

US006515314B1

(12) United States Patent

Duggal et al.

(10) Patent No.: US 6,515,314 B1

(45) **Date of Patent:** Feb. 4, 2003

(54) LIGHT-EMITTING DEVICE WITH ORGANIC LAYER DOPED WITH PHOTOLUMINESCENT MATERIAL

(75) Inventors: **Anil Raj Duggal**, Niskayuna, NY (US); **Alok Mani Srivastava**, Niskayuna, NY

(US); Steven Jude Duclos, Clifton

Park, NY (US)

(73) Assignee: General Electric Company,

Niskayuna, NY (US)

(*) Notice: Subject to any disclaimer, the term of this

patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/713,394

(22) Filed: Nov. 16, 2000

(51) Int. Cl.⁷ H01L 31/072

503, 506, 507

(56) References Cited

U.S. PATENT DOCUMENTS

4,769,292	А	-1-	9/1988	lang et al	428/690
5,126,214	A	*	6/1992	Tokailin et al	428/690
5,294,870	A		3/1994	Tang et al.	
5,683,823	A	*	11/1997	Shi et al	428/690
5,717,289	A	*	2/1998	Tanaka	313/503
5,813,753	A	*	9/1998	Vriens et al	362/293

5,943,354 A	* 8/1999	Lawandy	372/39
5,998,803 A	12/1999	Forrest et al.	
6,023,371 A	2/2000	Onitsuka et al.	
6.252,254 B1	* 6/2001	Soules et al	257/89

OTHER PUBLICATIONS

Junji Kido et al., "Multilayer White Light–Emitting Organic Electroluminescent Device," 267 Science 1332–1334 (1995).

"Encyclopedia of Physical Science and Technology," vol. 7, 230–231 (Robert A Meyers (Ed.), 1987).

H. Suzuki et al., "Near-Ultraviolet Electroluminescence From Polysilanes," 331 Thin Solid Films 64-70 (1998).

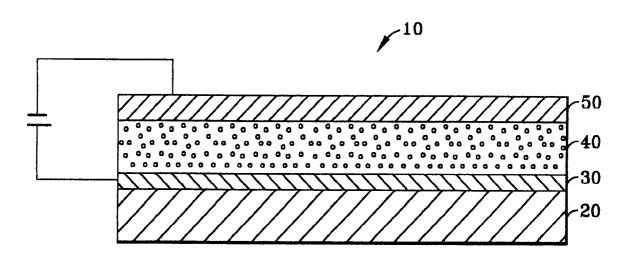
* cited by examiner

Primary Examiner—Nathan J. Flynn Assistant Examiner—Remmon R. Fordé (74) Attorney, Agent, or Firm—Toan P. Vo; Noreen C. Johnson

(57) ABSTRACT

A light-emitting device includes an anode, a cathode, and at least one organic electroluminescent ("EL") material positioned between the anode and the cathode. Nanoparticles of at least one photoluminescent material are dispersed in the organic EL material. The organic EL material emits a first electromagnetic ("EM") radiation having a first spectrum in response to an applied electrical field. The PL material absorbs a portion of the first EM radiation emitted by the organic EL material and emits a second EM radiation having a second spectrum. A plurality of the light-emitting devices are arranged on a transparent substrate to provide a panel display or a lighting source.

28 Claims, 6 Drawing Sheets



Feb. 4, 2003

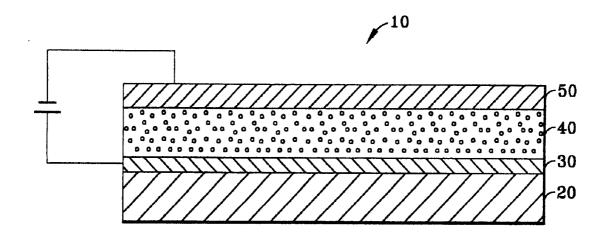
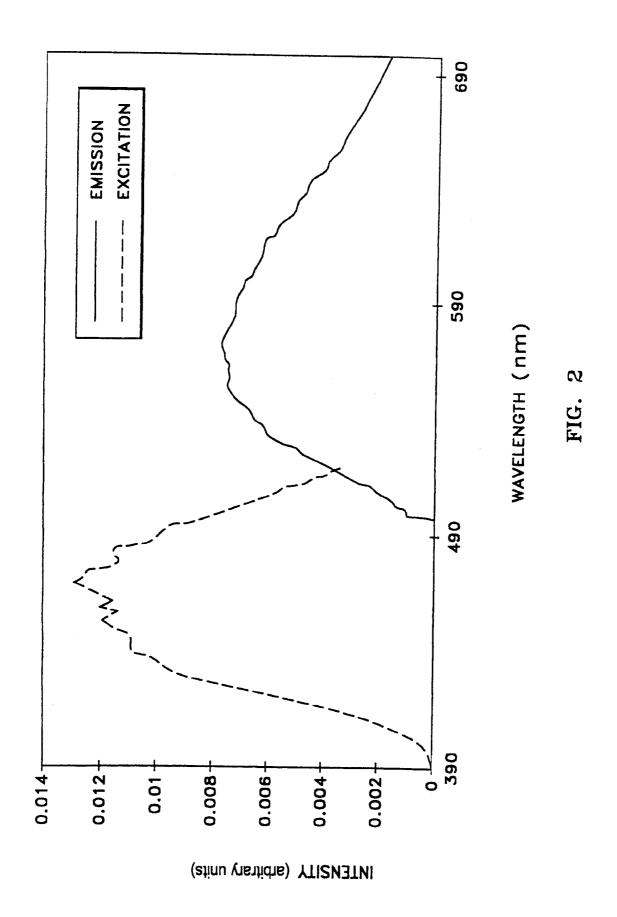
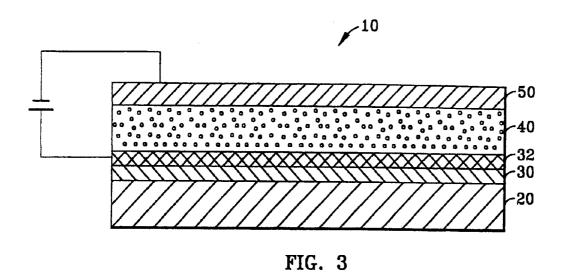
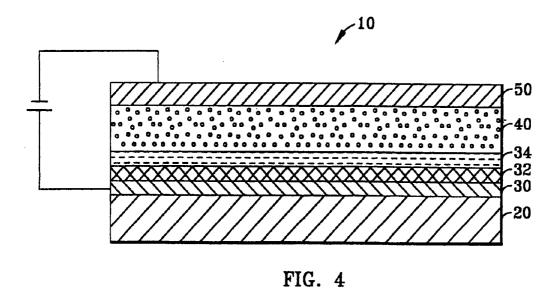


FIG. 1

Feb. 4, 2003







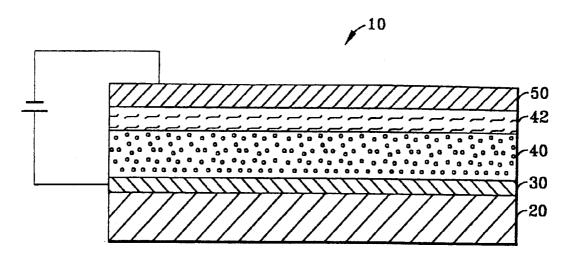
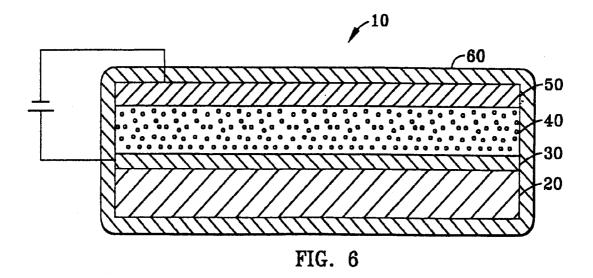


FIG. 5



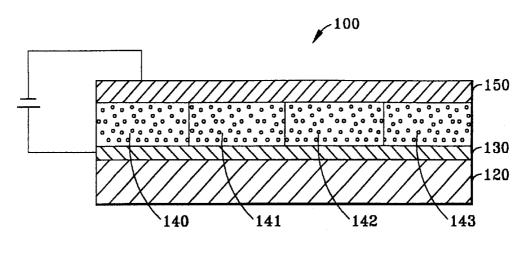


FIG. 7

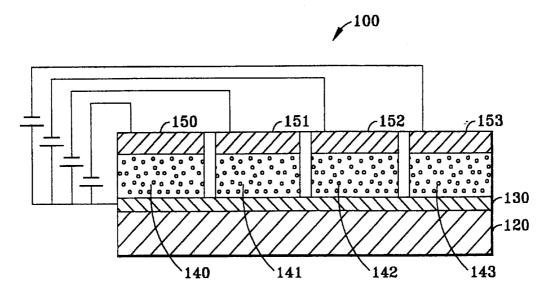


FIG. 8

Feb. 4, 2003

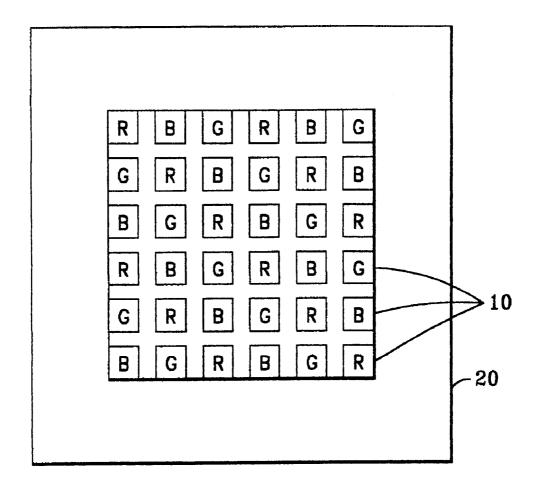


FIG. 9

LIGHT-EMITTING DEVICE WITH ORGANIC LAYER DOPED WITH PHOTOLUMINESCENT MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to lighting applications and, more particularly, to a light-emitting device having at least one organic luminescent layer doped with at least one photoluminescent material.

2. Description of the Related Art

Light-emitting diodes have gained increasing interest as sources for lighting. These devices are classified into inorganic light-emitting diodes ("LEDs") and organic lightemitting devices ("OLEDs"). The technology for LEDs has progressed significantly, and typical semiconductor-based LEDs now can emit a range of colors in the green-to-red wavelengths. LEDs emitting blue or violet light are rare. Commercial blue LEDs are based on gallium nitride (GaN) with phosphor particles to produce a mixture of the primary colors, resulting in white light. However, the manufacture of these devices is still complex and costly.

On the contrary, OLEDs offer the promise of low drive voltage requirement and simple manufacture. The simplest 25 OLEDs typically consist of three layers deposited on a transparent substrate: an anode layer, an active layer of electroluminescent ("EL") organic material, and a cathode layer. The EL organic material is either a low molecular weight organic material or a polymeric material having 30 unsaturated bonds. Individual OLEDs typically emit broadspectrum lights. To achieve a white light, prior-art devices incorporate closely arranged OLEDs emitting blue, green, and red light. These color lights are mixed to produce white light. An alternate scheme to produce white light is set forth 35 OLED. in U.S. Pat. No. 5,294,870 which describes an organic EL multicolor display device comprising an organic EL source emitting blue light with green- and red-emitting fluorescent materials applied to different subpixel areas. This device emits different colors from the different subpixel areas by 40 color shifting with the green- and red-emitting fluorescent materials. However, the manufacture of such microdevices is complex and requires sophisticated technologies.

Another example of an OLED is described in Junji Kido et al., "Multilayer White Light-Emitting Organic Electrolu- 45 minescent Device," 267 Science 1332-1334 (1995). This device includes three emitter layers with different carrier (or charge) transport properties, each emitting blue, green, or red light, which layers are used together to generate white light. However, the formation of successive layers requires 50 a high degree of care so that the interfaces between the layers do not introduce unnecessary barriers to charge transport. In this device, the layers emitting the different colors typically degrade over time at different rates. Consequently, the color of light emitted from the device is likely to change 55 over time. In addition, the uniformity of the light output over the emitting area of the device may be less than desirable because of imperfections at the interfaces between the layers.

Therefore, it is desirable to provide a light source based 60 on organic EL materials that emits light at controllable wavelengths and is simple to manufacture. It is also desirable to use such light sources to produce white light.

BRIEF SUMMARY OF THE INVENTION

Alight-emitting device of the present invention comprises an anode, a cathode, and at least one organic EL material that

is in contact with the anode and the cathode. The anode and the cathode are electrically isolated from one another. The organic EL material emits electromagnetic ("EM") radiation having a first spectrum in response to an electrical voltage or an electrical field applied through the anode and the cathode. The electrical voltage or electrical field is applied by connecting the anode to a first electrical potential and connecting the cathode to a second electrical potential that is lower than the first. The organic EL material includes at least one photoluminescent ("PL") material dispersed therein that absorbs a portion of the EM radiation emitted by the organic EL material and emits EM radiation having a second spectrum. When the EM radiation has the wavelength range in the visible spectrum (i.e, from about 380 nm to about 770 nm) the terms "light" and "EM radiation" are used interchangeably hereinafter. The organic EL material is formed into a thin film that is disposed between an anode and a cathode of the light-emitting device. The preferred PL materials comprise inorganic phosphors in the form of or indium gallium nitride (InGaN). LEDs have been coated 20 nanoparticles. The term "nanoparticles" as used in the present disclosure means particles having the largest dimension less than about 100 nm. The preferred largest dimension for the nanoparticles is less than about 50 nm. The inorganic phosphor nanoparticles are dispersed in the organic EL material prior to film formation. The PL material absorbs EM radiation having a shorter wavelength and emits EM radiation having a longer wavelength. In this case, the PL material is said to perform a down-conversion of the EM radiation. Other PL materials may be chosen to absorb EM radiation having a longer wavelength and emit EM radiation having a shorter wavelength. In this case, the PL material is said to perform an up-conversion of the EM radiation. Thus, the choice of the organic EL material and the PL material provides a control over the color of light emitted by the

BRIEF DESCRIPTION OF THE DRAWINGS

Other features and advantages of the present invention will be apparent from the following detailed description of the preferred embodiments and the accompanying drawings in which the same numerals refer to like elements.

FIG. 1 is a schematic diagram of a three-layer organic light-emitting device of the present invention.

FIG. 2 shows the absorption and PL spectra of the yittrium aluminum oxide garnet phosphor doped with gadolinium and cerium.

FIG. 3 is a schematic diagram of a four-layer organic light-emitting device of the present invention.

FIG. 4 is a schematic diagram of a five-layer organic light-emitting device of the present invention.

FIG. 5 is a schematic diagram of another embodiment of a four-layer organic light-emitting device of the present

FIG. 6 is a schematic diagram of the OLED of the present invention encapsulated in a protective shell.

FIG. 7 is a schematic diagram of a first embodiment of a flat panel display of the present invention.

FIG. 8 is a schematic diagram of a second embodiment of a flat panel display of the present invention.

FIG. 9 is a schematic diagram of an arrangement of the OLEDs to form a white light source.

DETAILED DESCRIPTION OF THE INVENTION

There has been an increasing need to have thin, flat, inexpensive, extended white light sources with a high color

55

rendition index ("CRI") and a color temperature in the range of 3000-6500° K for general illumination applications. In addition, the demand for flat panel displays having full color and high resolution also increases significantly with the explosive growth of television, computer terminals, and 5 portable electronic devices.

The present invention provides a light-emitting device that can emit light having a color temperature in the range of about 1000° K to over 10000° K, corresponding to red to blue color. A particular color temperature is achieved by the 10 choice of the particular organic EL material and the phosphor materials.

According to another embodiment of the present invention, a plurality of the light-emitting devices of the present invention is incorporated in a substantially flat panel display or a large lighting device for illumination of an area.

The color temperature of a light source refers to the temperature of a blackbody source having the closest color match to the light source in question. The color match is typically represented and compared on a conventional CIE (Commission International de l'Eclairage) chromaticity diagram. See, for example, "Encyclopedia of Physical Science and Technology," Vol. 7, 230-231 (Robert A. Meyers (Ed.), 1987). Generally, as the color temperature increases, the light becomes bluer. As the color temperature decreases, the light appears redder.

The CRI is a measure of the degree of distortion in the apparent colors of a set of standard pigments when measured with the light source in question as opposed to a standard 30 light source. The CRI can be determined by calculating the color shift; e.g., quantified as tristimulus values, produced by the light source in question as opposed to the standard light source. Typically, for color temperatures below 5000° appropriate temperature. For color temperatures greater than 5000° K, sunlight is typically used as the standard light source. Light sources having a relatively continuous output spectrum, such as incandescent lamps; typically have a high CRI, e.g. equal to or near 100. Light sources having a 40 multi-line output spectrum, such as high pressure discharge lamps, typically have a CRI ranging from about 50 to 80. Fluorescent lamps typically have a CRI greater than about

the organic EL material emits EM radiation having a wavelength in the range from UV to blue light (i.e., from about 300 nm to about 500 nm) in response to an applied voltage or an applied electrical field, and the inorganic phosphors ultraviolet to blue light and emit light having a wavelength in the range of blue to red light (i.e., from about 400 nm to about 770 nm). The source for the applied voltage may be a direct current ("DC") source or an alternating current ("AC") source.

The organic EL film or layer of the present invention is typically disposed between an anode layer and a cathode layer of the light-emitting device. The multilayer assemblage of anode, organic EL film, and cathode is typically supported on a substantially transparent substrate, such as 60 glass, quartz, or a substantially transparent polymeric material. The substrate allows at least 80%, preferably at least 95%, more preferably at least 99%, and most preferably at least 99.9%, light transmitted therethrough. Examples of polymeric materials suitable for use as the substrate are 65 polycarbonate, silicone, polyacrylate, polyethylene terephthalate, and epoxy resins. One or more additional

layers of other organic or metallic materials may be included between the anode and the cathode to increase the efficiency for injecting charges into or for carrying those charges to the active organic EL film. When an additional metallic film is used to facilitate the transport positive charges or holes to the active organic EL layer, their thickness is kept to a minimum, preferably less than 50 nm, so that light emitted from the organic layer can escape substantially unalterably. The thickness of any additional layer used to facilitate the transport of electrons to the active organic EL layer, on the other hand, may be larger as long as it is not excessive such that the layer presents an excessive barrier to the injection of electrons.

Exemplary embodiments of the present invention provide advantages over known devices. For example, the light emitted from the organic light emitting device is scattered because of the presence of the nanoparticles, and the light scattering provides improved uniformity in light output over the area of the light source. Also, because most phosphors are relatively stable over time, a light source according to exemplary embodiments of the invention has good color stability over time.

As examples of embodiments of the invention, the light source comprises an OLED that emits light in the blue or ultraviolet ("UV") spectral region (i.e., wavelengths in the 25 range of about 300 nm to about 500 nm). FIG. 1 is a schematic diagram of the first preferred embodiment of the light-emitting device of the present invention. The OLED 10 comprises three layers: an anode layer 30, a layer of organic EL material 40, and a cathode layer 50. The assemblage of the layers is disposed on a substantially transparent substrate 20 such as glass, quartz, or a substantially transparent polymer. The substrate allows at least 80%, preferably at least 95%, more preferably at least 99%, and most preferably 99.9%, light transmitted therethrough. The polymer K, the standard light source used is a blackbody of the 35 may be formed into a rigid or a flexible flat piece made of a polycarbonate, silicone, polyacrylate, polyethylene terephthalate, epoxy resin, or the like. However, in certain circumstances, it may be desirable to form the OLED on a curved substrate.

The anode layer 30 injects positive charge carriers (or holes) into the organic EL layer when an electrical voltage is applied across the OLED 10. The anode layer is preferably made of a metal having a high work function; e.g., greater than about 4.5 eV, preferably from about 4.5 eV to about 5.5 According to one embodiment of the present invention, 45 eV. Indium tin oxide ("ITO") is typically used for this purpose. The thickness of the ITO anode layer is typically in the range from about 50 nm to 400 nm, preferably from about 50 nm to about 200 nm. ITO is substantially transparent to light transmission and allows at least 80% light absorb EM radiation having a wavelength in the range of 50 transmitted therethrough. Therefore, light emitted from the organic EL layer 40 can easily escape through the ITO anode without being seriously attenuated. Other materials suitable for use as the anode layer are tin oxide, indium oxide, zinc oxide, indium zinc oxide, and mixtures thereof.

> The cathode layer 50 injects negative charge carriers (electrons) into the organic EL layer 40 when a voltage is applied across the OLED 10 and is selected from a material having a low work function; e.g, less than about 4 eV. Materials suitable for use as a cathode are K, Li, Na, Mg, La, Ce, Ca, Sr, Ba, Al, Ag, In, Sn, Zn, Zr, or mixtures thereof. Preferred materials for the manufacture of cathodes are Ag-Mg, Al-Li, In-Mg, and Al-Ca alloys. The thickness of the cathode layer is preferably kept in the range from about 50 nm to about 500 nm, preferably from about 50 nm to about 200 nm.

> The organic EL layer 40 serves as the transport medium for both holes and electrons. In this layer these excited

species combine and drop to a lower energy level, concurrently emitting EM radiation in the visible range. The preferred organic EL materials are those capable of electroluminescing in the range of UV to blue light. More preferably, the organic materials electroluminesce in the wavelength range from about 300 nm to about 450 nm. The thickness of the organic EL layer 40 is preferably kept in the range of about 100 to about 300 nm. The organic EL material may be a polymer, a copolymer, a mixture of polymers, or lower molecular-weight organic molecules having unsaturated bonds. Such materials possess a delocalized π -electron system, which gives the polymer chains or organic molecules the ability to support positive and negative charge carriers with high mobility. Suitable EL polymers are poly (N-vinylcarbazole) ("PVK", emitting violet-to-blue light in 15 the wavelengths of about 380–500 nm); poly(alkylfluorene) such as poly(9,9-dihexylfluorene) (410-550 nm), poly (dioctylfluorene) (wavelength at peak EL emission of 436 nm), or poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (400-550 nm); poly(praraphenylene) derivatives such as poly(2-decyloxy-1,4-phenylene) (400-550 nm). Mixtures of these polymers or copolymers based on one or more of these polymers and others may be used as long as the resulting polymeric material preferably emits blue light. For example, a copolymer of 2,7-dibromo-9,9-di-n-hexylfluorene and 9,10-dibromoanthracene emits light in the wavelength range of 400-525 nm.

Another class of suitable EL polymers is the polysilanes. Polysilanes are linear silicon-backbone polymers substituted quasi one-dimensional materials with delocalized σ-conjugated electrons along polymer backbone chains. Examples of polysilanes are poly(di-n-butylsilane), poly(din-pentylsilane), poly(di-n-hexylsilane), poly (methylphenylsilane), and poly[bis(p-butylphenyl)silane] 35 which are disclosed in H. Suzuki et al., "Near-Ultraviolet Electroluminescence From Polysilanes," 331 Thin Solid Films 64–70 (1998). These polysilanes emit light having wavelengths in the range from about 320 nm to about 420

Organic materials having molecular weight less than about 5000 that are made of a large number of aromatic units are also applicable. An example of such materials is 1,3,5tris[N-(4-diphenylaminophenyl) phenylamino] benzene, which emits light in the wavelength range of 380-500 nm. 45 The organic EL layer also may be prepared from lower molecular weight organic molecules, such as phenylanthracene, tetraarylethene, coumarin, rubrene, tetraphenylbutadiene, anthracene, perylene, coronene, or their derivatives. These materials generally emit light having 50 to Mn²⁺ ion. Thus, a larger total amount of light emitted by maximum wavelength of about 520 nm. Still other suitable materials are the low molecular-weight metal organic complexes such as aluminum-, gallium-, and indiumacetylacetonate, which emit light in the wavelength range of butyl)phenoxide] or scandium-(4-methoxypicolylmethylketone)-bis(acetylacetonate), which emits in the range of 420-433 nm. The preferred organic EL materials are those emit light predominantly below 450 nm such as PVK or polysilanes.

At least one phosphor material is dispersed uniformly in the organic EL layer. The phosphor material is preferably of an inorganic type and is in the form of nanoparticles. The nanoparticles have a particle size distribution such that more than 95 percent of the particles have the largest dimension 65 less than 100 nm, preferably less than 50 nm, and most preferably less than 30 nm. The smaller particle size is

preferred because the particles will disperse well in the organic medium and the resulting organic EL layer would have a smoother surface. The phosphor nanoparticles may be prepared from larger pieces of phosphor material by any grinding or pulverization method, such as ball milling using zirconia-toughened balls or jet milling. They also may be prepared by crystal growth from solution, and their size may be controlled by terminating the crystal growth at an appropriate time. The preferred phosphor materials efficiently absorb EM radiation emitted by the organic EL material in the ultraviolet-to-blue spectral region (i.e., wavelengths in the range from 100 nm to about 480 nm, preferably from about 350 nm to about 450 nm) and re-emit light in the blue-to-red spectral region (i.e., wavelength in the range from about 450 nm to about 770 nm). A particular phosphor material may be chosen to emit a desired color. A mixture of phosphors such as those emitting blue, green, and red light may be used if a white light is desired. An exemplary phosphor is the cerium-doped yttrium aluminum oxide Y₃Al₅O₁₂ garnet ("YAG"). Other suitable phosphors are based on YAG doped with more than one type of rare earth ions, such as $(Y_{1-x-y}Gd_xCe_y)_3Al_5O_{12}$ ("YAG:Gd,Ce"), $(Y_{1-x} Ce_x)_3 (Al_{1-y} Ga_y) O_{12} ("YAG:Ga,Ce"), (Y_{1-x-y} Gd_x Ce_y)$ $(Al_5 - Ga_2)O_{12}$ ("YAG:Gd,Ga,Ce"), and $(Gd_{1-x}Ce_x)$ $Sc_2Al_3O_{12}$ ("GSAG") where $0 \le x \le 1$, $0 \le y \le 1$, $0 \le z \le 5$ and $x+y \le 1$. For example, FIG. 2 shows the emission PL spectrum of the YAG:Gd,Ce phosphor. This material shows an absorption of light in the wavelength range from about 390 nm to about 530 nm (i.e., the blue spectral region) and an with a variety of alkyl and/or aryl side groups. They are 30 emission of light in the wavelength range from about 490 nm to about 700 nm (i.e., the green-to-red spectral region). The following are examples of phosphors that are efficiently excited by EM radiation emitted in the wavelength region of 300 nm to about 500 nm by polysilanes and their derivatives.

Green-emitting phosphors: $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}$, Mn^{2+} ; $GdBO_3:Ce^{3+}$, Tb^{3+} ; $CeMgAl_{11}O_{19}$: Tb^{3+} ; $Y_2SiO_5:Ce^{3+},Tb^{3+}$; and $BaMg_2Al_{16}O_{27}:Eu^{2+},Mn^{2+}$; Red-emitting phosphors: Y₂O₃:Bi³⁺,Eu³⁺; Sr₂P₂O₇:Eu²⁺ Mn^{2+} ; $SrMgP_2O_7:Eu^{2+},Mn^{2+}$; $(Y,Gd)(V,B)O_4:Eu^{3+}$; and 3.5MgO.0.5MgF₂.GeO₂:Mn⁴⁺;

Blue-emitting phosphors: BaMg₂Al₁₆O₂₇:Eu²⁺ and Sr₅ $(PO_4)_{10}Cl_2:Eu^{2+}$

Still other ions may be incorporated into the phosphor to transfer energy from the light emitted from the organic material to other activator ions in the phosphor host lattice as a way to increase the energy utilization. For example, when Sb³⁺ and Mn²⁺ ions exist in the same phosphor lattice, Sb³⁺ efficiently absorbs light in the blue region, which is not absorbed very efficiently by Mn²⁺, and transfers the energy the organic EL material is absorbed by both ions, resulting in higher quantum efficiency of the total device.

The phosphor nanoparticles are dispersed in the organic EL film-forming material. A phosphor composition of less 415-457 nm, aluminum-(picolymethylketone)-bis[2,6-di(t- 55 than about 30, preferably less than about 10, percent by volume of the mixture of organic material and phosphor is used. A solvent may be added into the mixture to adjust the viscosity of the organic material to a desired level. The mixture of the organic EL material and phosphor nanoparticles is applied by conventional techniques such as spin coating, spray coating, dip coating, roller coating, or ink-jet printing on the anode thin film that has been formed on the substantially transparent substrate. Spin coating is the preferred method when the mixture does not have very high viscosity. However, when it is desired to form the organic EL material on many small areas, the ink-jet printing method may be preferred.

In addition to the anode, organic EL, and the cathode layers, one or more additional layers may be included to increase the efficiency of the overall device. For example, these additional layers can serve to improve the injection (electron or hole injection enhancement layers) or transport (electron or hole transport layers) of charges into the organic EL layer. The thickness of each of these layers is kept to below 500 nm, preferably below 100 nm. Materials for these additional layers are typically low-to-intermediate molecular weight (less than about 2000) organic molecules. They 10 may be applied during the manufacture of the OLED by conventional methods such as spin coating, spray coating, dip coating, roller coating, ink-jet-printing, or physical or chemical vapor deposition. In another embodiment of the present invention, as shown schematically in FIG. 3, a hole 15 OLEDs with respect to the schedule or level of the power injection enhancement layer 32 is formed between the anode layer 30 and the organic EL layer 40 to provide a higher injected current at a given forward bias and/or a higher maximum current before the failure of the device. Thus, the hole injection enhancement layer facilitates the injection of 20 transparent ITO. In a preferred embodiment, a plurality of holes from the anode. Suitable materials for the hole injection enhancement layer are arylene-based compounds disclosed in U.S. Pat. No. 5,998,803; such as 3,4,9,10perylenetetra-carboxylic dianhydride or bis(1,2,5thiadiazolo)-p-quinobis(1,3-dithiole).

In another embodiment of the present invention, as shown schematically in FIG. 4, the OLED 10 further includes a hole transport layer 34 which is disposed between the hole injection enhancement layer 32 and the organic EL layer 40. The hole transport layer 34 has the functions of transporting 30 individual EL pixel, object, or figure may vary to provide the holes and blocking the transportation of electrons so that holes and electrons are optimally combined in the organic EL layer. Materials suitable for the hole transport layer are triaryldiamine, tetraphenyldiamine, aromatic tertiary amines, hydrazone derivatives, carbazole derivatives, triaz- 35 ole derivatives, imidazole derivatives, oxadiazole derivatives having an amino group, and polythiophenes as disclosed in U.S. Pat. No. 6,023,371.

In still another embodiment of the present invention, as shown schematically in FIG. 5, the OLED 10 includes an 40 additional layer 42 which is disposed between the cathode layer 50 and the organic EL layer 40. Layer 42 has the combined function of injecting and transporting electrons to the organic EL layer. Materials suitable for the electron injecting and transporting layer are metal organic complexes 45 such as tris(8-quinolinolato)aluminum, oxadiazole derivatives, perylene derivatives, pyridine derivatives, pyrimidine derivatives, quinoline derivatives, quinoxaline derivatives, diphenylquinone derivatives, and nitrosubstituted fluorene derivatives, as disclosed in U.S. Pat. No. 50 desired patterns. When one mask is applied, the cathode 6,023,371.

When one or more additional layers other than the organic EL laver are included in the OLED, such as for hole injection enhancement, hole transport, electron injection enhancement and transport, nanoparticles of one or more 55 between them, and a separate power supply may be provided phosphors disclosed above may be dispersed therein. An exemplary purpose for such an inclusion of phosphor nanoparticles is to further tune the color of the light emitted from the OLED.

In still another embodiment of the present invention, as 60 shown schematically in FIG. 6, the complete OLED 10 may be encapsulated in a substantially transparent and thin shell 60 of a polymeric material to retard the negative impact of oxygen and/or moisture on the useful life of the OLED 10. such as spray coating, dip coating, or chemical vapor deposition, followed by curing. The shell preferably has a

thickness less than about 100 nm after curing. Although the OLED 10 shown in FIG. 6 includes only the substrate, the anode, the organic EL layer, and the cathode, it should be appreciated that any or all of the hole injection enhancement layer, the hole transport layer, and the electron injection enhancement and transport layer also may be included before the formation of the protective shell **60**.

One or more OLEDs of the present invention may be included in a light-emitting flat panel display. The completed OLEDs may be attached to a common substrate or the layers of the individual OLEDs may be formed directly on defined areas of the common substrate. Each OLED or group of OLEDs may be provided with its own electrical power source, and the energization of different OLEDs or groups of applied may be controlled by a controller. An example is shown in FIG. 7. A flat panel color display 100 comprises a substantially transparent substrate 120 on which a thin anode layer 130 is formed. This anode layer is typically made of pixels (e.g., 140-143) of organic EL materials, each having one or more types of phosphor nanoparticles dispersed therein, is deposited on the anode layer at distinct positions. The organic EL materials are preferably applied by the 25 ink-jet printing method. This technique provides an inexpensive method of depositing the organic EL materials in very fine pixels.

Alternatively, larger objects or figures may be formed, for example, by spray coating or printing. The thickness of each optimum brightness and appearance of the display. The pixels, objects, or FIGS. may be deposited adjacently to one another to form a continuous layer. It may be desirable, in certain circumstances, to provide a partition between two adjacent pixels, objects, or figures. In this case, the partition is desirably made of an organic EL material that is different from the organic EL materials of the adjacent pixels, objects, or figures. In other circumstances, the partition may be desirably made of an organic material that is not electroluminescent. More than one layer of phosphor-dispersed organic EL material may be formed one on top of another to achieve the object of the display. A common cathode layer 150 is deposited on the exposed surface of the organic EL layer. In this case a common electrical power supplied is provided to the display. Alternatively, a separate cathode pixel or region may be deposited on each separate organic EL pixel or region as denoted by numerals 150-153 in FIG. 8. A convenient method of applying the separate cathode pixels or regions is by employing successive masks with the pixels are formed at the openings in the mask. Another mask is subsequently applied to form cathode pixels on other organic EL pixels. When separate cathode pixels or regions are formed, insulating partitions are preferably provided to each individual OLED which comprises the anode, the individual organic EL pixel or region, and the corresponding cathode pixel or region directly adjacent to it. In addition, additional layers for hole injection enhancement, hole transport, and electron injection enhancement and transport may be include as disclosed above. The various preferred materials disclosed in the foregoing are equally applicable to the manufacture of the flat panel display.

In another embodiment of the present invention, a white-This shell may be formed by any conventional technique 65 light source is produced by integrating a plurality of lightemitting devices, each emitting one of blue, green, or red color. The individual OLEDs are arranged adjacently on a

substantially transparent substrate such that two adjacent OLEDs emit two different colors. Preferably, the OLEDs are arranged in a matrix of rows and columns such that the OLEDs of each row or column form a periodic light color pattern; e.g, blue-green-red. In this way, the lights emitted by 5 adjacent OLEDs are mixed to produce a white light.

Methods of producing OLEDs, panel displays, and largearea light sources of the present invention are now described.

A substantially transparent substrate piece such as glass is 10 provided. The substrate piece may be previously cleaned with a compatible liquid, such as a dilute acid solution, and dried in a clean environment. An anode material, such as ITO, is sputter-deposited on the substrate piece to form an anode layer. The, anode layer may be patterned further by 15 etching. Preferably, the anode pattern is provided with an area from which a connection to an electrical voltage source may be made. The organic EL material is mixed with a desired amount of nanoparticles of at least one chosen PL material to produce a well-dispersed mixture. A quantity of 20 a compatible solvent may be added to the mixture to adjust its viscosity to a desired level for ease of application on the anode. The solvent is preferably an organic solvent having high a vapor pressure such that it can be easily removed from the organic EL layer after it has been formed. Suitable 25 solvents are acetone, low molecular weight alcohols, cyclohexane, toluene, or xylene. When the desired EL material is a polymeric material, monomers or oligomers of the polymeric material may be used in the mixture and a further polymerization of the monomers or oligomers may 30 be carried out after the film has been formed. The mixture is deposited on the anode by any conventional method such as spin coating, spray coating, dip coating, roller coating, or ink-jet printing. Spin coating and ink-jet printing are preferred. The partially formed device at this stage may be dried 35 at a low temperature, preferably under a sub-atmospheric pressure. The organic EL material may require a polymerization by an appropriate initiation. For example, EM radiation having an appropriate wavelength, such as in the UV range, or heat may complete the polymerization process. In 40 other instances, a soluble polymerization catalyst may be provided in the mixture before the film is formed. In still other instances, the catalyst may be applied on the organic EL layer to initiate the polymerization, for example, by spraying. When a catalyst is used for the polymerization, it 45 may be removed and the partially completed device may be dried in a clean environment. The cathode layer is next formed by sputter-depositing the cathode material, from one or more sources, on the organic EL layer. An electrical lead is attached to the cathode layer for a connection to the lower 50 EM radiation has a wavelength in the range from about 100 electrical potential of the voltage source. The device may be further encapsulated in a thin shell of a substantially transparent polymer. The shell may be formed by dip coating and curing the polymer. When additional layers of hole injection enhancement and transport material are included in the OLED, they may be applied on the appropriate previouslyformed layer by spin coating, spray coating, dip coating, roller coating, or ink-jet printing. The preferred method is ink-jet printing.

A plurality of the OLEDs thus made may be integrated together on a large-area transparent substrate to form a panel display or a light source for general lighting purposes. The individual OLEDs are attached to the substrate in a desired pattern with a thin layer of adhesive, such as a thermoplastic 65 alkylphenoxide; derivatives thereof; and mixtures thereof. material or an epoxy resin. To produce a large-area white light source, a plurality of OLEDs 10 are preferably attached

10

on the substrate 20 with a layer of adhesive in a matrix of rows and columns. The OLEDs are arranged such that two adjacent OLEDs 10 emit two different light colors selected from blue ("B"), green ("G"), and red ("R"); and the OLEDs 10 form a periodic pattern of colors, such as blue-green-red. FIG. 9 shows an example of such an arrangement. Alternatively, one single anode layer may be deposited on the substrate. Then the individual organic EL materials having nanoparticles dispersed therein are deposited on the anode layer in the desired pattern by ink-jet printing. Partitions of a non-conductive organic material are the deposited between the EL materials by, for example, ink-jet printing or chemical vapor deposition through an applied mask. Individual cathodes are then deposited on each individual organic EL material with non-conductive partitions provided between them. The cathodes in this case may be deposited by the conventional photolithography method.

While specific preferred embodiments of the present invention have been described in the foregoing, it will be appreciated by those skilled in the art that many modifications, substitutions, or variations may be made thereto without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

- 1. A light-emitting device comprising: an anode;
- a cathode; and
- at least one organic electroluminescent ("EL") material disposed between the anode and the cathode, the organic EL material having a plurality of nanoparticles of at least one inorganic photoluminescent ("PL") material dispersed therein, the organic EL material being capable of emitting a first electromagnetic ("EM") radiation having a first spectrum in response to an electrical voltage applied through the anode and the cathode, and the inorganic PL material being capable of absorbing a portion of the first EM radiation and emitting a second EM radiation having a second specfrum.
- 2. The light-emitting device of claim 1 wherein the anode, the cathode, and the organic EL material are formed as successive layers on a substantially transparent substrate.
- 3. The light-emitting device of claim 1 wherein the first spectrum has a range of shorter wavelengths than the second spectrum.
- 4. The light-emitting device of claim 1 wherein the first spectrum has a range of longer wavelengths than the second spectrum.
- 5. The light-emitting device of claim 3 wherein the first nm to about 480 nm and the second EM radiation has a wavelength in the range from about 400 nm to about 770 nm.
- 6. The light-emitting device of claim 5 wherein the organic EL material is capable of emitting EM radiation enhancement and transport material or electron injection 55 having a wavelength range from about 100 nm to about 480 nm and comprises a material selected from the group consisting of poly(N-vinylcarbazole); poly(alkylfluorene); poly(paraphenylene); polysilane; 1,3,5-tris[N-(4diphenylaminophenyl)phenylamino] benzene; anthracene; phenylanthracene; tetraarylethene; coumarin; rubrene; tetraphenylbutadiene; perylene; coronene; aluminum acetoacetonate; gallium acetoacetonate; indium acetoacetonate; scandium acetoacetonate; aluminum alkylphenoxide; gallium alkylphenoxide; indium alkylphenoxide; scandium
 - 7. The light-emitting device of claim 6 wherein the organic EL material comprises a material selected from the

11

group consisting of poly(N-vinylcarbazole), poly (alkylfluorene) and polysilanes.

- 8. The light-emitting device of claim 5 wherein said at least one inorganic PL material is capable of absorbing EM radiation having a wavelength range from about 100 nm to 5 about 480 nm and capable of emitting EM radiation having a wavelength range from about 400 nm to about 770 nm; said at least one inorganic PL material is selected from the group consisting of yttrium aluminum oxide garnet $Y_3Al_5O_{12}$, $(Y_{1-x-y}Gd_xCe_y)_3Al_5O_{12}$, $(Y_{1-x}Ce_x)_3(Al_{1-y}Ga_y)$ 10 O_{12} , $(Y_{1-x-y}Gd_xCe_y)(Al_{5-z}Ga_z)O_{12}$, $(Gd_{1-x}Ce_x)Sc_2Al_3O_{12}$, wherein $0 \le x \le 1$, $0 \le y \le 1$, $0 \le z \le 5$ and $x+y \le 1$; Ca_8Mg $(SiO_4)_4Cl_2:Eu^2+,Mn^2+;$ $GdBO_3:Ce^3+$, $Tb^3+;$ $CeMgAl_{1:1}O_{19}:Y_2SiO_5:Ce^3+$, $Tb^3+;$ $BaMg_2Al_{1:6}O_{27}:Eu^2+$, $Mn^2+;$ $(Y,Gd)(V,B)O_4:Eu^3+;$ 3.5MgO.0.5MgF₂GeO₂: Mn^{4+} ; $BaMg_2Al_{1:6}O_{27}:Eu^{2+}$; and $Sr_5(PO_4)_{1:0}Cl_2:Eu^{2+}$.
- 9. The light-emitting device of claim 5 wherein the anode is made of a material selected from the group consisting of 20 indium tin oxide, tin oxide, indium oxide, zinc oxide, indium zinc oxide, and mixtures thereof.
- 10. The light-emitting device of claim 5 wherein the cathode is made of a material selected from the group consisting of K, Li, Na, Mg, La, Ce, Ca, Sr, Ba, Al, Ag, In, 25 Sn, Zn, Zr, alloys thereof, and mixtures thereof.
- 11. The light-emitting device of claim 1 further comprising a hole injection enhancement material disposed between the anode and the organic EL material.
- 12. The light-emitting device of claim 11 further comprising at least one PL material dispersed in the hole injection enhancement material.
- 13. The light-emitting device of claim 11 wherein the hole injection enhancement material is selected from the group consisting of 3,4,9,10-perylenetetra-carboxylic dianhydride; 35 bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole); and mixtures thereof.
- 14. The light-emitting device of claim 13 further comprising a hole transport material disposed between the hole injection enhancement material and the organic EL material.
- 15. The light-emitting device of claim 14 further comprising at least one PL material dispersed in the hole transport material.
- 16. The light-emitting device of claim 14 wherein the hole transport material comprises a material selected from the 45 group consisting of 3,4,9,10-perylenetetra-carboxylic dianhydride; bis(1,2,5-thiadiazolo)-p-quinobis(1,3-dithiole); and mixtures thereof.
- 17. The light-emitting device of claim 1 further comprising an electron injection enhancement and transport material 50 disposed between the cathode and the organic EL layer.

12

- 18. The light-emitting device of claim 17 further comprising at least one PL material dispersed in the electron injection enhancement and transport material.
- 19. The light-emitting device of claim 15 wherein the electron injection enhancement and transport material comprises a material selected from the group consisting of tris(8-quinolinolato)aluminum, oxadiazole derives, quinoline derivatives, quinoxaline derivatives, diphenylquinone derivatives, nitro-substituted fluorene derivatives, and mixtures thereof.
- 20. The light-emitting device of claim 1 wherein the organic EL material having the PL nanoparticles dispersed therein is applied on the anode by a method selected from the group consisting of spin coating, spray coating, dip coating, roller coating, and ink-jet printing.
- 21. The light-emitting device of claim 20 wherein the organic EL material having the PL nanoparticles dispersed therein is applied on the anode by ink-jet printing.
- 22. The light-emitting device of claim 11 wherein the hole injection enhancement material is applied on the anode by a method selected from the group consisting of spin coating, spray coating, dip coating, roller coating, ink-jet printing, and chemical vapor deposition.
- 23. The light-emitting device of claim 22 wherein the hole injection enhancement material is applied on the anode by ink-jet printing.
- 24. The light-emitting device of claim 14 wherein the hole transport material is applied on the hole injection enhancement material by a method selected from the group consisting of spin coating, spray coating, dip coating, roller coating, ink-jet printing, and chemical vapor deposition.
- 25. The light-emitting device of claim 24 wherein the hole transport material is applied on the hole injection enhancement material by ink-jet printing.
- 26. The light-emitting device of claim 17 wherein the electron injection enhancement and transport material is applied on the organic EL material by a method selected from the group consisting of spin coating, spray coating, dip coating, roller coating, ink-jet printing, and chemical vapor deposition.
- 27. The light-emitting device of claim 17 wherein the electron injection enhancement and transport material is applied on the organic EL material by ink-jet printing.
- 28. The light-emitting device of claim 2 wherein at least two organic EL materials, each having nanoparticles of at least one PL material dispersed therein, are disposed as distinct and adjacent layers between the anode layer and the cathode layer.

* * * * *



专利名称(译)	具有掺杂光致发光材料的有机层的发光装置						
公开(公告)号	<u>US6515314</u>	公开(公告)日	2003-02-04				
申请号	US09/713394	申请日	2000-11-16				
[标]申请(专利权)人(译)	通用电气公司						
申请(专利权)人(译)	通用电气公司						
当前申请(专利权)人(译) 京东方科技集团股份有限公司.							
[标]发明人	DUGGAL ANIL RAJ						
	SRIVASTAVA ALOK MANI						
	DUCLOS STEVEN JUDE						
发明人	DUGGAL, ANIL RAJ						
	SRIVASTAVA, ALOK MANI						
	DUCLOS, STEVEN JUDE						
IPC分类号	H01L51/50 H01L27/28 H01L25/04 H01L27/32 H01L31/072						
CPC分类号	B82Y20/00 B82Y30/00 H01L51/50	0/00 H01L51/5036 H01L25/046 H01L27/3211 H01L2251/5369 H01L51/5048 H01L51					
	/5088 H01L51/5092 H01L2251/5361 H01L2924/0002						
外部链接	Espacenet USPTO						
			10				

摘要(译)

发光装置包括阳极,阴极和位于阳极和阴极之间的至少一种有机电致发光("EL")材料。至少一种光致发光材料的纳米颗粒分散在有机EL材料中。有机EL材料响应于施加的电场发射具有第一光谱的第一电磁("EM")辐射。 PL材料吸收由有机EL材料发射的第一EM辐射的一部分并发射具有第二光谱的第二EM辐射。多个发光装置布置在透明基板上以量提供面板显示器或光源。

