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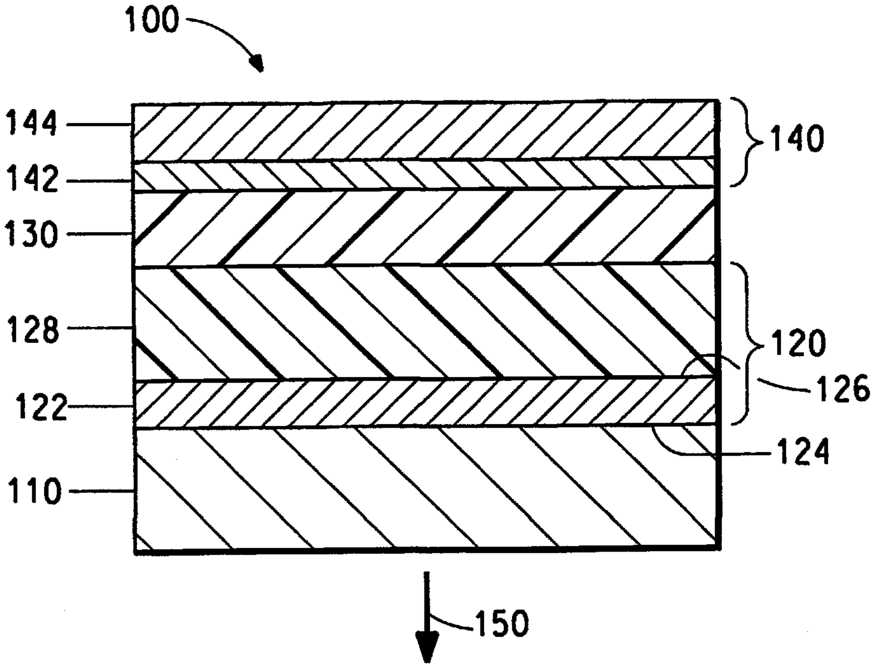
(54) Title: LONG-LIFETIME POLYMER LIGHT-EMITTING DEVICES WITH IMPROVED LUMINOUS EFFICIENCY AND RADIANCE



(57) Abstract: The luminous efficiency and radiance of light emitting diodes (LEDs) fabricated from organic emissive materials can be increased by using a multilayer cathode including a low work function layer and a high work function high reflectivity layer, in combination with a high work function, high reflectivity anode material in the device.

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TITLE

LONG-LIFETIME POLYMER LIGHT-EMITTING DEVICES WITH IMPROVED LUMINOUS EFFICIENCY AND RADIANCE

Field of the Invention

This invention relates to organic polymer light-emitting diodes with improved luminous efficiency and improved radiance.

Description of the Related Art

Diodes and particularly light emitting diodes (LEDs) fabricated with conjugated organic polymer layers have attracted attention due to their potential for use in display technology. A standard polymer LED architecture includes the following layers in contact sequence: a substrate with a coating of indium-tin oxide (ITO), a passivation layer, emissive polymer, followed by a single-layer cathode. In the field of organic polymer-based LEDs, it is common to employ a relatively high work function metal as the anode, which serves to inject holes into the otherwise filled π-band of the semiconducting, electroluminescent polymer. Relatively low work function metals are preferred as the cathode material, which serves to inject electrons into the otherwise empty π*-band of the semiconducting, electroluminescent polymer. The holes which are injected at the anode and the electrons which are injected at the cathode recombine radiatively within the active layer and light is emitted. Typical relatively high work function materials for use as anode materials include transparent conducting thin films of indium/tin-oxide Alternatively, thin films of polyaniline in the conducting emeraldine salt form can be used . Thin films of indium/tin-oxide and thin films of polyaniline in the conducting emeraldine salt form are traditionally preferred because, as transparent electrodes, both permit the emitted light from the LED to radiate from the device in useful levels.

Typical relatively low work function metals that are suitable for use as cathode materials are metals such as calcium, magnesium, and barium. Alkali metals tend to be too mobile and act to dope the emissive layer (e.g., electroluminescent polymer), thereby causing shorts and unacceptably short device lifetimes.

It is known in the art that cathodes in the form of an ultrathin layer of either a low work function metal [see Cao, Y.; PCT WO 98/57381 and Pichler, K., International Patent Application WO 98/10621] or an ultrathin layer of a low work function metal oxide [Cao, Y.; PCT Application No. 99 US/23775] yield LEDs which offer comparable or better initial performance (e.g., brightness and efficiency) and extended operating lifetime, as compared to similar LEDs which employ conventional thick film cathodes.

Despite the improvements in the fabrication of polymer LEDs, issues remain to be resolved. For example, the brightness and efficiency of polymer LEDs are sufficient for them to be used in certain display applications. However, in battery operated devices, the luminous efficiency is a critical parameter. Higher luminous efficiency results directly in a longer period of use without recharging the battery. More generally, higher luminous efficiency enables use in a wider range of display applications. Thus, a need exists for polymer LEDs with higher luminous efficiency. In specific applications, the light output is preferred to be in a narrow cone in the forward direction. In such applications, high radiance is especially important.

SUMMARY OF THE INVENTION

The present invention relates to a light-emitting diode including an anode that includes a semi-transparent layer having a high reflectivity and a high work function, and a cathode including at least one first cathode layer of a low work function material selected from metal, metal oxide and combinations thereof, and at least one second cathode layer having a high reflectivity and a high work function.

The invention achieves improved luminous efficiency and improved radiance. In a first embodiment, the semi-transparent layer or the second cathode layer has a reflectivity of at least 91.4% and a work function greater than about 4 eV. In a second embodiment, the semi-transparent layer and/or the second cathode layer has a reflectivity of at least 86% at an emission wavelength of between 400 nm and 500 nm. In a preferred embodiment, both the semi-transparent layer and the second cathode layer are silver.

As used herein, the phrase "adjacent to" does not necessarily mean that one layer is immediately next to another layer. An intermediate layer or layers may be provided between layers that are said to be adjacent.

As used herein the phrase "reflectivity...at wavelength of emission" refers to the reflectivity of a layer at a particular wavelength of light. The wavelength at which the reflectivity is quoted is that of the peak emission from the device. The reflectivity value is read from standard textbook tables, in "Optical Properties of metals and semiconductors". J.H. Weaver, H.P.R. Frederikse in CRC Handbook, Page 12-117;

As used herein the phrase "semi-transparent" is defined to mean capable of transmitting at least some light, preferably between about 4% and 25% of the amount of light of a particular wavelength of interest.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing of a polymer LED device configuration useful in the present invention. It is not intended to be to scale.

Figure 2 shows the sensitivity of the human eye to light, as a function of wavelength.

Figure 3 shows the electroluminescence spectrum of a comparative example polymer LED made using Covion PDO 122, with an ITO electrode and a Ba/Al electrode (i.e. Comparative Example A).

Figure 4 shows the electroluminescence spectrum of a polymer LED of the present invention, with a 300 Å silver anode and a Ba/Ag electrode (i.e., Example 3).

Figure 5 shows the electroluminescence spectrum of a comparative polymer LED made using Covion PDY 131 with an ITO electrode and a Ba/Al electrode (i.e., Comparative Example C).

Figure 6 shows the electroluminescence spectrum of a polymer LED of the present invention, made using Covion PDY 131, with a 300 Å silver anode and a Ba/Ag cathode (i.e., Example 4).

Figure 7 shows a plot of the luminance vs. voltage curves from devices of Example 4 and Comparative Example C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As best seen in Figure 1, an LED device 100 includes a substrate 110 and an anode 120. The anode 120 includes a semi-transparent layer 122 of a high reflectivity metal and an optional passivation layer 128. The semi-transparent layer 122 has a first surface 124 adjacent to the substrate 110 and an opposite second surface 126. At least one emissive layer 130 is disposed between the anode 120 and a cathode 140. The cathode 140 includes a first cathode layer 142 of a low-work function material and a second cathode layer 144 of a high reflectivity metal. Light is emitted through substrate 110 as shown by arrow 150.

Substrate

Suitable materials that can be used as a substrate 110 include, for example, glass and polymeric films.

Anode

While it is normal practice to utilize a transparent electrode such as ITO at the side of the device where light is emitted, in order to minimize transmission losses through the electrode the present invention replaces or augments the transparent electrode with a thin layer of high reflectivity metal layer 126 to increase the efficiency of the device. As best seen in Figure 1, the anode 120 can be a composite layer, made up of the semi-transparent layer 126 and the passivation layer 128 of conductive polymer coated on the second surface 124 of the semi-transparent layer 126.

In a first alternate embodiment (not shown), the anode includes only a conductive, current carrying layer that can serve as a hole-injecting layer, and does not include a passivation layer. In a second alternate embodiment (not shown), the anode includes a transparent conductive layer such as ITO adjacent to the first surface 124 of the semi-transparent layer 126 as well as the passivation layer 128. In a third alternate embodiment (not shown), the anode includes a transparent conductive layer such as ITO adjacent to the first surface 124 of the semi-transparent layer 126 and does not include a passivation layer. The semi-transparent layer 126 of the composite anode 120 or the alternative single anode layer (not shown) is made of an anode material selected from the group of high reflectivity metals of high work function (typically greater than about 4.0 eV). Examples of suitable metals include silver, gold, aluminum and copper. In a preferred embodiment, the semi-transparent layer 126 has a reflectivity of at least 91.4% at emission wavelength, is a good electrical conductor (having a conductivity of from about 10^2 to about 10^8 Ω^{-1} cm^{-1}, and being capable of forming into a smooth, contiguous film. In a second preferred embodiment, the semi-transparent layer has a reflectivity of more than about 92% at the wavelength emission. In a third preferred embodiment, the semi-transparent layer has a reflectivity of between about 92% and about 96.5% at the wavelength emission. In a fourth preferred embodiment, the semi-transparent layer has a reflectivity of between about 94% and about 96.5% at the wavelength emission. In a fifth preferred embodiment, the semi-transparent layer 126 has reflectivity greater than about 96% at the wavelength emission. In another preferred embodiment, the semi-transparent layer 126 has a reflectivity of at least 86% at an emission wavelength of from 400 nm to 500 nm. Examples of such anode material include silver, aluminum, gold and copper, as well as alloys of such metals.

The semi-transparent layer 126 can typically be fabricated using any of the techniques known in the art for deposition of thin films, including, for example, vacuum evaporation, sputter deposition, electron beam deposition, or chemical vapor deposition, using for example, pure metals or alloys or other film precursors. The thickness of the metal layer can be controlled by the rate and time of evaporation/deposition. A typical rate of evaporation/deposition is about 0.5 to 10 Å/sec. The thickness of the semi-transparent layer should be thin enough to transmit at least some light (so that it is semi-transparent), and thick enough to provide a continuous layer. Typically, the semi-transparent metal layer 126 has a thickness of from about 100 Å to about 500 Å. In a first preferred embodiment, the semi-transparent layer has a thickness of from about 250 to about 400 Å. In a second preferred embodiment, the semi-transparent layer has a thickness of from about 275 to about 350 Å. In a third preferred embodiment, the semi-transparent layer has a thickness of from about 275 to about 325 Å.

The optional passivation layer 128 of conductive material enables the use of high reflectivity metals with work functions that are not precisely matched with the emissive polymers being utilized. The exact form of conductive material useful in this invention may vary widely and is not critical. Examples of suitable conductive material include, but are not limited to, poly(aniline), poly(aniline) blends, polythiophenes, and polythiophene blends, Useful conductive poly(anilines) include the homopolymer, derivatives and blends with bulk polymers. Examples of useful poly(aniline) include those disclosed in U.S. Patent No. 5,232,631 and U.S. Patent No. 5,723,873. Useful conductive polythiophenes include the homopolymer, derivatives and blends with bulk polymers. Examples of useful polythiophenes include poly(ethylenedioxythiophenes) (PEDT), such as poly(3,4-ethylenedioxythiophene, and those disclosed in U.S. Patent No. 5,766,515 and U.S. Patent No. 5,035,926. The term "polyaniline" and "polythiophenes" are used herein generically to include substituted and unsubstituted materials. It is also used in a manner to include any accompanying dopants, particularly acidic materials used to render the material conductive.

Cathode

The first cathode layer 142 is selected from low work function metals or low work function metal-oxides (typically less than about 3.5 eV). Examples of suitable low work function materials include alkali, alkaline earth and lanthanide metals and oxides of alkali, alkaline earth and lanthanide metals. The term "alkali metal" is used herein in the conventional sense to refer to elements of Group IA of the periodic table. The term "alkali metal oxide" is used herein in the conventional sense to refer to compounds of an alkali metal and oxygen. For convenience, alkali metal oxides are referred to herein by the chemical formula of the corresponding simple oxide (*e.g.*, Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O); however, this reference to the simple oxide is intended to encompass other oxides, including mixed oxides and non-stoichiometric oxides (*e.g.*, Li_xO, Na_xO, K_xO, Rb_xO, and Cs_xO, where x is from about 0.1 to about 2).

The term "alkaline earth metal" is used herein in the conventional sense to refer to elements of Group IIA of the periodic table. Preferred alkaline earth metals include magnesium (*i.e.*, Mg), calcium (*i.e.*, Ca), strontium (*i.e.*, Sr), and barium (*i.e.*, Ba). The term "alkaline earth metal oxide" is used herein in the conventional sense to refer to compounds of an alkaline earth metal and oxygen. For convenience, alkaline earth metal oxides are referred to herein by the chemical formula of the corresponding simple oxide (*e.g.*, MgO, BaO, CaO, SrO, and BaO); however, this reference to the simple oxide is intended to encompass other oxides, including mixed oxides and non-stoichiometric oxides (*e.g.*, Mg_xO, Ba_xO,

Ca_xO, Sr_xO, and Ba_xO, where x is from about 0.1 to about 1.

The term "lanthanide metal" is used herein in the conventional sense to refer to elements of the lanthanide series of the periodic table, from cerium (*i.e.*, Ce) through lutetium (*i.e.*, Lu). Preferred lanthanide metals include samarium (*i.e.*, Sm), Ytterbium (*i.e.*, Yb), and neodymium (*i.e.*, Nd). The term "lanthanide metal oxide" is used herein in the conventional sense to refer to compounds of a lanthanide metal and oxygen. For convenience, lanthanide metal oxides are referred to herein by the chemical formula of the corresponding simple oxide of the +3 valency state (*e.g.*, Sm_2O_3, Yb_2O_3, and Nd_2O_3); however, this reference to the simple oxide is intended to encompass other oxides, including mixed oxides and non-stoichiometric oxides (*e.g.*, Sm_xO, Yb_xO, and Nd_xO), where x is from about 0.1 to about 1.5.

In a preferred embodiment, first cathode layer 142 includes low work function metal oxides. The first cathode layer 142 can typically be deposited by thermal vacuum evaporation. Typically, the first cathode layer 142 has a thickness of from about 10 to 200 Å. A typical rate of evaporation/deposition is from about 0.2 to about 4 Å per second.

Like the semi-transparent layer 126, the second cathode layer 144 has a high reflectivity and a high work function, and is made of a material that can be formed into a smooth, contiguous film. Typically the second cathode layer 144 has a work function of greater than 4 eV .In a preferred embodiment, the second cathode layer 144 has a reflectivity of at least 91.4% at emission wavelength. In a second preferred embodiment, the second cathode layer has a reflectivity of between 92% and 96.5% at the wavelength emission. In a third preferred embodiment, the second cathode layer has a reflectivity of between 94% and 96.5% at the wavelength emission. In a fourth preferred embodiment, the reflectivity of the second cathode layer is more than 96% at the wavelength emission. In another preferred embodiment, a metal that has a reflectivity of at least 86% at an emission wavelength of from 400 nm to 500 nm is used as the second cathode layer 144. As with the semi-transparent layer 126, the second cathode layer 144 includes a cathode material selected from metals and metal alloys. Examples of suitable high work function metals include aluminum, silver, copper, gold and the like, as well as alloys of such metals.

A preferred embodiment uses metal or metal alloy that has a reflectivity of at least 91.4% at the emission wavelength as both the semi-transparent layer 126 and as the second cathode layer 144. In another preferred embodiment, a metal that has a reflectivity of at least 86% at an emission wavelength of from 400 nm to 500 nm are used as both the semi-transparent layer 126 and as the second cathode layer 144.

In general, the second cathode layer 144 need not be the same material as used for the semi-transparent layer 126. For example, gold could be used for the high work function semi-transparent anode, and silver could be used as the high reflectivity metal layer in the bilayer cathode. In a preferred embodiment, the high reflectivity layer 142 has a metal with a reflectivity of at least 91.4%, or a reflectivity of at least 86% at an emission wavelength of from 400 nm to 500 nm, as both the second cathode layer 144 and as the semi-transparent layer 126. In a more preferred embodiment, silver (Ag) is used as both the high reflectivity metal layer in the bilayer cathode and as the semi-transparent anode.

Optionally, a multi-layer cathode system (not shown) can be used. For example, a first layer of high reflectivity cathode layer (preferably, of sufficient thickness to be opaque) may be covered by a layer of another high reflectivity cathode layer, which may be more or less reflective than the first high reflectivity cathode layer. In a tri-layer cathode-capping configuration, the uppermost metal may be any stable metal capable of forming a smooth, contiguous film, for example, aluminum or aluminum alloy. Subsequent layers can be added for specific function such as for example, for passivating and sealing of the device. Examples of layers useful for sealing the device include an air-stable capping layer. The term "air-stable" refers to the ability to protect the layers underneath the capping layer from ambient oxygen and moisture that may be present around the device. Suitable materials for air-stable capping layer include a metal or metal alloy.

As with the semi-transparent layer 126, the second cathode layer 144 can be fabricated using known deposition techniques. A typical rate of evaporation/deposition is from about 1 to 20 Å/sec. The thickness of the second cathode layer 144 should be thick enough to cover the first cathode layer and be opaque enough to give high reflectivity at the wavelength of interest. Typically, the second cathode layer has a thickness of at least about 800 Å.

Emissive layers

In the LEDs of the present invention, the at least one emissive layer 130 (also referred to as the luminescent layer or the electroluminescent layer) comprises an electroluminescent, semiconducting, organic material. Generally, materials for use as emissive layers in LEDs include polymeric or molecular materials that exhibitelectroluminescence, and still more specifically, materials that exhibit electroluminescence and that are soluble and processible from solution into uniform thin films.

Examples of useful molecular emissive materials include simple organic molecules such as anthracene, thiadiazole derivatives, and coumarin derivatives are known to show electroluminescence. In addition, complexes such as 8-hydroxyquinolate with trivalent metal ions, particularly aluminum are also suitable emissive materials, as described in, for example, Tang et al., U.S. Patent 5,552,678.

Examples of useful polymeric emissive materials include semiconductive conjugated polymers. Examples of suitable semiconductive conjugated polymers include poly(phenylene vinylene), PPV, and soluble derivatives of PPV such as poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, a semiconducting polymer with an energy gap E_g of ~ 2.1 eV. This material is described in more detail in Wudl, F., Hoger, S., Zhang, C., Pakbaz, K., Heeger, A. J., *Polymer Preprints*, **1993**, *34 (no. 1),* 197. Another material described as useful in this application is poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene), BCHA-PPV, a semiconducting polymer with an energy gap E_g of ~ 2.2 eV. This material is described in more detail in United States Patent No. 5,189,136. Other suitable polymers include, for example, the poly(3-alkylthiophenes) as described by Braun, D., Gustafsson, G., McBranch D., and Heeger, A. J., "Electroluminescence and electrical transport in poly(3-thiophene) diodes" *J. Appl. Phys.*, **1992**, *72*, 564; poly(para-phenylene) as described by Grem, G., Leditzky, G., Ullrich, B., and Leising, G., "Realization of blue-light-emitting device using poly(-p-phenylene)," *Adv. Mater.*, **1992**, *4*, 36, and its soluble derivatives as described by Yang, Z., Sokolik, I., and Karasz F. E., "Soluble blue light-emitting polymer," *Macromolecules*, **1993**, *26*, 1188; and polyquinoline as described by Parker, I. D., Pei, Q., Marrocco, M., "Efficient blue electroluminescence from a fluorinated polyquinoline" *Appl. Phys. Lett.*, **1994**, *65*, 1272. Blends of conjugated semiconducting polymers with non-conjugated host or carrier polymers are also useful as the active layer in polymer LEDs, as described by Zhang, C., von Seggern, H., Pakbaz, K., Kraabel, B., Schmidt, H.-W., and Heeger, A. J., "Blue electroluminescent diodes utilizing blends of poly(p-phenylphenylene vinylene) in poly(9-vinylcarbazole)," *Synthetic Metals*, **1994**, *62*, 35. Also useful are blends comprising two or more conjugated polymers, as described by Yu, G., and Heeger, A. J., "High efficiency photonic devices made with semiconducting polymers," *Synthetic Metals*, **1997**, *85*, 1183.

In one embodiment, the electroluminescent, organic material is an electroluminescent, semiconducting, organic polymer, which polymer is a π-conjugated polymer or is a co-polymer which contains segments of π-conjugated moieties. Conjugated polymers are well known in the art. Suitable examples of electroluminescent, semiconducting, organic polymers include, but are in no way limited to:

(i) poly(*p*-phenylene vinylene) and its derivatives substituted at various positions on the phenylene moiety;

(ii) poly(*p*-phenylene vinylene) and its derivatives substituted at various positions on the vinylene moiety;

(iii) poly(*p*-phenylene vinylene) and its derivatives substituted at various positions on the phenylene moiety and also substituted at various positions on the vinylene moiety;

(iv) poly(arylene vinylene), where the arylene may be such moieties as naphthalene, anthracene, furylene, thienylene, oxadiazole, and the like;

(v) derivatives of poly(arylene vinylene), where the arylene may be as in (iv) above, and additionally have substituents at various positions on the arylene;

(vi) derivatives of poly(arylene vinylene), where the arylene may be as in (iv) above, and additionally have substituents at various positions on the vinylene;

(vii) derivatives of poly(arylene vinylene), where the arylene may be as in (iv) above, and additionally have substituents at various positions on the arylene and substituents at various positions on the vinylene;

(viii) co-polymers of arylene vinylene oligomers, such as those in (iv), (v), (vi), and (vii) with non-conjugated oligomers;

(ix) poly(*p*-phenylene) and its derivatives substituted at various positions on the phenylene moiety, including ladder polymer derivatives such as poly(9,9-dialkyl fluorene) and the like;

(x) poly(arylenes) where the arylene may be such moieties as naphthalene, anthracene, furylene, thienylene, oxadiazole, and the like; and their derivatives substituted at various positions on the arylene moiety;

(xi) co-polymers of oligoarylenes such as those in (x) with non-conjugated oligomers;

(xii) polyquinoline and its derivatives;

(xiii) co-polymers of polyquinoline with *p*-phenylene substituted on the phenylene with, for example, alkyl or alkoxy groups to provide solubility;

(xiv) rigid rod polymers such as poly(*p*-phenylene-2,6-benzobisthiazole), poly(*p*-phenylene-2,6-benzobisoxazole), poly(*p*-phenylene-2,6-benzimidazole), and their derivatives;

and the like.

Also useful are combinations of semiconducting conjugated polymers with discrete molecules, with the discrete molecular compounds blended with the semiconducting conjugated polymer or covalently attached to via a covalent bond. Also useful are poly(fluorene) derivatives. See for example, US Pat. No. 5,777,070; U.S. Pat. No. 5,708,130; and U.S. Pat. No. 5,900,327.

In one embodiment, the electroluminescent, semiconducting, organic material is an electroluminescent, semiconducting, organic polymer. In preferred embodiments, the electroluminescent, semiconducting, organic material is selected from the group consisting of: poly(p-phenylene vinylene)s, poly(arylene vinylene)s, poly(p-phenylene)s, and poly(arylene)s.

The emissive layer may also comprise other materials, such as carrier polymers and additives. Typically, the emissive layer has a thickness of about 600 to about 1100 Å, depending on the desired wavelength of emission and hence the cavity size.

The emissive layer can typically be fabricated using any of the techniques known in the art, particularly those methods known in the art of organic molecular and organic polymer LEDs, including, for example, casting directly from solution, and casting of a polymer precursor followed by reaction (e.g., by heating) to form the desired polymer.

We have found that using a multi-layer cathode comprising at least one ultrathin layer of the low work function metal or metal-oxide (for efficient electron injection) capped with a high reflectivity metal, together with an anode comprising a semi-transparent, high reflectivity metal layer, one achieves excellent electron injection, high reflectivity, high Q in a microcavity architecture, and thereby improved luminous efficiency and improved radiance. It is believed that a microcavity effect enhances the luminous efficiency and brightness. The relatively high reflectivity of the semi-transparent metal anode and the cathode bilayer of the device result in the formation of the high performance polymer LED in a microcavity structure. The microcavity effect results in a narrowing of the bandwidth of light emitted. The result of this narrowing is to shift the wavelength of the majority of the photons emitted to an area where the human eye is more sensitive (see Figure 2) and thereby to significantly increase the luminous efficiency of the light emitting structure. The broad electroluminescence spectrum of a polymer LED fabricated in the traditional structure with the same luminescent polymer is shown for comparison in Figure 3.

Encapsulation

It is typically preferred to encapsulate the LEDs of the present invention to prevent long term degradation. Methods of encapsulation are well known in the art. For example, devices can be sealed between glass plates, or sealed between barrier polymer layers.

EXAMPLES

The following examples illustrate certain features and advantages of the present invention. They are intended to be illustrative of the invention, but not limiting.

In the Examples and Comparative Examples below, the following procedure was followed to determine the following measurements:

Efficiency:

Efficiencies were measured using a UDT S370 optometer (available from UDT, a part of Gamma Scientific, of San Diego, CA) which includes a photodiode that is calibrated using the procedure described below: The photodiode is calibrated as follows: A NIST calibrated light source, with a known, uniform light emission was used. A mask was used so that only a light beam the size of the pixel active area was emitted. The photodiode was placed at a given distance from the light, and the number of volts were recorded. Thus, the number of volts corresponding to a particular light intensity (340 cd/m^2) were known.

Radiance:

Radiance was measured using a Newport photodiode (available from Newport Corporation of Irvine, CA)

Lifetime:

For operational lifetime testing the LEDs were sealed using an epoxy resin and a glass cover. Lifetime testing was carried out, in air, on individual pixels in a device at constant current, 0.5 msec pulses, 0.5% duty cycle, at 5 mA per pixel. The time required for a pixel to decay to zero light output was measured using the UDT S370 optometer with the calibrated photodiode.

Comparative Example A

A polymer LED device was fabricated as follows: On a glass substrate partially coated with ITO was spin-coated at 6,000 rpm in air, a solution of poly(aniline) blend (general method of preparation is described in U.S. Patent No. 5,626,795). The resulting film was dried on a hot plate at 50 °C for 30 minutes and then overnight under vacuum at 70 °C. A toluene solution of Covion PDO 122, available from Covion Organic Semiconductors GmbH (Frankfurt, Germany), was spincoated at 1,800 rpm onto the pAni thin film (in a nitrogen glove box). The film was dried under vacuum at room temperature for 1 hour. A barium cathode was vapor deposited on the polymeric film of Covion PDO 122 to a thickness of 30 angstroms. A layer of aluminum was vapor deposited on top of the barium layer to a thickness of 3,000 Å.

Comparative Example B

A polymer LED device was fabricated as in Comparative Example A, except that the aluminum was replaced with a vapor deposited layer of silver at a thickness of 3,000 Å.

EXAMPLE 1

A polymer LED device was fabricated as in Comparative Example A, except that the ITO was replaced with a vapor deposited layer of silver at a thickness of 300 Å.

EXAMPLE 2

A polymer LED device was fabricated as in Comparative Example A, except that a layer of silver at a thickness of 300 Å was vapor deposited on top of the ITO. The performance of this device is similar to that of Example 1 and Example 3, as described below.

EXAMPLE 3

A polymer LED device was fabricated as described in Example 1 or Example 2 except that the aluminum layer was replaced with a vapor deposited layer of silver at a thickness of 3,000 Å. Efficiency of these devices were measured.

The performance of the devices is summarized in Table 1:

TABLE 1

Efficiency (cd/A) & Operating Voltage at 0.3 mA of Devices

Example No.	Efficiency at 0.3 mA (Cd/A)	Voltage (V)
Comp. Example A	5.25	11.3
Comp. Example B	4.54	9.6
Example 1	5.9	10.2
Example 3	9.5	10.4

Table 1 above shows that replacement of ITO with 300 Å of silver (but leaving the aluminum in place) improves the light output somewhat, yielding a 12% increase in brightness (i.e., Comparative Example A vs. Example 1). However, the most dramatic improvement is achieved in devices of the structure described by Example 3, where a silver anode is used, and silver is the high reflectivity metal used in the bilayer cathode structure. The device from

Example 3 is more than 80% brighter than that of the device in Comparative Example A. Table 1 also illustrates that simply replacing aluminum with silver at the cathode side (Comparative Example A vs. B) and leaving the anode side unchanged does not improve the efficiency of the device. In fact, there is a reduction in light output.

The emission from the devices of the Examples 1 and 3 was also be measured in radiometric units ($W/Sr/m^2$), which measurement ignores the effect of the human eye response and measures light output in absolute terms. Results are summarized in Table 2 below. Note that the radiance from the device fabricated according to this invention (Example 3) was 2.5 times greater than that from a device fabricated in the traditional polymer LED structure with the same luminescent polymer.

Figure 4 shows the electroluminesence spectrum of a device from Example 3. Note the narrowing of the electroluminescence emission relative to the spectrum seen in Figure 3, even though the same emissive polymer is used in both devices. It is believed that confinement of the Covion PDO 122 in the microcavity of Example 3 results in narrowing of the emission.

TABLE 2

Radiance of Devices

Example No.	Radiance at 0.3 mA (W/Sr/m2)
Comp. Example A	32
Comp. Example B	28
Example 1	41
Example 3	102

COMPARATIVE EXAMPLE C

A polymer LED device was fabricated as in Comparative Example A, except that the semi-conducting conjugated polymer employed was Covion PDY 131, available from Covion Organic Semiconductors GmbH (Frankfurt, Germany), and the film of Covion PDY 131 was spincoated at 3,000 rpm. The barium layer thickness was 15 Å.

The electroluminescence spectrum of this device is shown in Figure 5.

EXAMPLE 4

A polymer LED device was fabricated as in Example 3 except that the semi-conducting conjugated polymer employed was Covion PDY 131 and the film of Covion PDY 131 was spincoated at 3,000 rpm. The Ba thickness was 15 Å.

The electroluminescence spectrum of this device is shown in Figure 6.

TABLE 3

Efficiency (cd/A) & Operating Voltage

at 0.3 mA of Devices of the Examples

Example No.	Efficient (cd/A)	Voltage (V)
Comparative Example C	10.8	8.9
Example 4	27.4	10

TABLE 4

Radiance of Devices of the Examples

Example No.	Radiance at 0.3 mA (W/Sr/m^2)
Comparative Example C	36
Example 4	83

Tables 3 and 4 above show results from devices of Comparative Example C and Example 4. It is clear that the invention is not limited to one semi-conducting polymer, because major improvements in light output are also realized with another semi-conducting polymer, when the cathode capping metal is changed from aluminum to silver, and the ITO is replaced by silver at the anode side. The device from Example 4 exhibited a luminous efficiency that was 2.5 times greater than that of the device in Comparative Example C (Table 3).

The light output vs voltage (L-V) curves for the devices of Example 4 and Comparative Example C were measured and the measurement shown in Figure 7. The data in Figure 7 demonstrate that significantly higher brightness was obtained from the device fabricated in Example 4.

Table 5 below shows that the devices of Examples 1 and 3 have a longer lifetime and are more stable that the comparative device that includes an ITO anode layer.

TABLE 5

Lifetimes of Devices Under High Current (Stress) Conditions

Example No.	Time (h) to zero light output
Comparative Example A	2.5
Example 1	Not reached at end of test (15 hrs.)
Example 3	Not reached at end of test (15 hrs)

The devices of Examples 1 and 3 as well as Comparative Example A were tested under what is considered to be very high current conditions (0.5 msec pulses, 0.5% duty cycle, at 5 mA per pixel) in order to accelerate the aging process and thus enable testing of many devices. Of the three devices, the device of Comparative Example A emitted the least light and decreased to zero most rapidly (no light emission after 2.5 hours). The devices of Examples 1 and 3 exhibit very different behavior over their lifetimes. In each case, the brightness decreases to approximately 50% of the initial value and then remains at that level. In the cases of devices from Examples 1 and 3, the point of failure could not be reached before testing was deemed complete.

Therefore, while ITO is generally preferred over silver as the anode layer, the present invention obtains improved operating lifetimes with the silver structure than with ITO devices.

What is claimed is:

1. A light-emitting device (100) comprising an anode (120) comprising a semi-transparent layer (122) having a high reflectivity and a high work function, and a cathode (140) comprising at least one first cathode layer (142) of a low work function material selected from metal, metal oxide and combinations thereof, and at least one second cathode layer (144) having a high reflectivity and a high work function.

2. The device of Claim 1, wherein the semi-transparent layer has a work function of greater than 4 eV.

3. The device of Claim 1, wherein the semi-transparent layer includes an anode material selected from metals and metal alloys.

4. The device of Claim 1, wherein the second cathode layer has a work function of greater than 4 eV.

5. The device of Claim 1, wherein the second cathode layer includes a cathode material selected from metals and metal alloys.

6. The device of Claim 1 wherein at least one of device components selected from the semi-transparent layer and the at least one second cathode layer, has a reflectivity of at least 91.4% at the wavelength of emission.

7. The device of Claim 1 whereat least one of device components selected from the the semi-transparent layer and the at least one second cathode layer, has a reflectivity of at least 86% at a wavelength emission of from 400 nm to 500 nm.

8. The device of Claim 1 wherein at least one of device components selected from the semi-transparent layer and the at least one second cathode layer, comprises silver.

9. The device of Claim 1 wherein the semi-transparent layer has a first surface (124) adjacent to the cathode and an opposite second surface (126), and the anode further comprising a passivation layer (128) adjacent to the first surface, the passivation layer comprising a passivation material selected from poly(aniline), poly(aniline) blends, polythiophene, and polythiophene blends.

10. The device of Claim 1, wherein the semi-transparent layer has a first surface adjacent to the cathode and an opposite second surface and the anode further comprises a transparent layer of indium/tin oxide adjacent to the second surface of the semi-transparent layer.

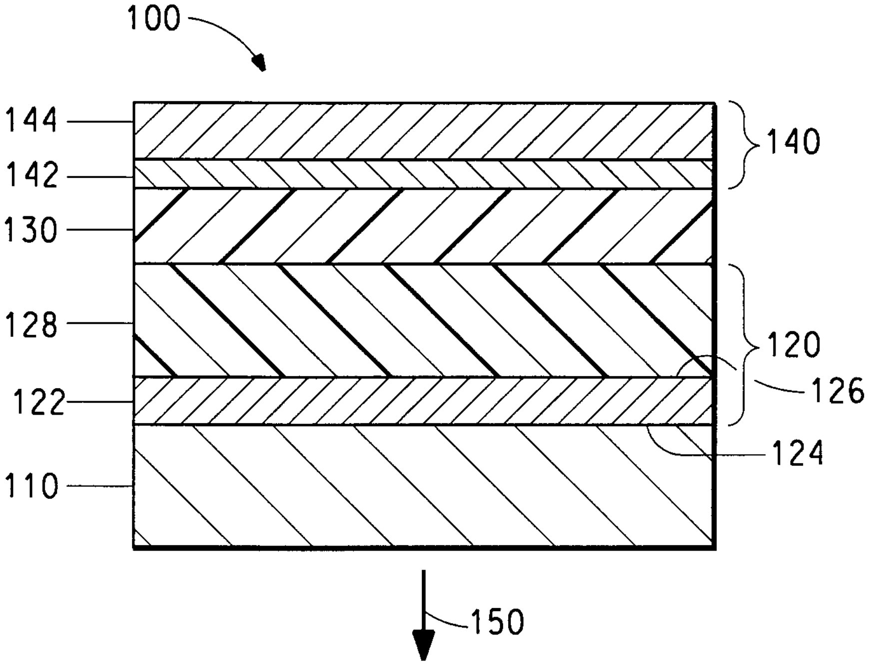
100
144
142
130
128
122
110
140
120
126
124
150

FIG. 1

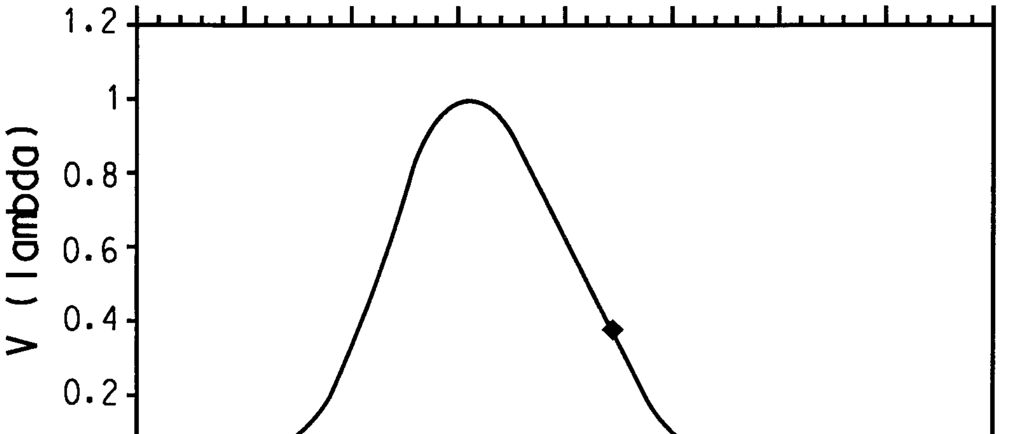
V (lambda)
1.2
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
700
750
800
WAVELENGTH (nm)

FIG. 2

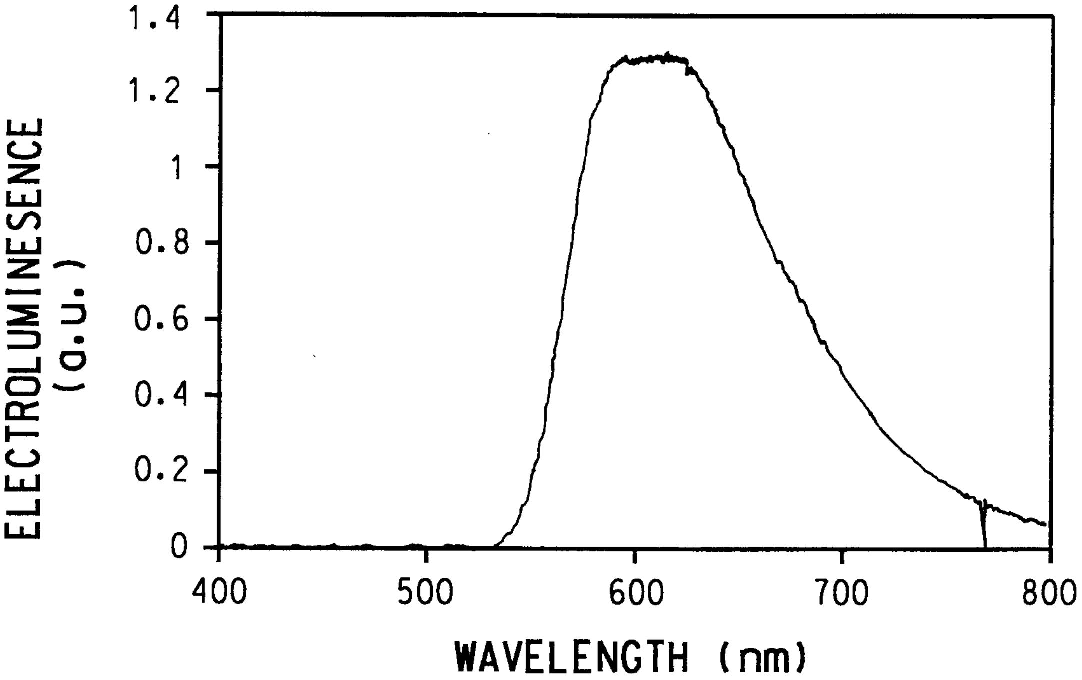

FIG. 3
(PRIOR ART)

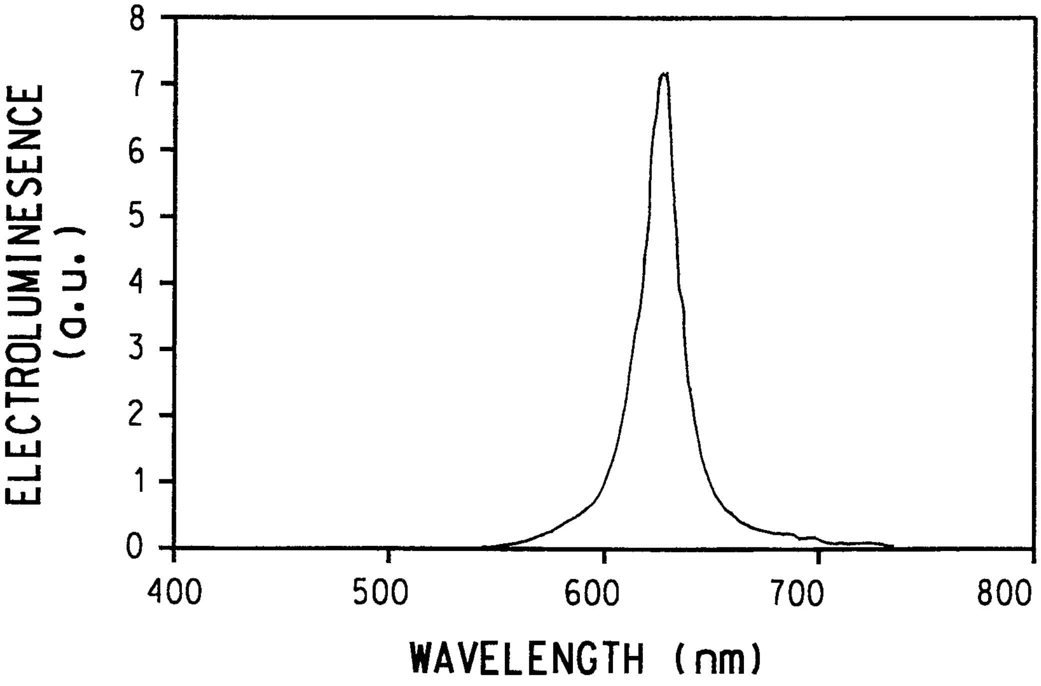

FIG. 4

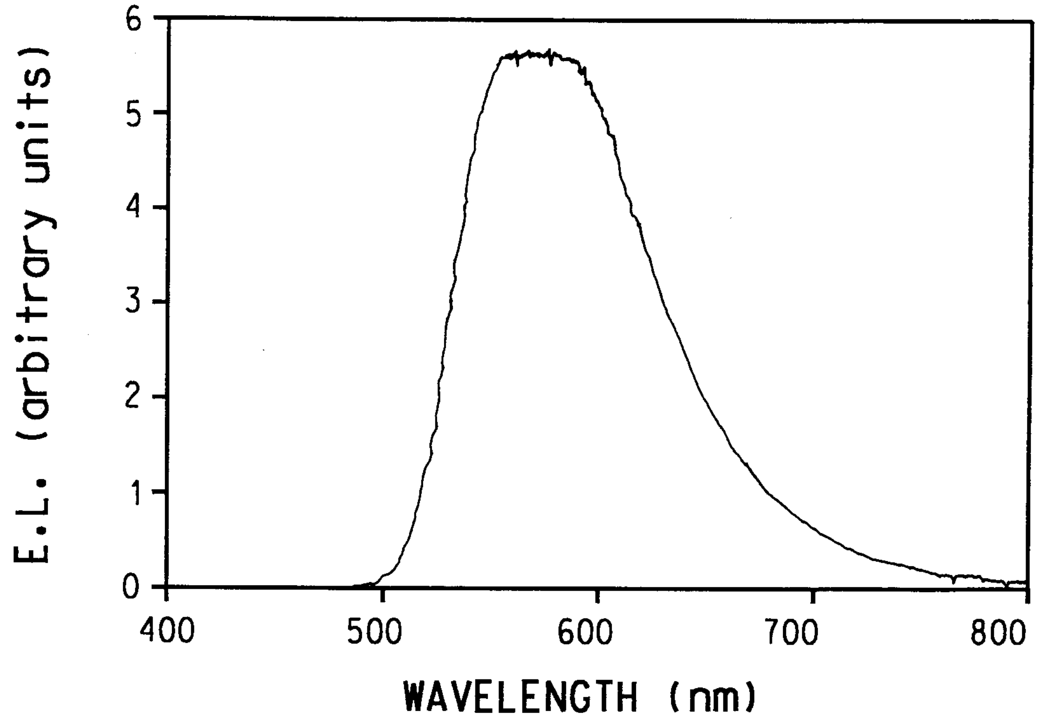

FIG. 5
(PRIOR ART)

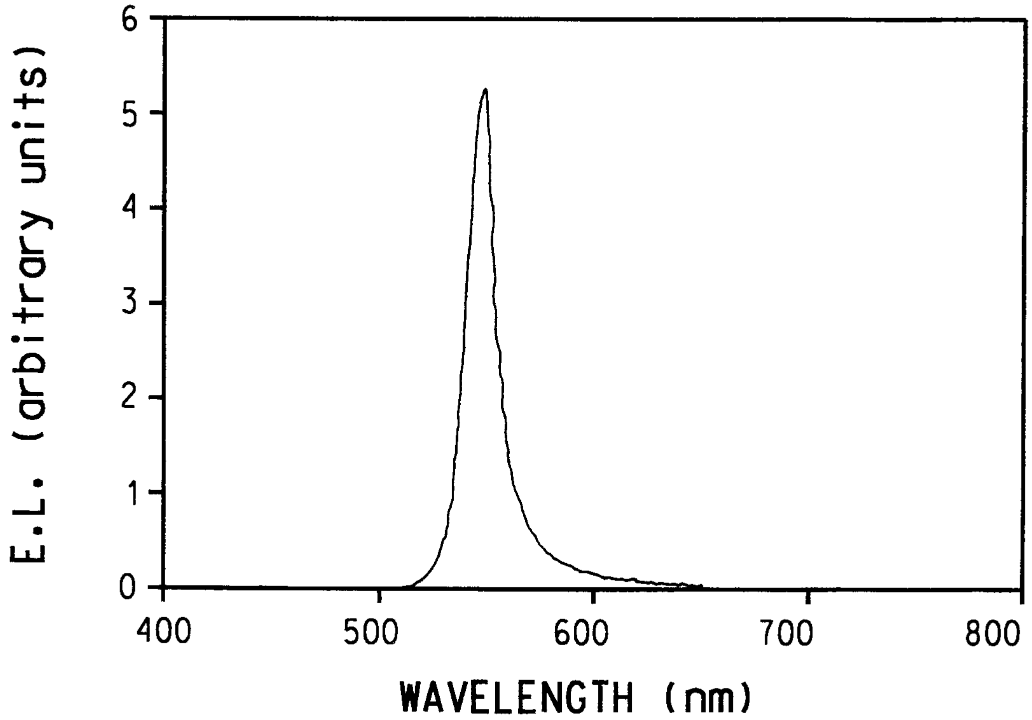

FIG. 6

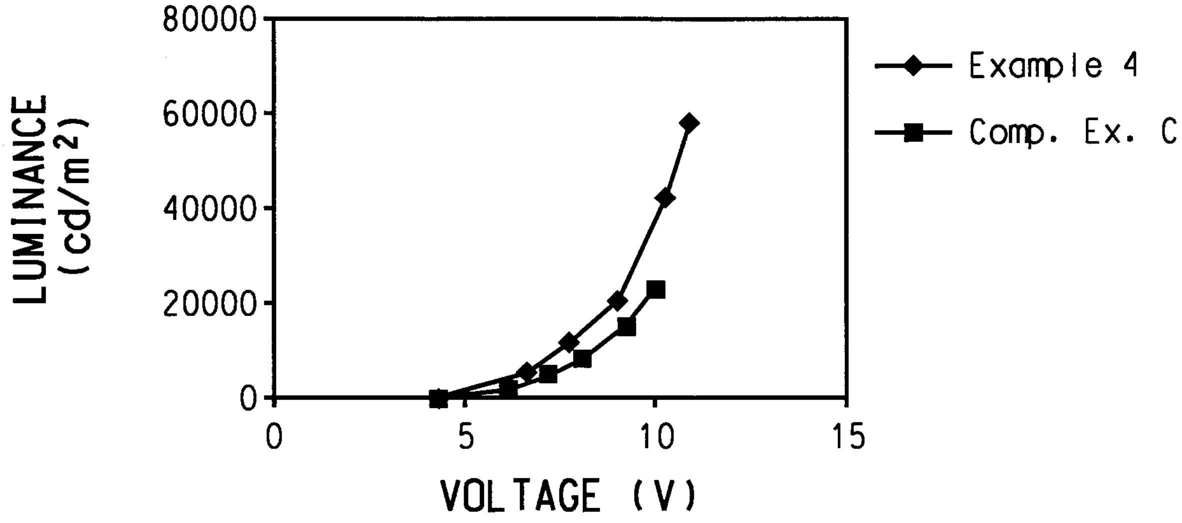
LUMINANCE (cd/m2)
80000
60000
40000
20000
0
0
5
10
15
VOLTAGE (V)
Example 4
Comp. Ex. C

FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/19476

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SCOTT J ET AL: "Hole limited recombination in polymer LEDs" APPLIED PHYSICS LETTERS, 15 MARCH 1999, vol. 74, no. 11, pages 1510-1512, XP002151227 ISSN: 0003-6951	1-5
A	page 1510, right-hand column, paragraph 2 -page 1511, left-hand column, paragraph 3 ---	6,7
X	KOWALSKY W ET AL: "Improved lifetime and efficiency of OLEDs" LED RESEARCH, MANUFACTURING, AND APPLICATIONS, SAN JOSE, 27-28 JAN 1999, vol. 3621, pages 103-114, XP000956290 ISSN: 0277-786X	1,2,4,5, 7,8,10
A	page 108, paragraph 3 -page 111 --- -/--	6,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search 26 October 2000	Date of mailing of the international search report 08/11/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer van der Linden, J.E.

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INTERNATIONAL SEARCH REPORT

Interna' 'l Application No
PCT/US 00/19476

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 668 620 A (AT & T CORP) 23 August 1995 (1995-08-23)	1-5
A	column 3, line 38 -column 8	6,7
X	JORDAN R ET AL: "Efficiency enhancement of microcavity OLEDs" APPLIED PHYSICS LETTERS, SEPT 1996, vol. 69, no. 14, pages 1997-1999, XP000636148 ISSN: 0003-6951 the whole document	1,2,4,5, 10
A	TAKADA N ET AL: "Control of emission characteristics in organic thin-film EL diodes using a microcavity structure" APPLIED PHYSICS LETTERS, OCT 1993, vol. 63, no. 15, pages 2032-2034, XP000397816 ISSN: 0003-6951 the whole document	1-3,5
A	WITTMANN H ET AL: "Microcavity effect in a single-layer polymer LED" ADVANCED MATERIALS, JUNE 1995, vol. 7, no. 6, pages 541-544, XP000508443 ISSN: 0935-9648 the whole document	1-7
P,X	WO 99 59379 A (FED CORP) 18 November 1999 (1999-11-18) page 3, paragraph 3 -page 5	1-5

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/19476

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0668620 A	23-08-1995	US 5619058 A JP 7263742 A	08-04-1997 13-10-1995
WO 9959379 A	18-11-1999	NONE	

专利名称(译)	长寿命聚合物发光器件，具有改善的发光效率和辐射性		
公开(公告)号	EP1196955A1	公开(公告)日	2002-04-17
申请号	EP2000947472	申请日	2000-07-18
申请(专利权)人(译)	UNIAX CORPORATION		
当前申请(专利权)人(译)	杜邦显示器，INC.		
[标]发明人	OREGAN MARIE B ZHANG CHI		
发明人	O'REGAN, MARIE, B. ZHANG, CHI		
IPC分类号	H05B33/28 H01L33/00 H01L51/50 H01L51/52 H05B33/24 H05B33/26 H01L51/20		
CPC分类号	H01L51/5203 H01L51/5265		
代理机构(译)	MATTHEWS，DEREK PETER		
优先权	60/144251 1999-07-19 US		
外部链接	Espacenet		

摘要(译)

通过使用包括低功函数层和高功函数高反射率层的多层阴极，结合高功函数，高反射率，可以增加由有机发光材料制造的发光二极管（LED）的发光效率和辐射亮度。装置中的阳极材料。