region to be formed from a thicker layer of the precursor material. The ionic material enables an electroluminescent device incorporating the light emitting region to be operated at lower voltages than in the case of a light emitting region from which such

materials are absent. As a result, the precursor material can be formed into a wide range of light emitting regions without the need for forming a light emitting layer on a substrate, and the possibility of forming thicker layers enables light emitting devices have light emitting regions incorporating the material to be prepared in less clean conditions than in the case of EP 1391944, thereby reducing the cost of production of such devices.

[0006] It will be appreciated by persons skilled in the art that the term "matrix material" is intended to cover a material from which a light emitting region can be formed and in which active components such as electroluminescent material and/or organic semiconductor material are embedded in the electroluminescent device.

[0007] At least one said ionic material may comprise at least one organic semiconductor material.

[0008] By providing at least one ionic material for use in electrochemical doping of the organic semiconductor material which itself comprises at least one organic semiconductor material, this provides the advantage of reducing the number of materials and processing steps, thereby simplifying the process of manufacturing light emitting devices from the precursor material.

[0009] The method may comprise heating at least part of at least one said matrix material to a molten state thereof and adding at least one said electroluminescent material and/or at least one said organic semiconductor material to said matrix material in said molten state.

[0010] This provides the advantage of reducing the risk of damage to the electroluminescent material and/or organic semiconductor material by heating.

[0011] At least one said electroluminescent material and/or at least one said organic semiconductor material may be added in solution form to said matrix material.

[0012] This provides the advantage of improving mixing of the electroluminescent material and/or organic semiconductor material with the matrix material.

[0013] The method may further comprise adding at least one plasticiser to at least one said matrix material.

[0014] This provides the advantage of reducing the temperature at which the matrix material becomes molten, thereby reducing the risk of damage to the electroluminescent material and/or organic semiconductor material by heating.

[0015] The method may further comprise causing solidification of at least part of said mixture.

[0016] This enables material to be stabilised in a suitable form, such as pellets or a sheet, for supplying to manufacturers making light emitting devices from the precursor material at a different location.

[0017] At least one said matrix material may comprise at least one polymer.

[0018] The mixture may include electrically conductive particles.

[0019] By adding electrically conductive particles to the mixture, this provides the advantage of increasing the efficiency of electroluminescent devices made from the precursor material. In particular, because the system

does not rely on matching the work functions of respective electrodes to energy levels of organic material, multi-domain devices can be achieved by introducing conductive particulate material into the system. The same particulate will see p-doping on one side and n-doping on the opposite side. Particles dispersed in the mixture therefore create multiple light emitting domains. The provision of multiple light emitting domains results in higher current efficiency for very similar voltage requirements.

[0020] According to another aspect of the present invention, there is provided a method of forming a light emitting region of an electroluminescent device from a precursor material provided by means of a method as defined above.

[0021] The method may comprise extruding at least part of said light emitting region.

[0022] The method may comprise moulding at least part of said light emitting region.

[0023] The method may further comprise applying an electric field to at least part of said mixture at a temperature at which ions in the system are mobile and capable of participating in the electrochemical doping and subsequently allowing the said mixture to cool so that electrochemically doped regions resulting from electric field application are maintained upon electric field removal.

[0024] This provides the advantage of enabling the electroluminescent device to be switched on and off more quickly than a device in which the ionic layers have to be formed each time the device is switched on.

[0025] A preferred embodiment of the invention will now be described, by way of example only and not in any limitative sense, with reference to the accompanying drawings, in which:-

Figure 1 is a schematic representation of a material processing apparatus for providing a precursor material by means of a process embodying the present invention;

Figure 2 is a plan view of an extruder device of the material processing apparatus of Figure 1;

Figure 3 is a side view of the extruder of Figure 2; and

Figures 4A to 4C explain the operation of a light emitting device having a light emitting region formed by means of the material processing apparatus of Figure 1.

[0026] Referring to Figure 1, a material processing apparatus 2 has a twin screw extruder 4 for providing a mixture of an electroluminescent organic semiconductor material, a matrix material such as a polymer, and an ionic material for supplying positive and negative ions for contributing to electrochemical doping of the organic semiconductor material, such that at least the matrix material, and preferably the entire mixture, is in a molten state. The molten mixture can then either be solidified

into pellets directly from the extruder 4 for subsequent processing at a different location, or fed to a sheet forming unit 6 which forms a sheet 8 of solidified electroluminescent mixture which can then be wound onto a roll 10 by means of a windup unit 12. In a preferred embodiment, the electroluminescent material is itself an organic semiconductor material, but it will be appreciated by persons skilled in the art that separate electroluminescent materials and organic semiconductor materials can be used. For example, inorganic electroluminescent materials, for example quantum dot materials such as cadmium sulphide, cadmium selenide, or cadmium selenide and zinc sulphide combinations can be used.

[0027] Referring to Figures 2 and 3, the extruder 4 comprises a pair of screws 14, 16 mounted for rotation about generally parallel axes 18, 20 respectively within a housing 22 having a series of heaters 24 and temperature sensors 26 to enable the temperature of different zones of the housing to be carefully controlled as the molten mixture is conveyed through the housing 22 by means of the screws 14, 16. The housing 22 defines a first feed zone 28 for receiving pellets of polymer matrix material (not shown) via a first inlet 30, and a melt zone 32 in which the polymer matrix material is subjected to shear by interleaved discs 34 of the screws 14, 16 and heated to bring the polymer matrix material to a molten state. The profile of the screws 14, 16 is inclined forwards in the first feed zone 28 so that material is conveyed towards the melt zone 32.

[0028] A part 36 of each screw 14, 16 is inclined backwards relative to the direction of propagation, in order to form a melt seal 38 to minimise leakage of molten material from the melt zone 32, and a liquid solution of electroluminescent organic semiconductor material containing ionic material for providing positive and negative ions for contributing to electrochemical doping of the organic semiconductor material dissolved in a suitable solvent such as toluene is injected into the molten polymer matrix material in a second feed zone 40 via a second inlet 42. The housing has a mix zone 44 in which the electroluminescent polymer solution and molten polymer matrix material are subjected to shear by means of interleaved discs 46 of the screws 14, 16, and excess solvent can be vented through an outlet 48 and recovered for reuse.

[0029] The molten mixture then passed to an extrusion zone 50 where it is discharged from an extrusion die 52 in the form of pellets or fed into the sheet forming unit 6 to form sheet 8 (Figure 1).

[0030] In order to form a light emitting device from the material generated by the material processing apparatus 2 shown in Figure 1, material from the previously solidified sheet 8 is dissolved in a suitable solvent such as toluene, or the molten mixture is formed directly from the extruder 4 or via a moulding device (not shown) into a suitable shape. A light emitting region 54 is then formed, as shown in greater detail in Figures 4A to 4C, by applying an electric field to the molten mixture by means of suitable electrodes 56, 58, as shown in Figure 4A, in which the

ionic material and electroluminescent material is initially distributed relatively uniformly throughout the molten mixture. As the electric field is applied, as shown in Figure 4B, charge is injected from the electrodes 56, 58 into the electroluminescent organic semiconductor, so that the semiconductor material becomes positively charged adjacent anode 56 and negatively charged adjacent cathode 58. At the same time, the ionic material supplies negative ions 60 which concentrate in the region adjacent the anode 56, and positive ions 62 which concentrate in the region adjacent the cathode 58, thereby neutralising the respective charges on the surrounding organic semiconductor material. As shown in Figure 4C, the applied voltage subsequently causes holes to move from the anode 56 towards the cathode 58, and electrons to move from the cathode 58 towards the anode 56, and between the regions 60, 62 of n and p type doping, holes and electrons combine to form neutral pairs 64, which radiatively decay and emit visible light. During application of the electric field, the mixture is allowed to set, as a result of which an excess of negative ions 60 remain located adjacent to the anode 56, and an excess of positive ions 62 remain located adjacent to the cathode 58. As a result, the electroluminescent device incorporating the light emitting region 54 switches on and off more quickly than a device in which the ionic material is uniformly distributed throughout the light emitting layer 54, since the layers 60, 62 of ions material adjacent to the respective electrodes 56, 58 do not need to be built up by application of a voltage.

[0031] The effect of the layers 60, 62 of ions is to increase the electrical conductivity of the respective regions in which they are located, which in turn has the effect of increasing the proportion of the applied voltage which is applied to the middle region containing the electron/hole pairs 62.

[0032] This therefore enables a thick layer of electroluminescent material to be operated at a lower applied voltage. In addition, conductive particles such as indium tin oxide (ITO), gold or aluminium can be distributed in the mixture. This enables multidomain devices to be achieved because particles will see p-doping on one side and n-doping on the opposite side. Particles dispersed in the mixture therefore create multiple light emitting domains. The provision of multiple light emitting domains results in higher current efficiency for very similar voltage requirements.

Example

[0033] Polystyrene pellets were fed into a twin screw extruder 4 at a rate of 0.6gm/minute, and the screws 14, 16 were caused to rotate at a rate of 50rpm. A solution consisting of 737.6mg of electroluminescent organic semiconductor material in the form of soluble phenyl-substituted PPV sold by Merck KGaA under the name PDY-132 (Superyellow), 4456.8mg of ionic liquid trihexyltetradecylphosphoniumbis (trifluoromethylsulfonyl) amide,

and a solvent consisting of 94ml of toluene were provided. The first feed zone 28 of the extruder 4 was maintained at a temperature of 165 degrees C, and the melt zone 32 and liquid feed zone 40 are maintained at a temperature of 172 degrees C. The above solution was then pumped into inlet 42 at a rate of 5ml/minute, and the mix zone 44 and extrusion zone 50 were maintained at a temperature of 175 degrees C and the extrusion die 52 at 120 degrees C. The extruded film material was then supplied to sheet forming unit 6 and the sheet 8 was then collected from the wind up unit 12 of the material processing apparatus 2.

[0034] 1.74gm of the sheet 8 was then dissolved in a solution of 30ml anhydrous toluene, and a sheet of indium tin oxide (ITO) coated glass was then cleaned using acetone, isopropyl alcohol and ultrasonic cleaning equipment and the substrate then baked dry. The toluene and sheet solution was placed in the centre of the glass and the glass was spun at 2000 rpm using a spin coater, in order to form a thin layer of film material. The toluene was then removed by evaporation and rotation of the substrate. The coated substrate was then placed in an evaporation system, the chamber of which was then pumped down to 3×10^{-6} mBar. Aluminium was then sublimated onto the substrate as it was rotated to ensure an even coverage, to form a light emitting layer for an electroluminescent device.

[0035] It will be appreciated by persons skilled in the art that the above embodiment has been described by way of example only, and not in any limitative sense, and that various alterations and modifications are possible without departure from the scope of the invention as defined by the appended claims. For example, certain electroluminescent or non-electroluminescent organic semiconductor materials also have ion supplying properties, as a result of which the addition of separate ionic material is not necessary.

Claims

1. A method of manufacturing a precursor material for use in forming a light emitting region of an electroluminescent device, the method comprising providing a mixture of at least one matrix material and at least one electroluminescent material, wherein at least part of at least one said matrix material is in a molten state and the mixture includes at least one organic semiconductor material and at least one ionic material for providing positive ions and negative ions for contributing to electrochemical doping of at least one said organic semiconductor material.
2. A method according to claim 1, wherein at least one said ionic material comprises at least one organic semiconductor material.
3. A method according to claim 1 or 2, further compris-

ing heating at least part of at least one said matrix material to a molten state thereof and adding at least one said electroluminescent material and/or at least one said organic semiconductor material to said matrix material in said molten state.

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4. A method according to any one of the preceding claims, wherein at least one said electroluminescent material and/or at least one said organic semiconductor material is added in solution form to said matrix material. 10
5. A method according to any one of the preceding claims, further comprising adding at least one plasticiser to at least one said matrix material. 15
6. A method according to any one of the preceding claims, further comprising causing solidification of said mixture. 20
7. A method according to any one of the preceding claims, wherein at least one said matrix material comprises at least one polymer.
8. A method according to any one of the preceding claims, wherein said mixture includes electrically conductive particles. 25
9. A method of forming a light emitting region of an electroluminescent device from a precursor material provided by means of a method according to any one of the preceding claims. 30
10. A method according to claim 9, comprising extruding at least part of said light emitting region. 35
11. A method according to claim 9 or 10, comprising moulding at least part of said light emitting region.
12. A method according to any one of claims 9 to 11, further comprising applying an electric field to at least part of said mixture at a temperature at which ions in the system are mobile and capable of participating in the electrochemical doping and subsequently allowing the said mixture to cool so that electrochemically doped regions resulting from electric field application are maintained upon electric field removal. 40 45

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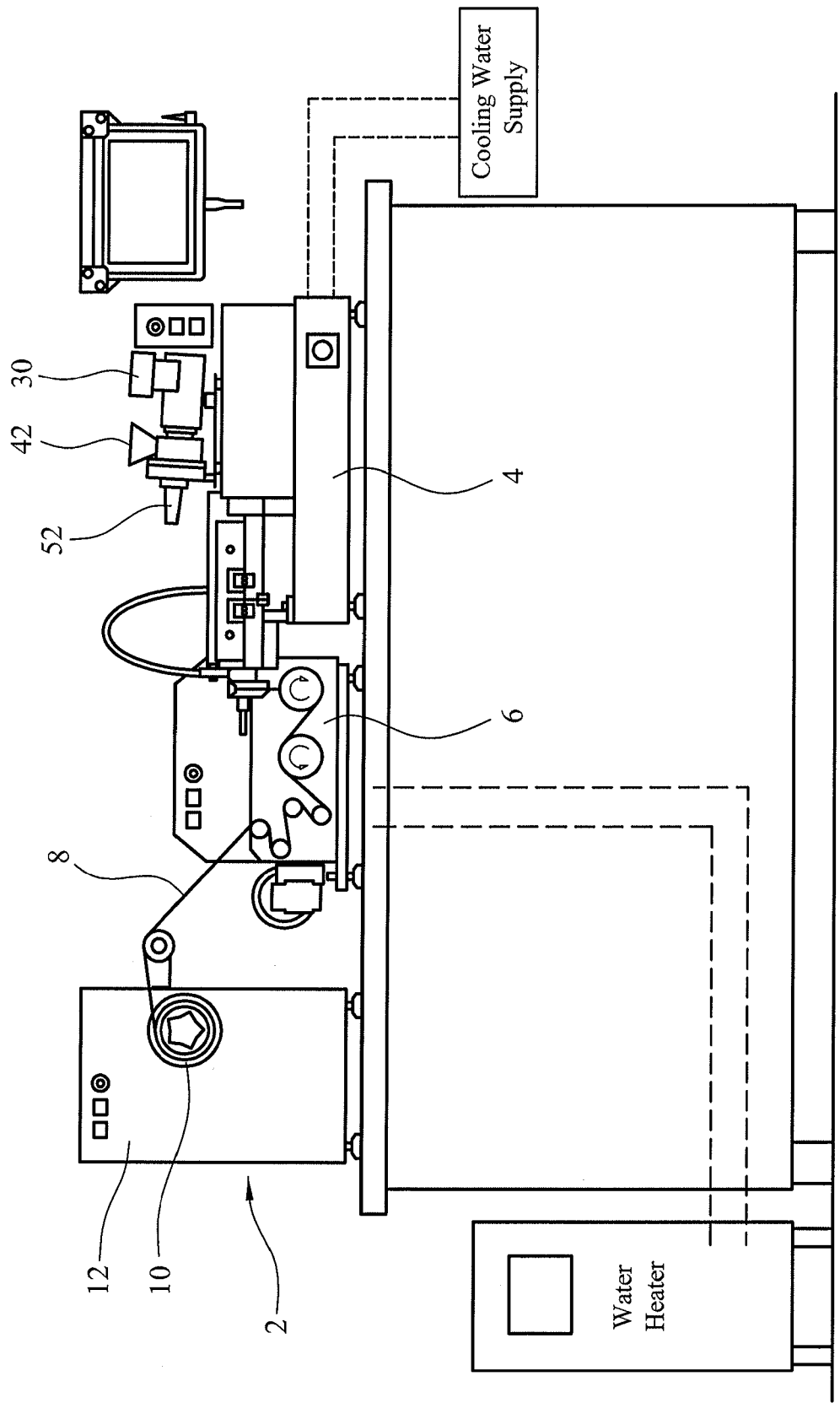


FIG. 1

FIG. 2

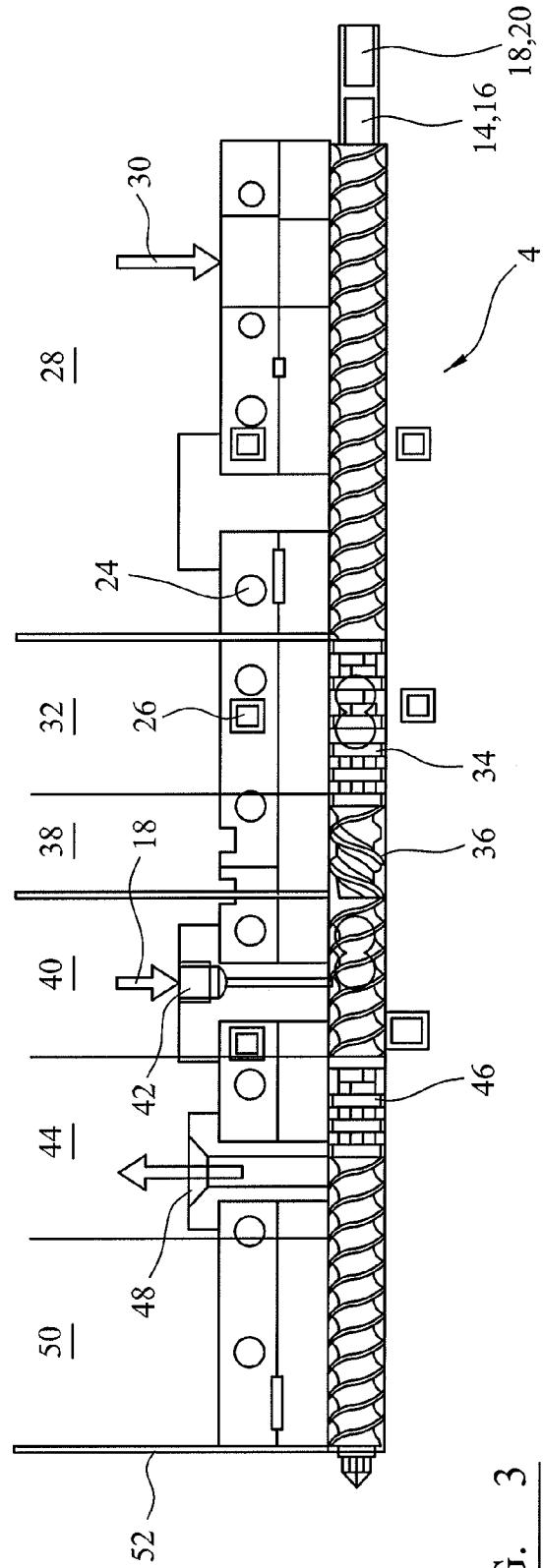
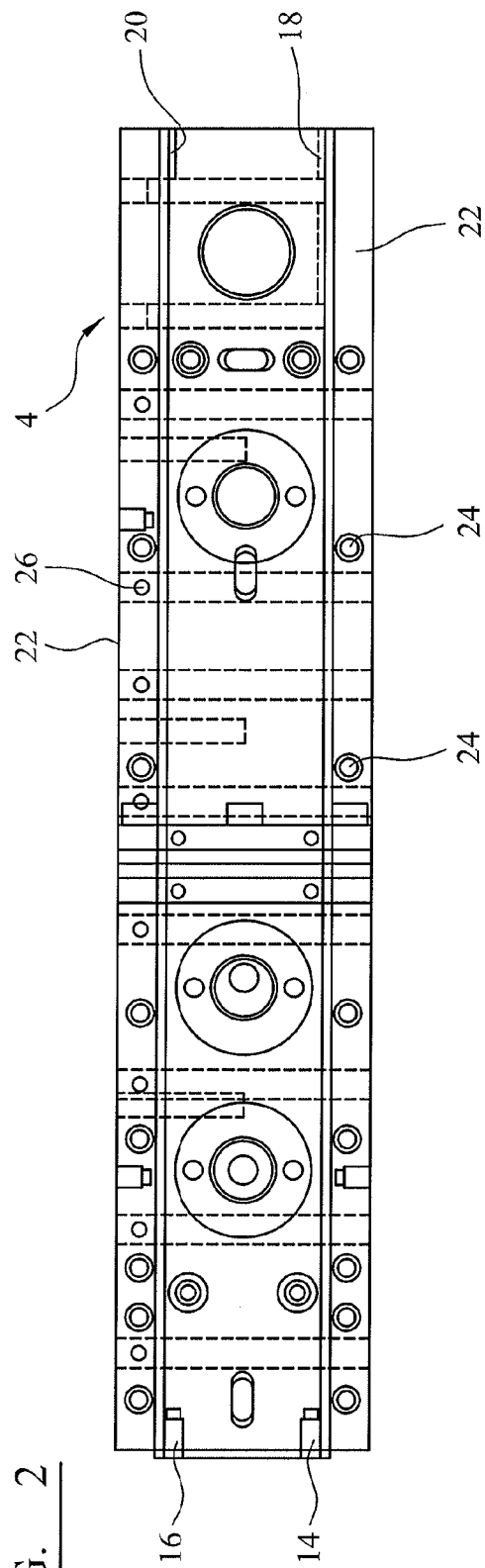


FIG. 3

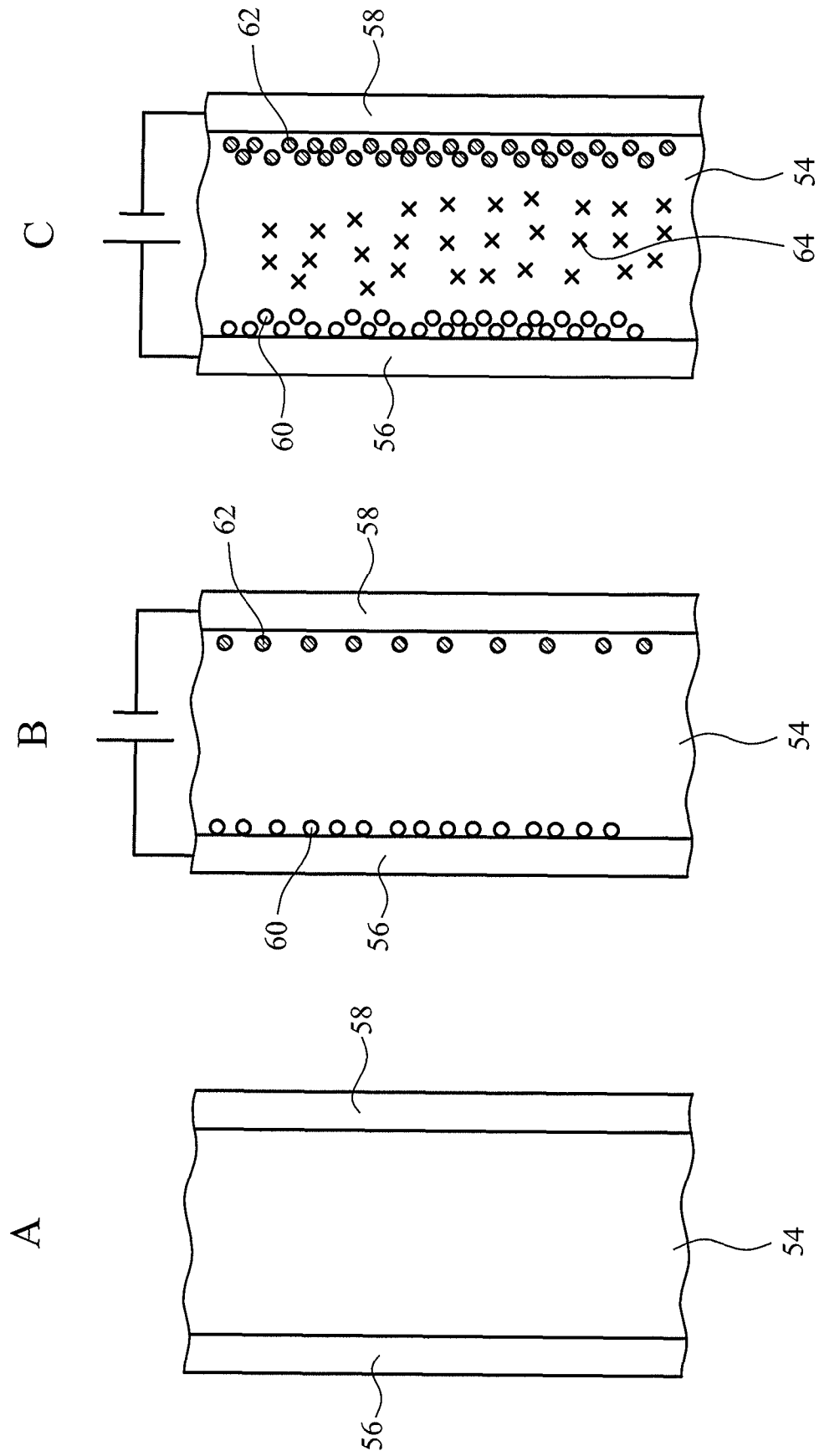


FIG. 4



EUROPEAN SEARCH REPORT

Application Number
EP 11 18 5550

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 96/00983 A1 (UNIAX CORP [US]) 11 January 1996 (1996-01-11)	1,2,4, 6-11	INV. H01L51/50
A	* page 11, line 5 - page 17, line 16 * * page 16, line 22 - line 24 * -----	12	H01L51/00
Y	WO 2006/077509 A1 (KONINKL PHILIPS ELECTRONICS NV [NL]; MEIJER EDUARD J [NL]; MEULENKAMP) 27 July 2006 (2006-07-27) * page 6, line 10 - line 25; figure 7 * -----	1-11	
Y	EP 1 965 451 A1 (SAMSUNG ELECTRONICS CO LTD [KR]) 3 September 2008 (2008-09-03) * paragraph [0051] * -----	1-11	
Y	EP 1 686 635 A1 (SAMSUNG SDI CO LTD [KR]) 2 August 2006 (2006-08-02) * abstract * -----	5	
Y	US 2006/270100 A1 (DEHAVEN PATRICK W [US] ET AL) 30 November 2006 (2006-11-30) * abstract * -----	3	
A	EP 2 017 306 A1 (TORAY INDUSTRIES [JP]) 21 January 2009 (2009-01-21) * the whole document * -----	1-11	TECHNICAL FIELDS SEARCHED (IPC) H01L
E	EP 2 381 503 A1 (POLYPHOTONIX LTD [GB]) 26 October 2011 (2011-10-26) * the whole document * -----	1-11	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 27 March 2012	Examiner Bernabé Prieto, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>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</p> <p>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</p>			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 11 18 5550

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The members are as contained in the European Patent Office EDP file on
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27-03-2012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9600983 A1	11-01-1996	AU 2911995 A	25-01-1996
		DE 69523755 D1	13-12-2001
		DE 69523755 T2	01-08-2002
		EP 0767974 A1	16-04-1997
		JP 4040674 B2	30-01-2008
		JP H10506747 A	30-06-1998
		US 5682043 A	28-10-1997
		WO 9600983 A1	11-01-1996
WO 2006077509 A1	27-07-2006	CN 101107728 A	16-01-2008
		EP 1844502 A1	17-10-2007
		JP 2008529267 A	31-07-2008
		KR 20070098929 A	05-10-2007
		US 2008265752 A1	30-10-2008
		WO 2006077509 A1	27-07-2006
EP 1965451 A1	03-09-2008	NONE	
EP 1686635 A1	02-08-2006	CN 1815698 A	09-08-2006
		EP 1686635 A1	02-08-2006
		JP 4308172 B2	05-08-2009
		JP 2006207023 A	10-08-2006
		KR 20060087915 A	03-08-2006
		US 2006172537 A1	03-08-2006
US 2006270100 A1	30-11-2006	NONE	
EP 2017306 A1	21-01-2009	EP 2017306 A1	21-01-2009
		KR 20080111018 A	22-12-2008
		US 2010273944 A1	28-10-2010
		WO 2007108501 A1	27-09-2007
EP 2381503 A1	26-10-2011	EP 2381503 A1	26-10-2011
		WO 2011131588 A1	27-10-2011

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 1391944 A [0002] [0005]

专利名称(译)	制造用于形成电致发光器件的发光区域的前体材料的方法		
公开(公告)号	EP2584624A1	公开(公告)日	2013-04-24
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[标]申请(专利权)人(译)	波利佛托尼克斯有限公司		
申请(专利权)人(译)	POLYPHOTONIX有限公司		
当前申请(专利权)人(译)	POLYPHOTONIX有限公司		
[标]发明人	ALLOTT RICHARD MARK BOLTON SEAN WILLIAM MIREMONT CHRISTOPHE OLIVIER SNELL THOMAS		
发明人	ALLOTT, RICHARD MARK BOLTON, SEAN WILLIAM MIREMONT, CHRISTOPHE OLIVIER SNELL, THOMAS		
IPC分类号	H01L51/50 H01L51/00		
CPC分类号	H01L51/5032 H01L51/0003		
外部链接	Espacenet		

摘要(译)

公开了一种制造用于形成电致发光器件的发光区域的前体材料的方法。该方法包括提供基质材料和电致发光材料的混合物，其中至少部分基质材料处于熔融状态，并且该混合物包括有机半导体材料和用于提供正离子和负离子的离子材料。电化学掺杂有机半导体材料。

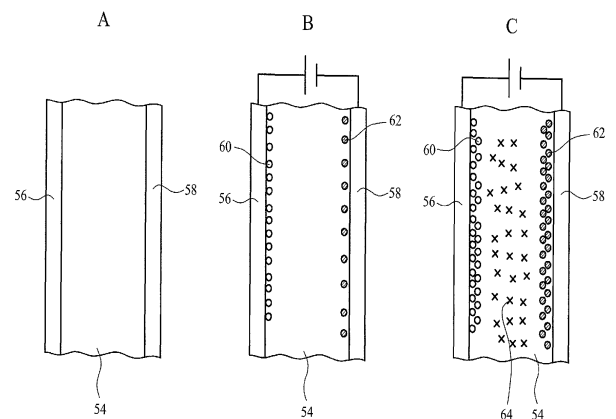


FIG. 4