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(54) **A FORMULATION FOR DEPOSITING A CONJUGATED POLYMER LAYER**

FORMULIERUNG ZUR ABLAGERUNG EINER KONJUGIERTEN POLYMERSCHICHT

FORMULATION PERMETTANT DE DEPOSER UNE COUCHE DE POLYMERE CONJUGUE

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Description

[0001] The present invention relates to a formulation for depositing a conjugated polymer layer in a light-emissive device (LED).

[0002] Light-emissive devices using as the light-emissive layer a semiconductive conjugated polymer are known. Figure 1 shows the construction of a simple light-emissive device. A glass or plastics substrate 2 is coated with an anode layer 4, for example in the form of indium tin oxide. The anode can be patterned in the form of elongate strips. The anode layer may be coated with a hole transport layer. A light-emissive polymer layer 6 is then deposited followed by the deposition of an electron transport layer. The device structure is then completed by the deposition of a cathode layer 8. By way of example, the cathode layer can be calcium or aluminium. The cathode layer 8 can be patterned in crosswise strips to define pixels P where the anode and cathode overlap. Alternatively with an unpatterned cathode, light emissive strips can be defined. Further alternatively, the pixels may be defined on an active matrix back-plane and the cathode may be patterned or unpatterned. When an electric field is applied between the anode and cathode, holes and electrons are injected into the light-emissive polymer layer 6. The holes and electrons recombine in the polymer layer and a proportion decay radiatively to generate light.

[0003] The hole transport layer can be comprised generally of any compound capable of sustaining hole transport. Examples of suitable materials are organic conductors such as the following conducting polymers: polyaniline, polyethylenedioxythiophene and other polythiophenes, polypyrrole, etc. in their doped forms. Other alternative materials are conjugated polyamines and also low molecular weight amines such as TPD.

[0004] The light-emissive layer may comprise any molecular or polymeric compounds which are capable of sustaining charge carrier transport and also capable of light emission under device driving conditions. Examples include fluorescent organic compounds and conjugated polymers such as Alq3, polyphenylenes and derivatives, polyfluorenes and derivatives, polythiophenes and derivatives, polyphenylene vinylenes and derivatives, polymers containing heteroaromatic rings, etc..

[0005] The electron transport layer may generally comprise any material capable of sustaining electron transport. Examples include perylene systems, Alq3, polyfluorenes or polyfluorene copolymers, polymers containing heteroaromatic rings, etc..

[0006] The device may contain any combination of the above layers provided it includes at least one light-emissive layer.

[0007] OLEDs are described in US Patent No. 5,247,190 or in US Patent No. 4,539,507, the contents of which are incorporated herein by reference. In US 5,247,190 the active organic layer is a light-emissive semiconductive conjugated polymer and in US 4,539,507 the active organic layer is a light-emissive sublimed molecular film.

[0008] Conventionally, the polymer layer was typically deposited by spin-coating or metered blade-coating a polymer solution onto the anode and then either allowing the solvent to evaporate at RTP, or driving off the solvent using heat treatment and/or reduced pressure. The polymer was the light-emissive polymer itself cast directly from solution, or a precursor to the polymer, which is converted to the light-emissive polymer during a heat treatment step. The polymer layer can comprise a blend of two or more materials, such as a blend of two or more polymers.

[0009] The polymer layer(s) may also be deposited by supplying a solution-processible material including the polymer through a plurality of elongate bores, either through the effect of gravity or under pressure or utilising the effect of surface tension. This facilitates direct deposition or patterning of the polymer films as required.

[0010] Deposition of the polymer layer(s) by means of an ink-jet method is a particularly preferred technique. The ink-jet method is described, for example, in EP0880303A1, the content of which is incorporated herein by reference.

[0011] It is desirable to use material formulations with which thin polymer films exhibiting excellent emission uniformity can be produced.

[0012] The present applicant's own previous publication WO 0 116 251 A discloses examples of formulations for depositing conjugated polymers based on polyalkylated benzenes such as cymene and isodurene.

[0013] It is also an aim of the present invention to provide formulations that facilitate the direct deposition of patterned polymer films. In particular, it is an aim of the present invention to provide a formulation with which conjugated polymer films that exhibit improved emission uniformity can be deposited.

[0014] According to a first aspect of the present invention, there is provided a formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a trialkyl- substituted aromatic hydrocarbon, at least two of the alkyl substituents being ortho to one another.

[0015] The solvent preferably includes one or more of 1,2,3-trialkylbenzene and 1,2,4-trialkylbenzene. 1,2,3-trialkylbenzene is particularly preferred.

[0016] According to a second aspect of the present invention, there is provided a formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a trialkylbenzene.

[0017] According to a third aspect of the present invention there is provided a method of depositing a polymer layer by supplying a solution processible formulation according to the first or second aspects of the present invention via a plurality of elongate bores onto

a substrate.

[0018] According to a fourth aspect of the present invention, there is provided a method of forming a polymer layer on a substrate comprising the step of depositing a formulation according to the first or second aspects of the present invention on a substrate by an ink-jet method.

[0019] For the purposes of this application, the term "polymer" includes homopolymers and copolymers, and also includes layers of polymer blends as well as layers of single polymers; and the term "polymer layer" includes a layer of relatively small dimensions, such as a layer having dimensions corresponding to a single pixel in a pixelated display, as well as layers of larger dimensions.

[0020] For the purposes of this application, the term "alkyl" refers to linear or branched alkyl substituents having up to 6 carbon atoms.

[0021] The resulting formulation preferably has a surface tension in the range of 25 to 40mN/m at 20°C, a viscosity of 2 to 8cPs at 20°C, and a w/v polymer concentration of 0.25 to 1.5%, preferably 0.5 to 1%. A formulation having such properties is particularly suited for deposition by ink-jet printing. The formulation should also have a contact angle appropriate for the substrate on which the deposition is carried out. For example, in the case of a polyimide substrate, the contact angle should be in the range of 30 to 60 degrees.

[0022] The formulation may include one or more additional types of solvents provided that the resulting formulation has the necessary fluid properties for the particular deposition technique. The presence of even a relatively small proportion of, for example, one or more trialkyl benzenes in the formulation can serve to improve the stability of the formulation and/or the fluid properties of the formulation.

[0023] For the purposes of this application, the term conjugated polymer refers to polymers, including oligomers such as dimers, trimers etc., which are fully conjugated (i.e. are conjugated along the entire length of the polymer chain) or are partially conjugated (i.e. which include non-conjugated segments in addition to conjugated segments).

[0024] The polymer may have an average molecular weight in the range of 10,000 to 500,000, more particularly in the range of 10,000 to 300,000.

[0025] The polymer may be a polymer suitable for use in a light-emissive layer, a hole transport layer or an electron transport layer in an organic light-emissive device.

[0026] In a preferred example, the conjugated polymer can be a light-emissive polymer, hole transport polymer or electron transport polymer itself, or a precursor to a light-emissive polymer, hole transport polymer or electron transport polymer. The conjugated polymer or its precursor can be any suitable polymer, and in particular can be any one of the following:

a) conducting polymers such as polyaniline (PANI) and derivatives, polythiophenes and derivatives, polypyrrole and derivatives, polyethylene dioxythiophene; doped forms of all these and particularly polystyrene sulphonic acid-doped polyethylene dioxythiophene (PEDT/PSS);

b) solution processible charge transporting and/or luminescent/electro-luminescent polymers, preferably conjugated polymers such as: polyphenylenes and derivatives, polyphenylene vinylenes and derivatives, polyfluorenes and derivatives, tri-aryl containing polymers and derivatives, precursor polymers in various forms, copolymers (including the above-named polymer classes), generally random and block copolymers, polymers with the active (charge transporting and/or luminescent) species attached as side-groups to the main chain, thiophenes and derivatives, etc..

[0027] The conjugated polymer may, for example, comprise a fluorene-based polymer, or a copolymer containing fluorene units with other units such as triarylamine units or benzylthiadiazole (BT) units, or a blend of two or more of such polymers.

[0028] For a better understanding of the invention and to show how the same may be carried into effect, embodiments of the present invention are described hereunder, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a diagram of a light-emissive device;
Figure 2 is a diagram illustrating a method of depositing various polymer layers; and
Figure 3 shows the structure of recurring units and polymers used in the examples.

[0029] Figure 2 illustrates a deposition technique for depositing a polymer layer 6 onto the patterned anode 4. A plurality of elongate bores 10 are illustrated, each aligned with a respective trough 8. The elongate bores 10 are connected via a conduit 12 to a reservoir 14 holding the solution to be deposited. The solution is supplied through the elongate bores 10 under pressure or by gravity to deposit the light emitting polymer layer 6.

[0030] Specific formulations according to the present invention are discussed herebelow.

Example 1

[0031] The first exemplified formulation is 1% w/v of a triblend containing approximately 14 wt.% of a ternary polymer containing fluorene (F8) units (shown in Figure 3a), benzylthiadiazole (BT) units (shown in Figure 3b) and triarylene units shown in Figure 3c, 56 wt.% of F8BT (shown in Figure 3d) and 30wt.% TFB (shown in Figure 3e) in 1,2,4 trimethylbenzene. The resulting formulation had a viscosity of 3.8cps at 20°C and a surface tension

of 28mN/m at 20°C.

Example 2

[0032] According to the second example, the formulation comprises 1% w/v of the triblend referred to in Example 1 in a solvent mixture containing 20vol.% 1,2,4-trimethylbenzene and 80vol.% xylene. The formulation had a solution viscosity of 2.9cps at 20°C and a surface tension of 28mN/m at 20°C.

[0033] A sample of the formulation was deposited on a substrate and was vacuum dried. The PL efficiency of the thus produced polymer layer was found to be 43%. Drying a layer of the same formulation at 80°C for 13.5 hours resulted in a polymer layer having a PL efficiency of 39%.

Example 3

[0034] According to a third example, the formulation comprises 1% w/v of the triblend referred to in Example 1 in a solvent mixture containing 50vol.% 1,2,4-trimethylbenzene and 50vol.% xylene. The formulation had a solution viscosity of 2.82cps at 20°C and a surface tension of 28mN/m at 20°C.

[0035] The addition of the trimethyl benzene is found to significantly increase the stability of the formulation.

[0036] 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene were also found to be good solvents for a fluorene-thiophene polymer having an average molecular weight of about 266,000.

Claims

1. A formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a trialkyl- substituted aromatic hydrocarbon, at least two of the alkyl substituents being ortho to one another.

2. A formulation according to claim 1 wherein the solvent includes a trialkyl-substituted benzene, at least two of the alkyl substituents being ortho to one another.

3. A formulation according to claim 1 or claim 2 wherein each alkyl substituent is independently a C1-C6 alkyl group.

4. A formulation according to claim 3 wherein each alkyl substituent is a methyl group.

5. A formulation according to claim 4 wherein the solvent includes 1,2,3-trimethylbenzene.

6. A formulation according to claim 2 wherein the solvent also includes xylene.

7. A formulation according to claim 6 wherein the solvent comprises 20% to 100% by weight of a trialkylbenzene and up to 80% by weight of xylene.

8. A formulation according to any preceding claim wherein the conjugated polymer is a light-emissive polymer.

9. A formulation according to any preceding claim wherein the polymer includes a fluorene-based, polymer.

10. A formulation according to any preceding claim wherein the polymer includes a polymer containing fluorene and triarylamine units.

11. A formulation according to any preceding claim wherein the polymer comprises a blend of a fluorene-based polymer and a polymer containing fluorene and triarylamine units.

12. A method of depositing a polymer layer by supplying a solution processible formulation according to any preceding claim via a plurality of elongate bores onto a substrate.

13. A method of forming a polymer layer on a substrate comprising the step of depositing a formulation according to any preceding claim on a substrate by ink-jet printing.

14. The use of a formulation according to any preceding claim in an ink-jet method of depositing a polymer layer.

Patentansprüche

1. Formulierung zur Abscheidung einer Polymerschicht bei der Herstellung einer lichtemittierenden Anordnung, wobei die Formulierung ein in einem Lösungsmittel gelöstes konjugiertes Polymer enthält, und wobei das Lösungsmittel einen trialkylsubstituierten aromatischen Kohlenwasserstoff enthält, bei dem mindestens zwei der Alkylsubstituenten orthoständig zueinander angeordnet sind.

2. Formulierung nach Anspruch 1, bei der das Lösungsmittel ein trialkylsubstituiertes Benzol enthält, bei dem mindestens zwei der Alkylsubstituenten orthoständig zueinander angeordnet sind.

3. Formulierung nach Anspruch 1 oder 2, worin jeder Alkylsubstituent, unabhängig voneinander, eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen ist.

4. Formulierung nach Anspruch 3, worin jeder Alkylsubstituent eine Methylgruppe ist.

5. Formulierung nach Anspruch 4, bei der das Lösungsmittel 1,2,3-Trimethylbenzol enthält.

6. Formulierung nach Anspruch 2, bei der das Lösungsmittel ferner Xylol enthält.

7. Formulierung nach Anspruch 6, bei der das Lösungsmittel 20 bis 100 Gew.-% eines Trialkylbenzols und bis zu 80 Gew.-% Xylol umfaßt.

8. Formulierung nach einem der vorhergehenden Ansprüche, bei der das konjugierte Polymer ein lichtemittierendes Polymer ist.

9. Formulierung nach einem der vorhergehenden Ansprüche, bei der das Polymer ein auf Fluoren basierendes Polymer enthält.

10. Formulierung nach einem der vorhergehenden Ansprüche, bei der das Polymer ein Fluoren- und Triarylamin-Einheiten enthaltendes Polymer enthält.

11. Formulierung nach einem der vorhergehenden Ansprüche, bei der das Polymer eine Mischung aus einem auf Fluoren basierenden Polymer und einem Fluoren- und Triarylamin-Einheiten enthaltenden Polymer umfaßt.

12. Verfahren zur Abscheidung einer Polymerschicht durch Zuführen einer als Lösung verarbeitbaren Formulierung gemäß einem der vorhergehenden Ansprüche über eine Vielzahl von Schlitzlöchern auf das Substrat.

13. Verfahren zur Bildung einer Polymerschicht auf einem Substrat, das die Abscheidung einer Formulierung gemäß einem der vorhergehenden Ansprüche auf ein Substrat mittels Farbstrahldrucken umfaßt.

14. Verwendung der Formulierung gemäß einem der vorhergehenden Ansprüche in einem Farbstrahl-Verfahren zur Abscheidung einer Polymerschicht.

Revendications

1. Formulation permettant le dépôt d'une couche de polymère dans la production d'un dispositif émetteur de lumière, la formulation incluant un polymère conjugué dissous dans un solvant, le solvant incluant un hydrocarbure aromatique substitué par un groupement trialkyle, au moins deux des substituants alkyles se trouvant en position ortho l'un par rapport à l'autre.

2. Formulation selon la revendication 1, dans laquelle le solvant inclut un benzène substitué par un groupement trialkyle, au moins deux des substituants alkyles se trouvant en position ortho l'un par rapport à l'autre.

3. Formulation selon la revendication 1 ou la revendication 2, dans laquelle un substituant alkyle est indépendamment un groupement alkyle en C1 à C6.

4. Formulation selon la revendication 3, dans laquelle chaque substituant alkyle est un groupement méthyle.

5. Formulation selon la revendication 4, dans laquelle le solvant inclut du 1,2,3-triméthylbenzène.

6. Formulation selon la revendication 2, dans laquelle le solvant inclut également du xylène.

7. Formulation selon la revendication 6, dans laquelle le solvant comprend de 20 % à 100 % en poids d'un trialkylbenzène et jusqu'à 80 % en poids de xylène.

8. Formulation selon l'une quelconque des précédentes revendications, dans laquelle le polymère conjugué est un polymère émetteur de lumière.

9. Formulation selon l'une quelconque des précédentes revendications, dans laquelle le polymère inclut un polymère à base de fluorène.

10. Formulation selon l'une quelconque des précédentes revendications, dans laquelle le polymère inclut un polymère contenant des unités fluorène et triarylamine.

11. Formulation selon l'une quelconque des précédentes revendications, dans laquelle le polymère comprend un mélange d'un polymère à base de fluorène et d'un polymère contenant des unités fluorène et triarylamine.

12. Procédé de dépôt d'une couche de polymère par apport d'une formulation pouvant être traitée en solution selon l'une quelconque des précédentes revendications via un grand nombre de trous allongés sur un substrat.

13. Procédé de formation d'une couche de polymère sur un substrat, comprenant l'étape de dépôt d'une formulation selon l'une quelconque des précédentes revendications sur un substrat par impression à jet d'encre.

14. Utilisation d'une formulation selon l'une quelconque des précédentes revendications dans un procédé à jet d'encre de dépôt d'une couche de polymère.

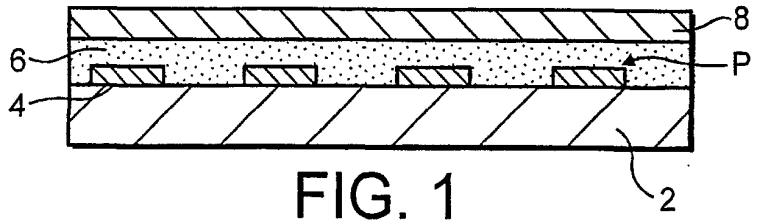

FIG. 1

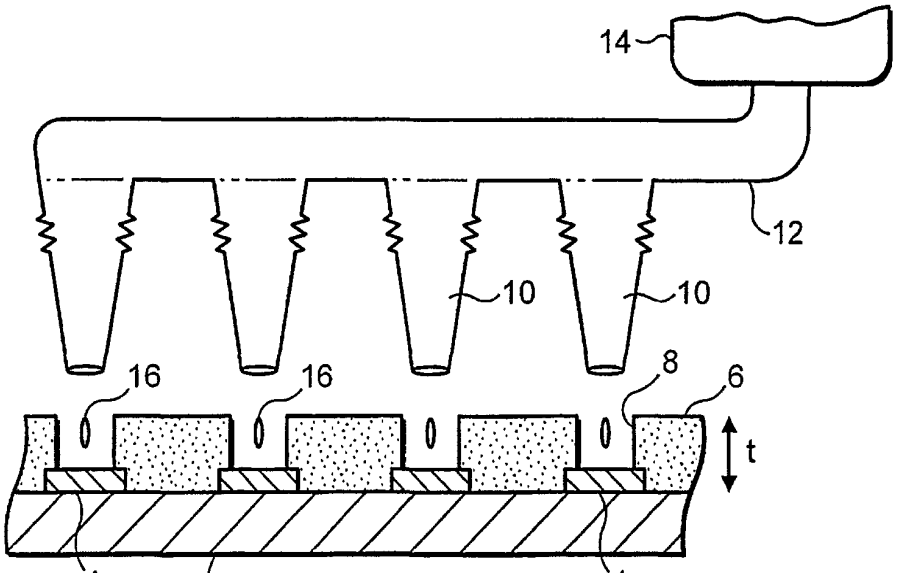

FIG. 2

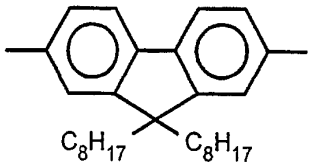

FIG. 3a

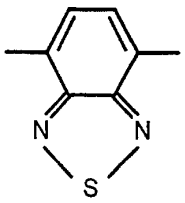

FIG. 3b

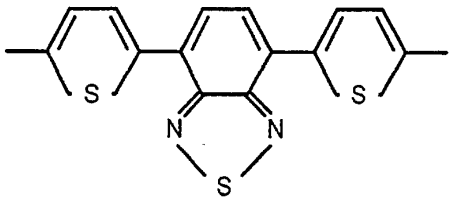

FIG. 3c

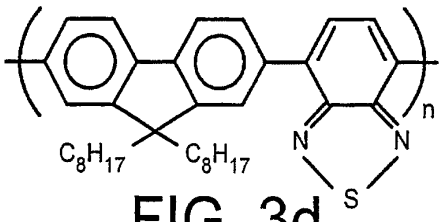

FIG. 3d

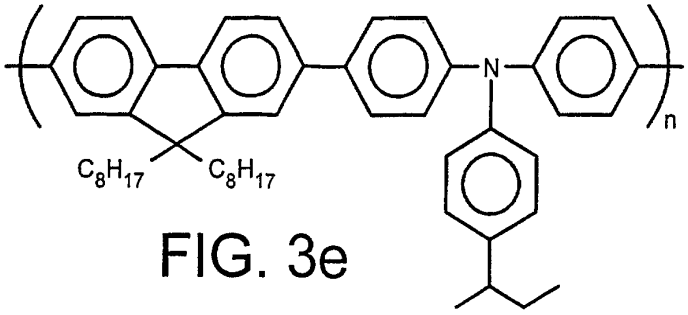

FIG. 3e

专利名称(译)	用于沉积共轭聚合物层的配方		
公开(公告)号	EP1313822B1	公开(公告)日	2004-11-10
申请号	EP2001907930	申请日	2001-02-28
[标]申请(专利权)人(译)	剑桥显示技术有限公司		
申请(专利权)人(译)	剑桥显示科技有限公司		
当前申请(专利权)人(译)	剑桥显示科技有限公司		
[标]发明人	GRIZZI ILLARIA CAMBRIDGE DISPLAY TECH LTD LYON PETER CAMBRIDGE DISPLAY TECH LIMITED		
发明人	GRIZZI, ILLARIA, CAMBRIDGE DISPLAY TECHNOLOGY LTD. LYON, PETER, CAMBRIDGE DISPLAY TECHNOLOGY LIMITED		
IPC分类号	C09K11/06 C08K5/01 C08L45/00 H01L51/00 H01L51/40 H01L51/50 H05B33/14		
CPC分类号	H01L51/0005 H01L51/0007 H01L51/0036 H01L51/0039 H01L51/0043 H01L51/5012 H01L51/56		
优先权	PCT/GB2000/003349 2000-08-30 WO		
其他公开文献	EP1313822A1		
外部链接	Espacenet		

摘要(译)

用于在制造发光装置中沉积聚合物层的配方，该配方包括溶解在溶剂中的共轭聚合物，该溶剂包括二烷基 - 或三烷基 - 取代的芳烃，至少两个烷基取代基是邻位的彼此;以及这种配方在通过喷墨方法在基板上沉积聚合物层的用途。

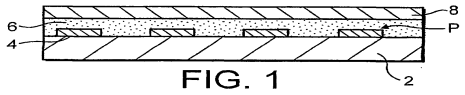

FIG. 1

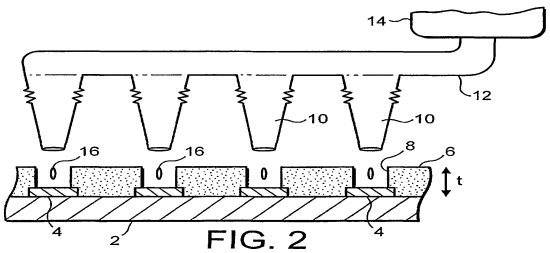

FIG. 2