(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 624 504 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
12.10.2016 Bulletin 2016/41

(51) Int Cl.:
H01L 51/50 *(2006.01)* ***H01L 51/52*** *(2006.01)*

(21) Application number: **05107135.5**

(22) Date of filing: **02.08.2005**

(54) **OLEDs having inorganic material containing anode capping layer**

OLEDs mit einer ein anorganisches Material enthaltender Anode-Abdeckschicht

OLEDs ayant une couche recouvrant l'anode composée d'un materiau inorganique

(84) Designated Contracting States:
DE FR GB

(30) Priority: **02.08.2004 US 909691**

(43) Date of publication of application:
08.02.2006 Bulletin 2006/06

(60) Divisional application:
16163236.9 / 3 057 152

(73) Proprietor: **LG Display Co., Ltd.**
Yeongdeungpo-gu
Seoul
07336 (KR)

(72) Inventors:
- **Aziz, Hany**
  L6H 7L6, Oakville (CA)
- **Popovic, Zoran D.**
  L5L 2Z8, Mississauga (CA)
- **Coggan, Jennifer A.**
  N3C 4L6, Cambridge (CA)

(74) Representative: **Ter Meer Steinmeister & Partner**
Patentanwälte mbB
Nymphenburger Straße 4
80335 München (DE)

(56) References cited:
EP-A- 1 017 118 **EP-A- 1 167 488**
WO-A-03/055275 **WO-A-03/088718**
US-A1- 2003 116 772

- **PATENT ABSTRACTS OF JAPAN vol. 2003, no. 12, 5 December 2003 (2003-12-05) -& JP 2004 139981 A (DAINIPPON PRINTING CO LTD; KIDO JUNJI), 13 May 2004 (2004-05-13)**

EP 1 624 504 B1

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

[0001] Organic Light Emitting Devices (referred herein as "OLED" or "OLEDs") represent a promising technology for display applications. For full color display applications, red-emitting, green-emitting and blue-emitting OLEDs with satisfactory performance are desired. Although in terms of efficiency and brightness, OLEDs can be utilized in the majority of display applications, their luminance stability continues to be a limiting factor, especially for blue-emitting OLEDs. Although recent advances have led to the realization of red-emitting and green-emitting OLEDs with a half-life exceeding 10,000 hours, thus making them suitable for a number of commercial applications (e.g., avionic and automotive displays, and personal and hand held electronics), luminance stability of blue-emitting OLEDs is still limited in many instances to about 1,000 hours, rendering them unsuitable for many of these applications. Therefore, there is still a need, addressed by embodiments of the present invention, to increase the luminance stability of OLEDs emitting in various colors in general, and in blue in particular, to make them suitable for utilization in a wide variety of commercial applications. Document US 2003/116772 A1 relates to a light emitting device made of a cathode, an organic compound layer and an anode, wherein a protection film is formed in an interface between the anode that is a light exit electrode and the organic compound layer. Document EP-A-1 167 488 relates to an organic electroluminescence device comprising a layer of an organic light emitting medium, which is disposed between a pair of electrodes and comprises:

(A) a mono-, di-, tri- or tetrastyryl derivative containing amine and
(B) an anthracene derivative having a specific structure.

[0002] Document JP 2004 139981 A relates to a display element and its manufacturing method, wherein the display element comprises a first electrode, a luminescent layer, a second electrode, and a transparent base material. The first electrode is composed of a metal layer, and a corrosion-resistant charge-injection promoting layer.

[0003] Document EP-A-1 017 118 relates to an organic electroluminescent element comprising at least a light emitting layer containing an organic light emitting material placed between the anode and a cathode, wherein the element has, between the anode and the light emitting layer, at least a hole transporting layer containing a hole transporting material and an acceptor, and an electron injection restraining layer restraining the injection of electrons from the light emitting layer into the hole transporting layer, from the anode side, and/or, between the light emitting layer and the cathode, at least an electron transporting layer containing an electron transporting material and a donor, and a hole injection restraining layer restraining the injection of holes from the light emitting layer into the electron transporting layer, from the cathode side (c.f. abstract).

[0004] Document WO 03/055275 A discloses an electrode structure for electronic and optoelectronic devices. Such a device comprises a first electrode substantially having a conductive layer, a non-metal layer formed on the conductive there, a fluorocarbon layer formed on the non-metal layer, and a second electrode formed on the structure.

[0005] WO03/088718 discloses an electroluminescent device wherein the anode can comprise a metal-organic mixed layer.

SUMMARY OF THE DISCLOSURE

[0006] In embodiments of the present invention, there is provided an organic light emitting device as defined in claim 1. Preferred embodiments of the present invention are defined in the dependent claims 2 to 4.

DETAILED DESCRIPTION

[0007] As used herein, "luminance stability" or "stability" refers to the length of time that an OLED emits light; unless otherwise noted, any recited value for the "luminance stability" is the half-life in hours of the OLED where half-life is the length of time that the emitted light drops in intensity by 50 % after the initial bum-in period.

[0008] The term "layer" indicates a single coating generally having a composition that differs from the composition of an adjacent layer.

[0009] One, two, three or more adjacent layers may be collectively referred to as a "region."

[0010] The term "zone" refers to a functional area in a layer where there may be one, two, three or more "zones" (i.e., functional areas) in a layer.

[0011] For convenience, the layer including an organic electroluminescent material is referred herein as "electroluminescent layer."

[0012] For convenience, the layer including an electron accepting material is referred herein as "electron accepting layer."

[0013] For certain layers, there may not be a universally accepted classification system for designating those layers as belonging to a particular region of the OLED (such as "Cathode," Light Emitting Region," "Anode Capping Region," "Anode," and "Substrate"). For example, the anode capping layer is described in the section pertaining to the "Anode Capping Region" but the anode capping layer (and the "Anode Capping Region") could alternatively have been designated as part of the "Anode." In addition, in certain embodiments, the electron accepting layer may be described as part of the "Light Emitting Region," whereas in other embodiments the electron accepting layer may be described as part of the "Anode Capping Region." While the OLED region names is a useful classification system, it is recognized that the present invention is not limited by any arbitrary designation of certain layers as being part of one region or as part of another adjacent region.

[0014] Embodiments of the present invention encompass one or more additional layers in the OLED configurations inserted in the sequence before or after each of the electroluminescent layer, the electron accepting layer and the anode capping layer while maintaining the general sequence (referred herein as "General Sequence") of the cathode, the electroluminescent layer, the electron accepting layer, the anode capping layer, and the anode, wherein the substrate can be before the cathode or after the anode. For example, in embodiments where there are two anode capping layers, the electron accepting layer may be sandwiched between the two anode capping layers; in such embodiments, the presence of the additional anode capping layer before the electron accepting layer does not break the General Sequence since the electron accepting layer is still after the electroluminescent layer and there is an anode capping layer after the electron accepting layer.

[0015] The layers of the present OLEDs may be transparent (light transmissive) or opaque (non-light transmissive) depending on the side of the OLED that is facing the viewer. In embodiments, either the anode side, the cathode side, or both the anode side and the cathode side may be light transmissive. In embodiments, light transmissive layers of the present OLEDs have a degree of light transmission of visible light of for example at least 70 %, or at least 90 %. Illustrative materials will now be discussed in constructing embodiments of the present OLED.

CATHODE

[0016] A cathode is composed of one, two, or more layers. The thickness of the cathode can range from, for example, 10 nanometers to 1,000 nanometers. Thicknesses outside of this range can also be used.

[0017] The cathode can comprise suitable electron injecting materials, such as metals, including high work function components, such as metals with, for example, a work function from 4 eV to 6 eV, or low work function components, such as metals with, for example, a work function of from 2 eV to 4 eV. The cathode can comprise a combination of a low work function (less than 4 eV) metal and at least one other metal. Effective proportions of the low work function metal to the second or other metal are from less than 0.1 weight percent to 99.9 weight percent. Illustrative examples of low work function metals include, but are not limited to, alkaline metals such as lithium or sodium; Group 2A or alkaline earth metals such as beryllium, magnesium, calcium or barium; and Group III metals including rare earth metals and the actinide group metals such as scandium, yttrium, lanthanum, cerium, europium, terbium or actinium. Lithium, magnesium and calcium are preferred low work function metals. The Mg-Ag alloy cathodes described in US Patent 4,885,211, US Patent 4,720,432, and US Patent 5,703,436 are exemplary cathode materials for forming the cathodes. In embodiments, the cathode includes a metal-organic mixed layer (MOML) as described in US Patent Application Publication 2002/0180349 A1. Other exemplary cathodes are described in US Patent 5,429,884. The cathodes can be formed from lithium alloys with other high work function metals such as aluminum and indium.

[0018] Optionally, the cathode may further include a separate electron injection layer, contacting the light emitting region. Examples of suitable materials that can be used in the electron injection layer include the alkaline earth metal oxides like SrO, CaO, BaO, Li_2O and others such as those disclosed in US Patents 5,457,565 and 5,739,635 and other metal oxides such as Al_2O_3, SiO and SiO_2. A preferred class of metal compounds that can be utilized in the electron injection layer is the alkaline metal halides such as, for example, LiF, LiCl, NaCl, KF, KCl, CsF, and others disclosed in the above referenced US Patent 5,739,635 and also those disclosed in US Patent 5,776,622.

[0019] A substantially transparent, light transmissive cathode can comprise very thin substantially transparent metallic layer or layers comprising a metal with a work function ranging from 2 eV to 4 eV, such as Mg, Ag, Al, Ca, In, Li, Ba, Cs and their alloys such as Mg:Ag alloys, comprised of, for example, from 80 to 95 volume percent of Mg and 20 to 5 volume percent of Ag, and Li:Al alloys, comprised of, for example, from 90 to 99 volume percent of Al, and from 10 to 1 volume percent of Li, and the like, having a thickness, for example, from 10 Å to 200 Å, and, particularly, from 30 Å to 100 Å. Of course, a thickness outside of this range can also be used.

[0020] In embodiments of the OLED, the cathode can be opaque (i.e., non-light transmissive) where the anode is light transmissive. Such an opaque cathode is fabricated from the materials described herein and having a thickness ranging for example from 50 nm to 2 mm.

LIGHT EMITTING REGION

1. Electroluminescent Material and Charge Transport Material

[0021] The light emitting region is composed of an organic electroluminescent material, and optionally other materials described herein, wherein the light emitting region contains one, two, or more layers. One layer of the light emitting region is the electroluminescent layer which includes one, two, or more organic electroluminescent materials.

[0022] Where there are present in a layer two or more organic electroluminescent materials, each organic electroluminescent material may be present at any suitable volume ratio such as for example from 99(first material): 1 (second material) to 1 (first material):99(second material).

[0023] Suitable organic electroluminescent materials include, for example, polyphenylenevinylenes, such as poly(p-phenylenevinylene) ("PPV"), poly(2-methoxy-5-(2-ethylhexyloxy)1,4-phenylenevinylene) ("MeHPPV") and poly(2,5-dialkoxyphenylenevinylene) ("PDMeOPV"), and other materials disclosed in US Patent 5,247,190; polyphenylenes, such as poly(p-phenylene) ("PPP"), ladder-poly-paraphenylene ("LPPP"), and poly(tetrahydropyrene) ("PTHP"); and polyfluorenes, such as poly(9,9-di-n-octylfluorene-2,7-diyl), poly(2,8-(6,7,12,12-tetraalkylindenofluorene) and copolymers containing fluorenes such as fluorene-amine copolymers (see e.g., Bernius et al., "Developmental Progress of Electroluminescent Polymeric Materials and Devices," Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices III, Denver, Colorado, July 1999, Volume 3797, p. 129).

[0024] Another class of suitable organic electroluminescent materials includes, but is not limited to, the metal oxinoid compounds as disclosed in US Patents 4,539,507; 5,151,629; 5,150,006; 5,141,671 and 5,846,666. Illustrative examples include tris(8-hydroxyquinolinate) aluminum ("AlQ3"), which is one preferred example, and bis(8-hydroxyquinolato)-(4-phenylphenolato) aluminum ("Balq") which is another preferred example. Other examples of this class of materials include tris(8-hydroxyquinolinate) gallium, bis(8-hydroxyquinolinate) magnesium, bis(8-hydroxyquinolinate) zinc, tris(5-methyl-8-hydroxyquinolinate) aluminum, tris(7-propyl-8-quinolinolato) aluminum, bis[benzo{f}-8-quinolinate]zinc, bis(10-hydroxybenzo[h]quinolinate) beryllium, and the like, and metal thioxinoid compounds disclosed in US Patent 5,846,666, such as metal thioxinoid compounds of bis(8-quinolinethiolato)zinc, bis(8-quinolinethiolato)cadmium, tris(8-quinolinethiolato)gallium, tris(8-quinolinethiolato)indium, bis(5-methylquinolinethiolato)zinc, tris(5-methylquinolinethiolato)gallium, tris(5-methylquinolinethiolato)indium, bis(5-methylquinolinethiolato)cadmium, bis(3-methylquinolinethiolato)cadmium, bis(5-methylquinolinethiolato)zinc, bis[benzo{f}-8-quinolinethiolato]zinc, bis[3-methylbenzo {f}-8-quinolinethiolato]zinc, bis[3,7-dimethylbenzo{f}-8-quinolinethiolato]zinc. Preferred materials are bis(8-quinolinethiolato)zinc, bis(8-quinolinethiolato)cadmium, tris(8-quinolinethiolato)gallium, tris(8-quinolinethiolato)indium and bis[benzo{f}-8-quinolinethiolato]zinc.

[0025] More specifically, a class of suitable organic electroluminescent materials comprises stilbene derivatives, such as those disclosed in US Patent 5,516,577. A preferred stilbene derivative is 4,4'-bis(2,2-diphenylvinyl)biphenyl.

[0026] Another class of suitable organic electroluminescent materials is the oxadiazole metal chelates disclosed in US Application No. 08/829,398, corresponding to US Patent 5,925,472. These materials include bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1 ,3,4-oxadiazolato]beryllium; bis[5-biphenyl-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]zinc; bis[5-biphenyl-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]beryllium; bis(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]lithium; bis[2-(2-hydroxyphenyl)-5-p-tolyl-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-p-tolyl-1,3,4-oxadiazolato]beryllium; bis[5-(p-tert-butylphenyl)-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]zinc; bis[5-(p-tert-butylphenyl)-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(3-fluorophenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazolato]beryllium; bis[5-(4-chlorophenyl)-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxy-4-methylphenyl)-5-phenyl-1,3,4-oxadiazolato]zinc; bis[2- -(2-hydroxynaphthyl)-5-phenyl-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-p-pyridyl-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-p-pyridyl-1,3,4-oxadiazolato]beryllium, bis[2-(2-hydroxyphenyl)-5-(2-thiophenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-thiadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-thiadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-thiadiazolato]zinc; and bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-thiadiazolato]beryllium; and the triazines including those disclosed in US Application No. 09/489,144, filed on January 21, 2000 and US Patent 6,057,048y.

[0027] A blue organic electroluminescent material is described herein and may be for example a polyfluorene such as those mentioned above, an anthracene derivative, such as, those described, for example, in US Patent 6,479,172, US Patent 6,562,485, US Patent 6,465,115, and US Patent 6,565,996, like 9,10-diphenylanthracene ("DPA"), 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene ("ADN"), and tertiary-butyl substituted 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene ("TBADN" also sometimes given the acronym "BH2"), a stilbene derivative such as those described above, a triazine derivative, such as those described in US Patent 6,229,012, a carbazole derivative including bicarbazole derivatives, or a binaphtyl derivative, such as those described in US Application Serial No. 10/774,577, filed February 10, 2004.

[0028] A red organic electroluminescent material is described herein and may be for example a polyfluorene, such as those mentioned above, a poly phenylene vinylene, such as MeHPPV, or others as described above. In embodiments, certain red emitting OLEDs utilize an electroluminescent material that by itself would emit green or blue, but is doped with one or two red luminescent materials.

[0029] A green organic electroluminescent material is described herein and may be for example, a polyfluorene, as those described above, a poly phenylenevinylene as those described above, or a metal chelate such as tris(8-hydroxyquinoline) aluminum ("AlQ3"), or others as those described above. In embodiments, certain green emitting OLEDs utilize an electroluminescent material that by itself would emit blue, but is doped with one or two green luminescent materials.

[0030] The light emitting region (in the electroluminescent layer and/or other layer(s) of the light emitting region) can further include from 0.01 weight percent to 25 weight percent of a luminescent material as a dopant. In embodiments, the dopant is an organic luminescent material including but not limited to electroluminescent materials of the type described herein, where the organic luminescent dopant may be for instance an organometallic compound. Examples of dopant materials that can be utilized in the light emitting region are fluorescent materials, such as, for example, coumarin, dicyanomethylene pyranes, polymethine, oxabenzanthrane, xanthene, pyrylium, carbostyl, perylene. Another preferred class of fluorescent materials are quinacridone dyes. Illustrative examples of quinacridone dyes include quinacridone, 2-methylquinacridone, 2,9-dimethylquinacridone, 2-chloroquinacridone, 2-fluoroquinacridone, 1,2-benzoquinacridone, N,N'-dimethylquinacridone, N,N'-dimethyl-2-methylquinacridone, N,N'-dimethyl-2,9-dimethylquinacridone, N,N'-dimethyl-2-chloroquinacridone, N,N'-dimethyl-2-fluoroquinacridone, N,N'-dimethyl-1,2-benzoquinacridone as disclosed in US Patents 5,227,252; 5,276,381 and 5,593,788. Another class of fluorescent materials that may be used is fused ring fluorescent dyes. Exemplary suitable fused ring fluorescent dyes include perylene, rubrene, anthracene, coronene, phenanthrecene, pyrene, as disclosed in US Patent 3,172,862. Also, fluorescent materials include butadienes, such as 1,4-diphenylbutadiene and tetraphenylbutadiene, and stilbenes, as disclosed in US Patents 4,356,429 and 5,516,577. Other examples of fluorescent materials that can be used are those disclosed in US Patent 5,601,903.

[0031] Additionally, luminescent dopants are the fluorescent dyes disclosed in US Patent 5,935,720, such as, for example, 4-(dicyanomethylene)-2-I-propyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB); the lanthanide metal chelate complexes, such as for example, tris(acety lacetonato)(phenanthroline) terbium, tris(acetyl acetonato)(phenanthroline) europium, and tris(thenoyl trisfluoroacetonato)(phenanthroline) europium, and those disclosed in Kido et al., "White light emitting organic electroluminescent device using lanthanide complexes," Jpn. J. Appl. Phys., Volume 35, pp. L394-L396 (1996; and phosphorescent materials, such as, for example, organometallic compounds containing heavy metal atoms that lead to strong spin-orbit coupling, such as those disclosed in Baldo et al., "Highly efficient organic phosphorescent emission from organic electroluminescent devices," Letters to Nature, Volume 395, pp. 151-154 (1998. Examples include 2,3,7,8,12,13,17,18-octaethyl-21H23H-phorpine platinum(II) (PtOEP) and fac tris(2-phenylpyridine)iridium (Ir(ppy)3).

[0032] A light emitting region that generates white light can, for example, comprise two or more layers where at least one layer generates blue emission and at least one layer generates yellow, orange or red emission. The one or more layers generating blue emission can, for example, comprise one or more of the blue electroluminescent materials described herein, and the one or more layers generating the yellow, orange or red emission can be comprised of any electroluminescent material capable of emission at the desired color range or by adding luminescent dopants, as those described herein, in a suitable electroluminescent material. Alternatively, a white emitting region that generates white light can consist of a single layer comprised of a blue electroluminescent material that further includes a yellow, orange or red luminescent dopant in a low concentration, for example less than 2 % by volume, and typically, less than 1 % by volume, and sometimes even less than 0.5 % by volume, where the low concentration of dopant allows the partial retention of blue emission from the blue electroluminescent material, which when combined with the yellow, orange or red emission components from the dopant, gives the white emission.

[0033] In embodiments, the light emitting region optionally further includes one, two, or more charge transport materials (in the electroluminescent layer and/or other layer(s) of the light emitting region). Where there are present in a layer two or more charge transport materials, each charge transport material may be present at any suitable volume ratio such as for example from 99(first material): 1(second material) to 1 (first material):99(second material). For two or more charge transport materials, each may transport the same or different charge type (that is, whether holes or electrons). The volume ratio of the electroluminescent material and the charge transport material ranges for example from 99(electroluminescent material): 1(charge transport material) to 1 (electroluminescent material):99(charge transport material), or 90(electroluminescent material): 10(charge transport material) to 90(electroluminescent material): 10(charge transport material), or 60(electroluminescent material):40(charge transport material) to 40(electroluminescent material):60(charge transport material).

[0034] It is understood that an electroluminescent material inherently possesses a certain degree of charge transport capability. In embodiments of the present invention, if a material is electroluminescent, then such a material is considered an electroluminescent material regardless of its charge transport capability (whether holes or electrons).

[0035] Examples of hole-transporting materials that can be utilized in the light emitting region include polypyrrole, polyaniline, poly(phenylene vinylene), polythiophene, polyarylamine as disclosed in US Patent 5,728,801 and their derivatives, and known semiconductive organic materials like porphyrin derivatives such as 1,10,15,20-tetraphenyl-21H,23H-porphyrin copper (II) disclosed in US Patent 4,356,429; copper phthalocyanine, copper tetramethyl phthalocyanine; zinc phthalocyanine; titanium oxide phthalocyanine; magnesium phthalocyanine.

[0036] A specific class of hole transporting materials are the aromatic tertiary amines such as those disclosed in US Patent 4,539,507. Suitable exemplary aromatic tertiary amines include, but are not limited to, bis(4-dimethylamino-2-methylphenyl)phenylmethane, N,N,N-tri(p-tolyl)amine, 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane, 1,1-bis(4-di-p-tolylaminophenyl)-4-phenyl cyclohexane, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-l,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-bis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine, N,N,N',N'-tetra-p-tolyl-1,1'-biphenyl-4,4'-diamine, N,N'-di-1-naphthyl-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine, N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine ("NPB"), mixtures thereof. Another class of aromatic tertiary amines are polynuclear aromatic amines. Examples of these polynuclear aromatic amines include, but are not limited to, N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenylyl]aniline; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenylyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenylyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenylyl] aniline; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenylyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenylyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-p-chlorophenylamino)-4-biphenylyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-chlorophenylamino)-4-biphenylyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-chlorophenylamino)-4-biphenylyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenylyl]-p-chloroaniline; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenylyl]-m-chloroaniline; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenylyl]-1-aminonaphthalene, mixtures thereof and the like; 4,4'-bis(9-carbazolyl)-1,1'-biphenyl compounds, such as, for example 4,4'-bis(9-carbazolyl)-1,1'-biphenyl and 4,4'-bis(3-methyl-9-carbazolyl)-1,1'-biphenyl.

[0037] A specific class of the hole transporting materials are the indolocarbazoles, such as those disclosed in US Patents 5,942,340 and 5,952,115 such as, for example, 5,11-di-naphthyl-5,11-dihydroindolo[3,2-b]carbazole, and 2,8-dimethyl-5,11-di-naphthyl-5,11-dihydroindolo[3,2-b]carbazole; N,N,N'N'-tetraarylbenzidines, wherein aryl may be selected from phenyl, m-tolyl, p-tolyl, m-methoxyphenyl, p-methoxyphenyl, 1-naphthyl, 2-naphthyl. Illustrative examples of N,N,N'N'-tetraarylbenzidine are N,N;-di-1-naphthyl-N,N'- diphenyl-1,1'-biphenyl-4,4'-diamine, which is more preferred; N,N'-bis(3-methylphenyl) -N,N'- diphenyl-1,1'-biphenyl-4,4'-diamine; N,N'-bis(3-methoxyphenyl) - N,N'- diphenyl-1,1'-biphenyl-4,4'-diamine. Preferred hole transporting materials are the naphtyl-substituted benzidine derivatives.

[0038] In embodiments, the light emitting region can also include one or more electron transport materials. Exemplary electron transport materials include polyfluorenes, such as poly(9,9-di-n-octylfluorene-2,7-diyl), poly(2,8-(6,7,12,12-tetraalkylindenofluorene) and copolymers containing fluorenes such as fluorene-amine copolymers, as described in Bernius et al., Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices III, Denver, Colorado, July 1999, Volume 3797, p. 129.

[0039] Other examples of electron transport materials are the metal oxinoid compounds, the oxadiazole metal chelate compounds, the triazine compounds and the stilbene compounds, examples of which have been described above in detail. Other examples of electron transport materials are the arylimidazole derivatives such as those described in US Application Serial No. 10/702,859, filed November 6, 2003.

[0040] In embodiments where the light emitting region includes a hole transport material and/or electron transport material in addition to the organic electroluminescent material, the organic electroluminescent material, the hole transport material, and/or the electron transport material can be formed in separate layers, such as, for example, the OLEDs disclosed in US Patents 4,539,507; 4,720,432 and 4,769,292; or in the same layer thus forming a mixed layer of two or more materials, such as, for example, the OLEDs disclosed in US Patent 6,130,001, and in US Application Nos. 09/357,551 (corresponding to US Patent 6,392,339); 09/606,670 (corresponding to US Patent 6,392,250); and 09/770,159 (corresponding to US Patent 6,614,175). [0043] In embodiments where the electroluminescent layer includes both an organic electroluminescent material and a charge transport material, such a layer may be referred to as a mixed electroluminescent layer.

2. Electron Accepting Layer

[0041] In embodiments, the electron accepting layer containing the electron accepting material may be considered a hole injection layer which reduces the hole injection barrier between the anode capping layer and the electroluminescent layer. In embodiments, the electron accepting layer contacts the electroluminescent layer. The electron accepting layer may be composed of one, two, or more electron accepting materials. Where the electron accepting layer includes two or more electron accepting materials, each electron accepting material may be present at any suitable volume ratio such as for example from 99(first material): 1(second material) to 1 (first material):99(second material).

[0042] The inclusion of the electron accepting layer may, in some embodiments, lower the driving voltage of the OLED and/or increase device efficiency relative to a comparison device that is in all regards identical except for the omission of the electron accepting layer.

[0043] Suitable electron accepting materials include a wide variety of compounds that have a high electron affinity. Suitable organic electron accepting materials include electron deficient compounds such as, for example as described in US Patent Application Publication 2004/0004433 by Lamansky et al., tetracyanoquinodimethane compounds where this term collectively refers to tetracyanoquinodimethane and its derivatives; thiopyranylidine compounds where this term collectively refers to thiopyranylidine and its derivatives; polynitrofluorenone compounds where this term collectively refers to polynitrofluorenone and its derivatives; tetracyanoethylene compounds where this term collectively refers to tetracyanoethylene (TCNE) and its derivatives; chloranil compounds where this term collectively refers to chloranil and its derivatives; and other compounds commonly used as electron acceptors. Specific examples of electron accepting materials include tetracyanoquinodimethane (TCNQ), tetrafluoro-tetracyanoquinodimethane (F4TCNQ), tetracyanoethylene, chloranil, 2-(4-(1-methylethyl)phenyl-6-phenyl-4H-thiopyran-4-ylidene)-propanedinitrile-1,1-dioxyide (PTYPD), and 2,4,7-trinitrofluorenone. Other possible organic electron accepting materials could be those described in US Patent Application Publication 2004/0009418 by Main et al., such as carboxylfluorenone malonitrile compounds where this term collectively refers to carboxylfluorenone malonitrile (CFM) and its derivatives; N,N'bis(dialkyl)-1,4,5,8-naphthalenetetracarboxylic diimide compounds where this term collectively refers to N,N'bis(dialkyl)-1,4,5,8-naphthalenetetracarboxylic diimide and its derivatives; or N,N'bis(diaryl)-1,4,5,8-naphthalenetetracarboxylic diimide compounds where this term collectively refers to N,N'bis(diaryl)-1,4,5,8-naphthalenetetracarboxylic diimide and its derivatives; carboxybenzylnaphthaquinone compounds where this term collectively refers to carboxybenzylnaphthaquinone and its derivatives; or diphenoquionone compounds where this term collectively refers to diphenoquionone and its derivatives. The electron accepting material can also be inorganic compounds such as Lewis acid compounds like $FeCl_3$, $AlCl_3$, $InCl_3$, $SbCl_5$, $GaCl_3$ etc, as reported by Endo et al. in Jpn. J Appl Phys. 41, L358 (2002. Other electron accepting materials can be fullerene compounds where this term collectively refers to fullerene (e.g., C_{60}) and its derivatives.

[0044] In embodiments, the electron accepting layer optionally further includes one, two, or more organic materials. Where there are present two or more organic materials, each organic material may be present at any suitable volume ratio such as for example from 99(first material): 1 (second material) to 1 (first material):99(second material). The volume ratio of the organic material and the charge accepting material ranges for example from 99(organic material): (charge accepting material) to 1 (organic material):99(charge accepting material), particularly from 90(organic material): 10(charge accepting material) to 10(organic material):90(charge accepting material).

[0045] Suitable organic materials include for example hole transport materials, such as tertiary aromatic amine derivatives, indolocarbazole derivatives, and porphyrin derivatives, including copper phthalocyanine, copper tetramethyl phthalocyanine; zinc phthalocyanine; titanium oxide phthalocyanine; magnesium phthalocyanine, such as those described above. Other suitable materials include polypyrrole, polyaniline, poly(phenylene vinylene), polythiophene, polyarylamine.

[0046] The thickness of the light emitting region, and the thickness of each layer (e.g., electroluminescent layer, hole transport layer, electron transport layer, and electron accepting layer) of the light emitting region, can vary from for example, 1 nm to 1000 nm, typically from 5 nm to 200 nm, and especially from 10 nm to 150 nm.

ANODE CAPPING REGION

1. Anode Capping Layer(s)

[0047] In embodiments, the anode capping layer(s) is intended to enhance one or more properties of the present OLEDs such as for example to increase the luminance stability. In embodiments, the anode capping layer contacts either the electron accepting layer or the anode, or both the electron accepting layer and the anode. The anode capping layer consists of the materials as defined in claims 1. Where the anode capping layer(s) is composed of two or more inorganic materials, each inorganic material may be present at any suitable volume ratio such as for example from 99(first material): 1(second material) to 1 (first material):99(second material), as not defined otherwise in claim 1.

[0048] In embodiments involving two or more anode capping layers, the anode capping layers may be the same or different from one another for each of the aspects making up the anode capping layers such as for example the material(s), the material concentration where two or more materials are present, and the layer thickness.

[0049] In embodiments, when elemental metal and/or metal alloy are used in the anode capping layer(s), there may possibly occur a partial or even total chemical transformation of the elemental metal and metal alloy to one or more metal containing compounds (e.g., a metal oxide), where the transformation may occur during, immediately after (1 hour or less) or even long after (more than I hour) the anode capping layer(s) is formed, possibly as a result of interaction with other materials present in the fabrication environment or with other materials in the anode capping layer(s) or the rest of the OLED.

2. Electron Accepting Layer

[0050] In embodiments, the same electron accepting layer described herein with respect to the Light Emitting Region may be designated part of the Anode Capping Region, especially when the electron accepting layer is sandwiched between two or more anode capping layers.
[0051] The anode capping layer is disposed between the layer including a hole transport material and the anode capping layer.
[0052] The thickness of the anode capping region, and the thickness of each layer (e.g., anode capping layer and electron accepting layer) of the anode capping region, can vary from for example, 0.1 nm to 100 nm, typically from 0.5 nm to 50 nm, and especially from 0.5 nm to 15 nm.
[0053] Embodiments of this invention include an anode capping region which is transparent or translucent, and therefore the present OLEDs in embodiments are suitable for applications when transparent anode (e.g., anodes with transmission at least 70 % in the visible range, and typically at least 90 % in the visible range) such as in bottom emitting OLEDs or transparent (see-through) OLEDs is desired. In transparent or translucent embodiments of the anode capping region, the optical transmission of the anode capping region can be made to be at least 50 % in the visible range, and typically at least 70 % in the visible range, and preferably at least 90 % in the visible range, by means of using thin layers such as, for example, each layer is 200 Angstroms or less, and preferably, each layer is 100 Angstroms or less, such that the optical transmission of the entire anode capping region is in the desired range. These transparent embodiments are particularly suitable for anode-emitting (also sometimes called bottom emitting) OLEDs, such as, for example in passive matrix OLED displays, and some active matrix displays, when device emission is required to be transmitted through the anode, or in other applications involving transparent and/or transparent or translucent substrates (rigid transparent substrates such as glass, or flexible transparent substrates such as plastic substrates).
[0054] In embodiments, when the anode capping region is used in an OLED with a non-transparent anode, and hence maximizing its optical transmission becomes less important, thicker layer(s) of the anode capping region, for example, layer(s) in the range of 100 Angstroms to 2,000 Angstroms can be used, and may provide additional advantages, such as, for example, increased mechanical robustness, optical reflectivity, or electrical conduction. In embodiments, a transparent anode capping region can be used, and are sometimes even desirable, with a non-transparent anode, such as, with reflective anodes with reflectance of for example, at least 80 % in the visible range, or with non-reflective anodes, such as anodes of for example not more than 50 % reflectance in the visible range.

ANODE

[0055] Any suitable anode may be used including optically transparent, translucent, opaque, reflective and non-reflective anodes. The anode is a single layer or a plurality of layers composed of for example indium tin oxide (ITO), tin oxide, gold or platinum, or a mixture thereof. Other suitable materials for forming the anode include, but are not limited to, electrically conductive carbon, -conjugated polymers such as polyaniline, polythiophene, polypyrrole, having, for example, a work function equal to, or greater than, 4 eV, or from 4 eV to 6 eV. In embodiments, the anode can be ZnO-Based anodes described by Zugang et al, J. Phys. Condens. Matter 8, 3221 (1996) and by Kim et al., Appl. Phys. Lett. 83, 3809 (2003) or conducting polymer anodes like glycerol-doped poly (3,4-ethylenedioxy-thiophene)-poly(styrene sulfonate) ("PEDOT:PSS") or polyaniline ("PANI") as described by Kim et al., Appl. Phys. Lett. 80, 3844 (2002) and by Carter et al. Appl. Phys. Lett. 70, 2067 (1997.
[0056] The anode can have any suitable form. A thin conductive layer can be coated onto a light transmissive substrate, such as, for example, a transparent or substantially transparent glass plate or plastic film. Embodiments of organic light emitting devices can comprise a light transmissive anode formed from tin oxide or indium tin oxide coated on glass. Also, very thin light-transparent metallic anodes having a thickness, for example, of less than 200 A, and, especially, from 75 Å to 150 Å can be used. These thin anodes can comprise metals such as gold, palladium. In addition, transparent or semitransparent thin layers of conductive carbon or conjugated polymers such as polyaniline, polythiophene, polypyrrole can be used to form anodes. These thin layers can have a thickness of, for example from 50 Å to 175 Å. Additional suitable forms of the anode are disclosed in US Patent 4,885,211. In embodiments, the anode includes a metal-organic mixed layer (MOML) as described in US Patent Application Publication 2002/0180349 A1.
[0057] In embodiments of a light transmissive anode, the thickness of the anode can range for example from 1 nm to 5000 nm or from 30 nm to 300 nm. The thickness range of the anode is dependent on the optical constants of the anode material.
[0058] In embodiments of the OLED, the anode can be opaque (i.e., non-light transmissive or non-transparent). Such an opaque anode is fabricated from the materials described herein and having a thickness ranging for example from 10 nm to 2 mm. Non-transparent anodes can comprise for example Si, Ni, Au, Ag, Cu and/or Pt , which may also be highly reflective as described, for example, in Chen et al. Appl. Phys. Lett. 83, 5127 (2003), or non-reflective as described, for example, in US Patent Application Publication 2002/0180349 A1. Embodiments of the present OLED with a non-trans-

parent anode include cathode-emitting OLEDs (e.g., OLEDs with transparent cathodes, where cathode transmission is at least 70 %, in the visible range, and typically, is at least 80 % in the visible range; also sometimes called top-emitting OLEDs) commonly used in active-matrix OLED displays, and others.

SUBSTRATE

[0059] The substrate may be rigid or flexible and may be composed of one, two, three or more layers. The substrate may have a thickness ranging for example from 10 to 5,000 micrometers, and more particularly from 25 to 1,000 micrometers.

[0060] A substantially transparent substrate can comprise various suitable materials including, for example, polymeric components, glass, quartz. Suitable polymeric components include, but are not limited to polyesters such as MYLAR®, polycarbonates, polyacrylates, polymethacrylates, polysulfones. Other substrate materials can also be selected provided, for example, that the materials can effectively support the other layers, and do not interfere with the device functional performance.

[0061] An opaque substrate can comprise various suitable materials including, for example, polymeric components like polyesters such as MYLAR®, polycarbonates, polyacrylates, polymethacrylates, polysulfones, which contain coloring agents or dyes such as carbon black. The substrate can also be comprised of silicon such as amorphous silicon, polycrystalline silicon, single crystal silicon. Another class of materials that can be used in the substrate are ceramics such as metallic compounds like metal oxides, halides, hydroxides, sulfides.

[0062] In embodiments, the present OLED uses a conductive substrate such as amorphous- Si, poly-Si, or flexible metallic foils and belts (e.g., stainless steel belts or Ni belts).

[0063] Exemplary configurations of the present OLEDs are now described where the various configurations have the recited sequence. In embodiments, one or both of the cathode and anode are light transmissive.

Configuration 1:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
second anode capping layer including organic material (anode capping region) first anode capping layer including inorganic material (anode capping region) anode
substrate

Configuration 2:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
anode capping layer including inorganic material (anode capping region) anode
substrate

Configuration 5:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
fifth anode capping layer including inorganic material (anode capping region) fourth anode capping layer including organic material (anode capping region) third anode capping layer including inorganic material (anode capping region) second anode capping layer including organic material (anode capping region) first anode capping layer including inorganic material (anode capping region) anode
substrate

Configuration 6:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
third anode capping layer including inorganic material (anode capping region) second anode capping layer including organic material (anode capping region) first anode capping layer including inorganic material (anode capping region) anode
substrate

Configuration 7:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
second anode capping layer including inorganic material (anode capping region) first anode capping layer including organic material (anode capping region) anode
substrate

Configuration 8:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
fourth anode capping layer including organic material (anode capping region) third anode capping layer including inorganic material (anode capping region) second anode capping layer including organic material (anode capping region) first anode capping layer including inorganic material (anode capping region) anode
substrate

Configuration 9:

cathode
electron transport layer (light emitting region)
electroluminescent layer (light emitting region)
hole transport layer (light emitting region)
electron accepting layer (light emitting region)
second anode capping layer including inorganic material (anode capping region) first anode capping layer including inorganic material (anode capping region) anode
substrate

[0064] The layers of the present OLEDs can be formed by any suitable technique. There can be employed various thin film forming methods such as, for example, thermal vapor deposition in vacuum. Electron beam deposition and sputtering deposition are also among the suitable vacuum deposition methods. Chemical vapor deposition can also be used as a deposition method. The deposition rate of the various materials can be for example 0.1 to 100 Angstroms per second ("A/s"), or from 1 to 10 A/s. In some cases it is possible to form one or more OLED layers by spin coating, printing (e.g., inkjet printing) or other coating techniques.

[0065] For embodiments of the present OLEDs, the following exemplary luminance stability values (half-life with L_o of about 100 cd/m^2) are provided:

[0066] Blue light emitting OLEDs: at least 2,000 hours, at least 4,000 hours, or at least 6,000 hours.

[0067] Green light emitting OLEDs: at least 5,000 hours, at least 10,000 hours, or at least 15,000 hours.

[0068] Red light emitting OLEDs: at least 2,000 hours, at least 4,000 hours, or at least 6,000 hours.

[0069] White light emitting OLEDs: at least 4,000 hours, at least 8,000 hours, or at least 12,000 hours.

[0070] In the present invention, the anode capping layer(s) is selected such that the luminance stability ratio of the present OLEDs is greater than 1, preferably greater than 2, greater than 5, or greater than 10. The luminance stability ratio refers to the ratio between (1) the time of operation elapsed before the luminance of the present OLED containing the anode capping layer(s) drops by a certain factor (e.g., 10 %, 20 %, 50 %, etc.) of the initial luminance Lo (where, for example, Lo=100 cd/m^2 , 300 cd/m^2 , 500 cd/m^2 , or 1000 cd/m^2), and (2) the time of operation elapsed before the luminance of a comparison OLED (which is in all respects identical except for the absence of the anode capping layer(s)) drops by the same factor when operated at the same initial luminance L_o, under the same testing conditions, where the test can be performed anytime after the known initial bum-in period of the devices. In embodiments, for the present OLEDs at a given initial luminance L_o, the luminance stability ratio may or may not significantly vary depending on the particular luminance dropoff factor chosen (e.g., the stability ratio measured at 10 % dropoff factor may or may not significantly differ from the stability ratio measured at 50 %). In certain embodiments, the luminance stability ratio will be relatively consistent regardless of the particular dropoff factor used (i.e., in embodiments, the luminance stability ratio is relatively independent of the particular dropoff factor used). For those embodiments where the luminance stability ratio is dependent on the particular dropoff factor used and it is important to precisely determine the luminance stability ratio, the dropoff factor of 10 % should be used. This dropoff factor of 10 % is picked to enable a faster determination, as compared with the length of time required for a dropoff factor of 50 % (half-life).

[0071] For those embodiments where the luminance stability ratio is dependent on the particular initial luminance L_o used and it is important to precisely determine the luminance stability ratio, the following initial luminance L_o should be used (all using AC driving at an average forward current density of about 31.25 mA/cm^2):

Blue light emitting OLEDs: 300 cd/m^2;
Green light emitting OLEDs: 1,000 cd/m^2;
Red light emitting OLEDs: 150 cd/m^2; and
White light emitting OLEDs: 1,000 cd/m^2;

[0072] The burn-in period depends on the initial luminance of an OLED where, in general, the higher the initial luminance at which an OLED is operated, the shorter the bum-in period. For example, for an OLED operated at an initial luminance of 100 cd/m^2, the bum-in period is usually the first 100 hours and typically the first 500 hours of operation of the OLED; for an OLED operated at an initial luminance of 300 cd/m^2, the burn-in period is usually the first 35 hours and typically the first 175 hours of operation of the OLED; for an OLED operated at an initial luminance of 500 cd/m^2, the bum-in period is usually the first 20 hours and typically the first 100 hours of operation of the OLED; and for an OLED operated at an initial luminance of 1000 cd/m^2, the bum-in is usually the first 10 hours and typically the first 50 hours of operation of the OLED.

[0073] The term "selected" in the context of providing the anode capping layer(s) with the specified luminance stability ratio refers to the choices to be made for the aspects making up the anode capping layer(s) such as for example the material(s), the material concentration where two or more materials are present, the layer thickness, and the number of anode capping layers, which enable the present OLEDs to exhibit the specified luminance stability ratio. Exemplary embodiments of the anode capping layer(s) are discussed herein to illustrate "selected".

[0074] A longer time demonstrated by the present OLED before its luminance drops by a certain fraction from the same initial value relative to the comparison OLED renders the luminance stability ratio >1, and represents an increase in device luminance stability. In embodiments, the driving voltage of the present OLED may be lower than, the same as, or higher than the driving voltage needed to achieve the same level of current density and/or luminance of a comparison OLED that is in all regards identical except for the omission of the anode capping layer(s). In embodiments, the driving voltage of the present OLED is not significantly higher (i.e., does not exceed by more than 5 Volts, or does not exceed by more than 3 Volts) than the driving voltage needed to achieve the same level of current density and/or luminance of the comparison OLED that is in all regards identical except for the omission of the anode capping layer(s).

[0075] In embodiments, the present OLEDs may exhibit one or more of the following attributes relative to a comparison OLED that is in all regards identical except for the omission of the anode capping layer(s): more stable luminance; and more stable driving voltage.

[0076] The invention will now be described in detail with respect to specific exemplary embodiments thereof, it being understood that these examples are intended to be illustrative only and the invention is not intended to be limited to the materials, conditions, or process parameters recited herein. All percentages and parts are by volume unless otherwise indicated.

EXAMPLES

[0077] In the Examples below, the configuration of the OLEDs is as follows: substrate / anode / anode capping layer(s) / electron accepting layer / one layer of the light emitting region / another layer of the light emitting region / cathode.

[0078] In the Examples below, where there are multiple layers indicated, the convention is that when the layers are read from left to right, the first recited layer is closer to the anode than the other layer. For example, regarding "Layers of light emitting region for Group I: NPB(600) / AlQ3(750)," the NPB layer is closer to the anode than the AlQ3 layer.
[0079] The numbers in brackets are a layer thickness in Angstroms. Numbers separated by a colon (e.g., "1:1:) indicate a material ratio by volume.
[0080] The following terms are explained:

"ITO": indium tin oxide.
"NPB": *N*,*N'*-di(naphthalene-1-yl)-*N*,*N'*-diphenyl-benzidine.
"AlQ3": tris(8-hydroxyquinolinate) aluminum; also referred to as tris(8-hydroxyquinoline) aluminum or tris(8-hydroxyquinolinato) aluminum.
"F4TCNQ": tetrafluoro-tetracyanoquinodimethane.
"CuPc": copper phthalocyanine; this organometallic compound is considered organic.
"BH2": tertiary-butyl substituted 9,10-bis[4-(2,2-diphenylethenyl)phenyl]anthracene; also represented by the acronym TBADN.
"BD2": tertiary-butyl substituted perylene.
"Rub": 5,6,11,12-tetraphenylnaphthacene; also called Rubrene.

[0081] All OLEDs of all groups (Groups I through IX) were fabricated using physical vapor deposition in vacuum (5 x 10-6 Torr) on ITO-coated glass substrates, that were pre-cleaned using UV-ozone cleaning. All devices had identical anodes which were ITO having a thickness of about 200 nm. All devices had identical cathodes composed of Mg and Ag (9:1 volume ratio) having a thickness of about 120 nm.
[0082] Unless otherwise noted, the values provided in the column titled "Luminance Stability Ratio (vs Comp.)" were calculated based on the following:

Initial luminescence (L_o) using AC driving at an average forward current density of about 31.25 mA/cm2;

[0083] Initial voltage (V_o) was within about 5V from that of the comparison example.
[0084] The luminance stability test was carried out by operating the OLEDs in a nitrogen atmosphere using AC driving at an average forward current density of about 31.25 mA/cm^2, and monitoring the gradual decrease in device luminance using a photodiode. Time elapsed for 10 % decay from L_o, subsequent to the initial bum-in period of about 20 hours, was recorded. Time for 10 % decay from L_o = 100 cd/m^2 was calculated from time for 10 % decay from L_o measured above using the relationship:

$$\text{Time for 10 \% decay from } L_o=100 \text{ cd/m}^2 = (\text{Time for 10 \% decay from } L_o \text{ measured above}) \times (L_o \text{ measured above}) / 100.$$

[0085] Luminance stability ratio (vs comp.) was obtained by dividing the "Time for 10 % decay from L_o=100 cd/m^2 obtained from an inventive example device" over "Time for 10 % decay from L_o=100 cd/m^2 obtained from a comparison example device that was in all respects identical except for the omission of the anode capping layer(s). "

Group I Examples (Electroluminescent color: Green):

[0086]

Layers of light emitting region for Group I: NPB(600) / AlQ3(750)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
I-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
I-2 (Comp.)	Au:Pd (5)	NPB+F4TCNQ (9:1)(100)	3.5	Large increase in luminance stability compared to comparison example

(continued)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
I-3	Au:Pd (5) / NPB+Mg(1:1)(50)	NPB+F4TCNQ (9:1)(100)	7.1	Large increase in luminance stability compared to comparison example

Group II Examples (Electroluminescent color: Green):

[0087] Layers of light emitting region for Group II:

NPB(200) / NPB+AlQ3(1:1)(800)/AlQ3(200)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
II-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
II-2 (Comp.)		NPB+F4TCNQ (9:1)(100)	2	Large increase in luminance stability compared to comparison example II-1.

Group III Examples (Electroluminescent color: Green):

[0088]

Layers of light emitting region for Group III: NPB(600) / AlQ3(750)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
III-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
III-2	CuPc+Mg(1:1)(25)	NPB+F4TCNQ (9:1)(100)	17.7	Large increase in luminance stability compared to comparison example III-1
III-3	CuPc+Mg(1:1)(150)	NPB+F4TCNQ (9:1)(100)	53.3	Large increase in luminance stability compared to comparison example III-1
III-4	Mg(25) / CuPc(150)	NPB+F4TCNQ (9:1)(100)	18.3	Large increase in luminance stability compared to comparison example III-1
III-5 (Comp.)	CuPc(150)	NPB+F4TCNQ (9:1)(100)	1.1	Marginally increased luminance stability compared to comparison example III-1. Increase in stability was much less for this comparative example (Mg absent; and only organic material in the Anode Capping Layer(s)) than compared with other examples which include Mg in the Anode Capping Layer(s).

Group IV Examples (Electroluminescent color: Green):

[0089] Layers of light emitting region for Group IV:

NPB(600) / AlQ3(750)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
IV-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
IV-2 (Comp.)	Cr (7)	NPB+F4TCNQ (9:1)(100)	36.4	Large increase in luminance stability compared to comparison example
IV-3 (Comp.)	Cr (7) / NPB (25) / Cr (7)	NPB+F4TCNQ (9:1)(100)	132.6	Large increase in luminance stability compared to comparison example
IV-4 (Comp.)	NPB (25) / Cr (7)	NPB+F4TCNQ (9:1)(100)	27.7	Large increase in luminance stability compared to comparison example

Group V Examples (Electroluminescent color: Green):

[0090] Layers of light emitting region for Group V:

NPB(600) / AlQ3(750)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. comp.)	Remarks
V-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
V-2	Mg (50)	NPB+F4TCNQ (9:1)(100)	18.6	Large increase in luminance stability compared to comparison example
V-3	Mg (25)	NPB+F4TCNQ (9:1)(100)	58	Large increase in luminance stability compared to comparison example
V-4	Mg (25) / NPB (25) / Mg (25)	NPB+F4TCNQ (9:1)(100)	17.5	Large increase in luminance stability com pared to comparison example

Group VI Examples (Electroluminescent color: Green):

[0091] Layers of light emitting region for Group VI:

NPB(600) / AlQ3(750)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
VI-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
VI-2 (Comp.)	Ag(7)	NPB+F4TCNQ (9:1)(100)	0.36	Decreased luminance stability compared to comparison example VI-1. Illustrates that not every Anode Capping Layer can result in increased luminance stability.
VI-3 (Comp.)	Ag (25)	NPB+F4TCNQ (9:1)(100)	0.25	Decreased luminance stability compared to comparison example VI-1. Illustrates that not every Anode Capping Layer can result in increased luminance stability.

(continued)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
VI-4 (Comp.)	Ag+NPB (1:1)(50)	NPB+F4TCNQ (9:1)(100)	0.25	Decreased luminance stability compared to comparison example VI-1. Illustrates that not every Anode Capping Layer can result in increased luminance stability.
VI-5 (Comp.)	Sm (5)	NPB+F4TCNQ (9:1)(100)	N/A (unable to determine stability ratio due to poor performance)	Decreased luminance stability compared to comparison example VI-1. Illustrates that not every Anode Capping Layer can result in increased luminance stability.

Group VII Examples (Electroluminescent color: Blue):

[0092] Layers of light emitting region for Group VII:

NPB(300)/NPB+BH2+BD2(49:49:2)(300)/BH2(50)/AlQ3(250)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
VII-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
VII-2	NPB+Mg (1:1)(10)	NPB+F4TCNQ (9:1)(100)	4.9	Large increase in luminance stability compared to comparison example
VII-3	NPB+Mg (1:1)(50)	NPB+F4TCNQ (9:1)(100)	6.25	Large increase in luminance stability compared to comparison example

Group VIII Examples (Electroluminescent color: Blue):

[0093] Layers of light emitting region for Group VIII:

NPB(300) / BH2 (300) / AlQ3(300)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
VIII-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
VIII-2 (Comp.)	CuPc (150)	NPB+F4TCNQ (9:1)(100)	1.3	Marginally increased luminance stability compared to comparison example VIII-1. Increase in stability was much less for this comparative example (Mg absent; and only organic material in the Anode Capping Layer(s)) than compared with example VIII-5 which included Mg in the Anode Capping Layer(s).

(continued)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
VIII-3 (Comp.)	NPB (150)	NPB+F4TCNQ (9:1)(100)	1.5	Marginally increased luminance stability compared to comparison example VIII-1. Increase in stability was much less for this comparative example (Mg absent; and only organic material in the Anode Capping Layer(s)) than compared with example VIII-5 which included Mg in the Anode Capping Layer(s).
VIII-4 (Comp.)	NPB+Ag (1:1)(50)	NPB+F4TCNQ (9:1)(100)	0.38	Decreased luminance stability compared to comparison example VIII-1. Illustrates that not every Anode Capping Layer can result in increased stability.
VIII-5 (Comp.)	NPB+Mg+Ag (48:48:4)(50)	NPB+F4TCNQ (9:1)(100)	7.15	Large increase in luminance stability compared to comparison example VIII-1.

Group IX Examples (Electroluminescent color: White):

[0094] Layers of light emitting region for Group IX:

NPB(300)/NPB+BH2+Rub(49:49:2)(300)/BH2(300)/AlQ3(300)

Ex. #	Anode Capping Layer(s)	Electron Accepting Layer	Luminance Stability Ratio (vs. Comp.)	Remarks
IX-1 (Comp.)	None	NPB+F4TCNQ (9:1)(100)	1	Comparison example
IX-2	NPB+Mg (1:1)(50)	NPB+F4TCNQ (9:1)(100)	20	Large increase in luminance stability compared to comparison example

[0095] The above examples are intended to be illustrative only.

Claims

1. An organic light emitting device having a sequence comprising:

a cathode;
a layer including an organic electroluminescent material;
a layer including a hole transport material;
a layer including an electron accepting material,
selected from the group consisting of:

tetracyanoquinodimethane compounds; thiopyranylidine compounds; polynitrofluorenone compounds; tetracyanoethylene compounds; chloranil compounds; carboxylfluorenone malonitrile compounds; N,N'bis(dialkyl)-1,4,5,8-naphthalenetetracarboxylic diimide compounds; N,N'bis(diaryl)-1,4,5,8-naphthalenetetracarboxylic diimide compounds; carboxybenzylnaphthaquinone compounds; diphenoquionone compounds, inorganic Lewis acid compounds, and fullerene compounds, and a mixture thereof;
an anode capping layer consisting of Mg, a stack of Au:Pd/NPB+Mg(1:1), CuPc+Mg(1:1), a stack of Mg/CuPc, a stack of Mg/NPB/Mg or NPB+Mg(1:1);
an anode; and
a substrate in the sequence before the cathode or after the anode,

wherein the layer including an electron accepting material is disposed between the layer including a hole transport material and the anode capping layer,
wherein the anode capping layer is selected to provide the device with a luminance stability ratio that is greater than 1,
wherein the luminance stability ratio refers to the ratio between

(1) the time of operation elapsed before the luminance of the device containing the anode capping layer drops by a certain factor of the initial luminance L_0, and
(2) the time of operation elapsed before the luminance of a comparison device, which is in all respects identical except for the absence of the anode capping layer, drops by the same factor when operated at the same initial luminance L_0, under the same testing

2. The device of claim 1, wherein the anode comprises indium tin oxide.

3. The device of claim 1, wherein the electron accepting layer further includes an organic material.

4. The device of claim 1, wherein the electroluminescent layer is capable of emitting blue light.

Patentansprüche

1. Organische lichtemittierende Vorrichtung mit einer Reihenfolge, umfassend:

eine Kathode;
eine ein organisches elektrolumineszentes Material beinhaltende Schicht;
eine ein Lochtransportmaterial beinhaltende Schicht;
eine ein Elektronen annehmendes Material beinhaltende Schicht, gewählt aus der Gruppe, bestehend aus:

Tetracyanochinodimethanverbindungen; Thiopyranylidinverbindungen; Polynitrofluorenonverbindungen; Tetracyanoethylenverbindungen; Chloranilverbindungen; Carboxyfluorenonmalonitrilverbindungen; N,N'-Bis(dialkyl)-1,4,5,8-naphthalintetracarbonsäurediimidverbindungen; N,N'-Bis(diaryl)-1,4,5,8-naphthalintetracarbonsäurediimidverbindungen; Carboxybenzylnaphthachinonverbindungen; Diphenochinonverbindungen; anorganische Lewissäure-Verbindungen und Fullerenverbindungen und eine Mischung hiervon;
eine Anode-Abdeckschicht, bestehend aus Mg, einem Stack aus Au:Pd/NPB+Mg(1:1), CuPc+Mg(1:1), einem Stack aus Mg/CuPc, einem Stack aus Mg/NPB/Mg oder NPB+Mg(1:1);
eine Anode; und
ein Substrat in der Reihenfolge vor der Kathode oder nach der Anode,
wobei die ein Elektronen annehmendes Material beinhaltende Schicht zwischen der ein Lochtransportmaterial beinhaltendenden Schicht und der Anode-Abdeckschicht angeordnet ist,
wobei die Anode-Abdeckschicht so gewählt ist, um die Vorrichtung mit einem Leuchtdichte-Stabilitätsverhältnis, das größer als 1 ist, zu versehen,
wobei das Leuchtdichte-Stabilitätsverhältnis sich bezieht auf das Verhältnis zwischen

(1) der Betriebszeit, die verstrichen ist, bevor die Leuchtdichte der Vorrichtung, enthaltend die Anode-Abdeckschicht, durch einen bestimmten Faktor auf die anfängliche Leuchtdichte L_0 abfällt, und
(2) der Betriebszeit, die verstrichen ist, bevor die Leuchtdichte einer Vergleichsvorrichtung, die in jeder Hinsicht identisch ist, ausgenommen der Abwesenheit der Anode-Abdeckschicht, um den gleichen Faktor abfällt, wenn sie unter den gleichen Testbedingungen bei der gleichen Anfangs-Leuchtdichte L_0 betrieben wird.

2. Vorrichtung nach Anspruch 1, wobei die Anode Indiumzinnoxid umfasst.

3. Vorrichtung nach Anspruch 1, wobei die Elektronen annehmende Schicht weiterhin ein organisches Material beinhaltet.

4. Vorrichtung nach Anspruch 1, wobei die elektrolumineszente Schicht in der Lage ist, blaues Licht zu emittieren.

Revendications

1. Un dispositif électroluminescent organique ayant une séquence comprenant:

   une cathode;
   une couche comprenant un matériau électroluminescent organique;
   une couche comprenant un matériau de transport de trous;
   une couche comprenant un matériau accepteur d'électrons,
   choisi parmi le groupe constitué par:

      les composés tétracyanoquinodiméthane; les composés thiopyranylidine; les composés polynitrofluorenone; les composés tétracyanoéthylène; les composés de chloranile; les composés malonitrile de carboxylfluorenone; les composés diimide N,N'-bis(dialkyl)-1,4,5,8-naphtalènetétracarboxylique; les composés diimide N,N'-bis(diaryl)-1,4,5,8-naphtalènetétracarboxylique ; les composés carboxybenzylnaphthaquinone; les composés diphenoquionone, des composés d'acides de Lewis inorganiques, et les composés de fullerène, et un mélange de ceux-ci ;
      une couche de recouvrement d'anode constitué par du Mg, un empilement de Au : Pd / NPB + Mg (1:1), CuPc + Mg (1:1), un empilement de Mg / CuPc, un empilement de Mg / NPB / Mg ou de NPB + Mg (1:1) ;
      une anode ; et
      un substrat dans la séquence avant la cathode ou après l'anode,
      dans lequel la couche comprenant un matériau accepteur d'électrons est disposée entre la couche comprenant un matériau de transport de trous et la couche de recouvrement d'anode,
      dans lequel la couche de recouvrement d'anode est choisie afin de fournir le dispositif avec un rapport de la stabilité de la luminance qui est supérieur à 1,
      dans lequel le rapport de la stabilité de la luminance se réfère au rapport entre

         (1) le temps de fonctionnement écoulé avant que la luminance du dispositif comprenant la couche de recouvrement d'anode baisse d'un certain facteur à partir de la luminance initiale L_0, et
         (2) le temps de fonctionnement écoulé avant que la luminance d'un dispositif de comparaison, qui est identique à tous égards, sauf pour l'absence de la couche de recouvrement d'anode, baisse par le même facteur lorsqu'il est actionné à la même luminance initiale L_0, sous les mêmes conditions de test.

2. Le dispositif selon la revendication 1, dans lequel l'anode comprend de l'oxyde d'étain et d'indium.

3. Le dispositif selon la revendication 1, dans lequel la couche acceptant des électrons comprend en outre un matériau organique.

4. Le dispositif selon la revendication 1, dans lequel la couche électroluminescente est capable d'émettre de la lumière bleue.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 2003116772 A1 **[0001]**
- EP 1167488 A **[0001]**
- JP 2004139981 A **[0002]**
- EP 1017118 A **[0003]**
- WO 03055275 A **[0004]**
- WO 03088718 A **[0005]**
- US 4885211 A **[0017] [0056]**
- US 4720432 A **[0017] [0040]**
- US 5703436 A **[0017]**
- US 20020180349 A1 **[0017] [0056] [0058]**
- US 5429884 A **[0017]**
- US 5457565 A **[0018]**
- US 5739635 A **[0018]**
- US 5776622 A **[0018]**
- US 5247190 A **[0023]**
- US 4539507 A **[0024] [0036] [0040]**
- US 5151629 A **[0024]**
- US 5150006 A **[0024]**
- US 5141671 A **[0024]**
- US 5846666 A **[0024]**
- US 5516577 A **[0025] [0030]**
- US 08829398 B **[0026]**
- US 5925472 A **[0026]**
- US 09489144 B **[0026]**
- US 6057048 A **[0026]**
- US 6479172 B **[0027]**
- US 6562485 B **[0027]**
- US 6465115 B **[0027]**
- US 6565996 B **[0027]**
- US 6229012 B **[0027]**
- US 77457704 A **[0027]**
- US 5227252 A **[0030]**
- US 5276381 A **[0030]**
- US 5593788 A **[0030]**
- US 3172862 A **[0030]**
- US 4356429 A **[0030] [0035]**
- US 5601903 A **[0030]**
- US 5935720 A **[0031]**
- US 5728801 A **[0035]**
- US 1101520 A **[0035]**
- US 5942340 A **[0037]**
- US 5952115 A **[0037]**
- US 70285903 A **[0039]**
- US 4769292 A **[0040]**
- US 6130001 A **[0040]**
- US 09357551 B **[0040]**
- US 6392339 B **[0040]**
- US 09606670 B **[0040]**
- US 6392250 B **[0040]**
- US 09770159 B **[0040]**
- US 6614175 B **[0040]**
- US 20040004433 A, Lamansky **[0043]**
- US 20040009418 A, Main **[0043]**

Non-patent literature cited in the description

- **BERNIUS et al.** Developmental Progress of Electroluminescent Polymeric Materials and Devices. *Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices III,* July 1999, vol. 3797, 129 **[0023]**
- **KIDO et al.** White light emitting organic electroluminescent device using lanthanide complexes. *Jpn. J. Appl. Phys.,* 1996, vol. 35, L394-L396 **[0031]**
- **BALDO et al.** Highly efficient organic phosphorescent emission from organic electroluminescent devices. *Letters to Nature,* 1998, vol. 395, 151-154 **[0031]**
- **BERNIUS et al.** *Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices III,* July 1999, vol. 3797, 129 **[0038]**
- **ENDO et al.** *Jpn. J Appl Phys.,* 2002, vol. 41, 358 **[0043]**
- **ZUGANG et al.** *J. Phys. Condens. Matter,* 1996, vol. 8, 3221 **[0055]**
- **KIM et al.** *Appl. Phys. Lett.,* 2003, vol. 83, 3809 **[0055]**
- **KIM et al.** *Appl. Phys. Lett.,* 2002, vol. 80, 3844 **[0055]**
- **CARTER et al.** *Appl. Phys. Lett.,* 1997, vol. 70, 2067 **[0055]**
- **CHEN et al.** *Appl. Phys. Lett.,* 2003, vol. 83, 5127 **[0058]**

专利名称(译)	具有包含阳极覆盖层的无机材料的OLED		
公开(公告)号	EP1624504B1	公开(公告)日	2016-10-12
申请号	EP2005107135	申请日	2005-08-02
[标]申请(专利权)人(译)	乐金显示有限公司		
申请(专利权)人(译)	LG.飞利浦液晶CO.，LTD.		
当前申请(专利权)人(译)	LG DISPLAY CO.，LTD.		
[标]发明人	AZIZ HANY POPOVIC ZORAN D COGGAN JENNIFER A		
发明人	AZIZ, HANY POPOVIC, ZORAN D. COGGAN, JENNIFER A.		
IPC分类号	H01L51/50 H01L51/52		
CPC分类号	H01L51/5088 H01L51/50 H01L51/506 H01L51/5206 Y10S428/917		
优先权	10/909691 2004-08-02 US		
其他公开文献	EP1624504A3 EP1624504A2		
外部链接	Espacenet		

摘要(译)

一种有机发光器件，包括：阴极;包含有机电致发光材料的层;包含电子接受材料的层;阳极覆盖层，包括无机材料;阳极;在阴极之前或阳极之后的序列中的基板，其中选择阳极盖层以使器件具有大于1的亮度稳定性比。

$$\text{Time for 10 \% decay from } L_0 = 100\ cd/m^2 = (\text{Time for 10 \% decay from } L_0 \text{ measured above}) \times (L_0 \text{ measured above}) / 100.$$