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(54) MULTILAYER CATHODE FOR ENHANCED STABILITY OF PLATINUM AND PALLADIUM BASED OLEDS

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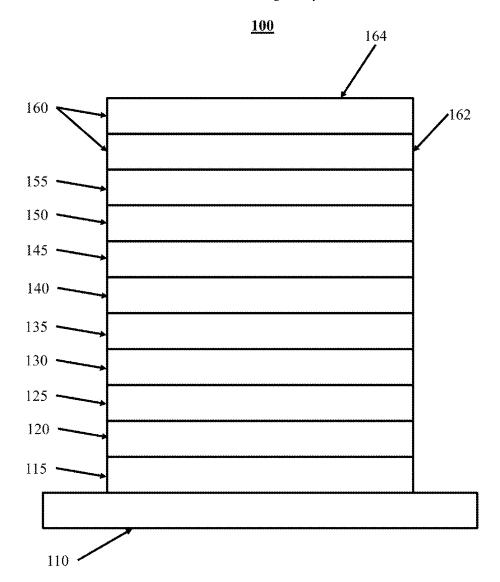
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(57) ABSTRACT

An organic optoelectronic device comprises an anode, an emitting layer positioned over the anode, and a multi-layer cathode positioned over the emitting layer, the multi-layer cathode comprising a first metal layer positioned over the emitting layer, an organic layer positioned over the first metal layer, and a second metal layer positioned over the organic layer.



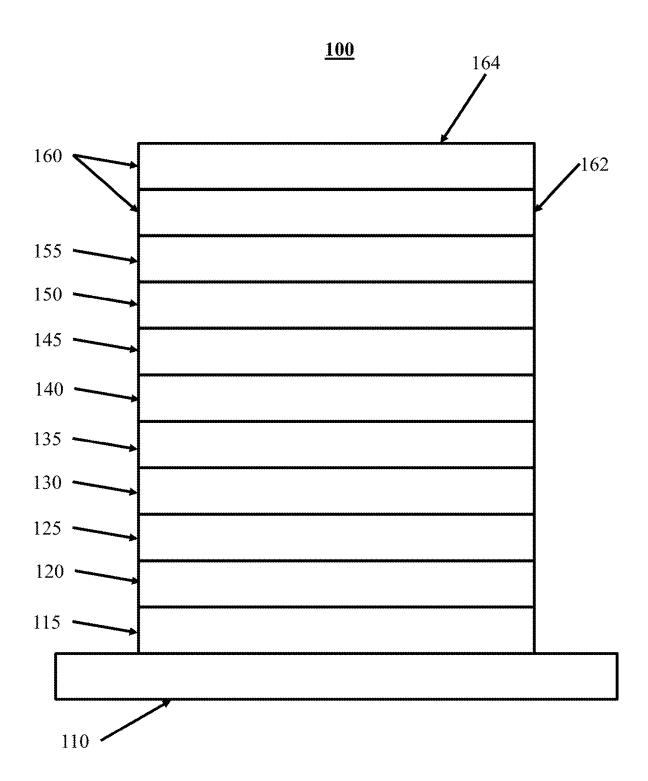


Fig. 1

<u>200</u>

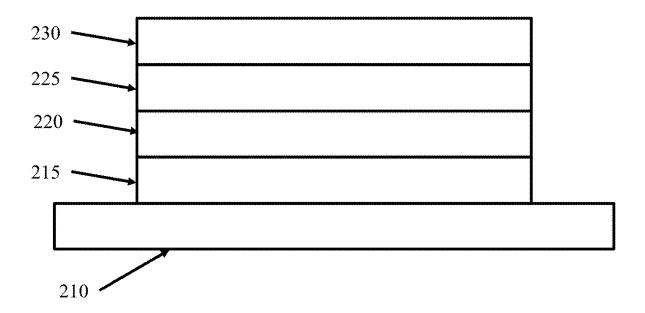
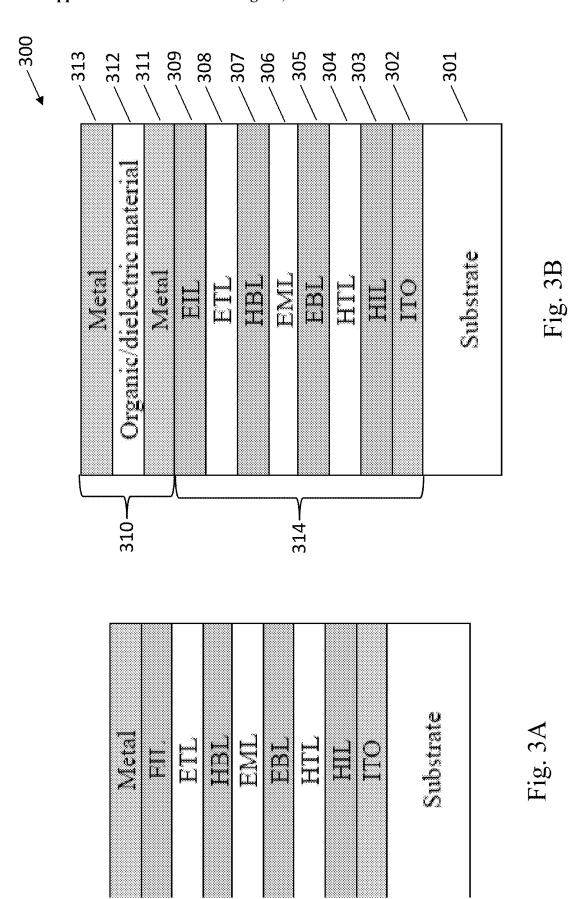
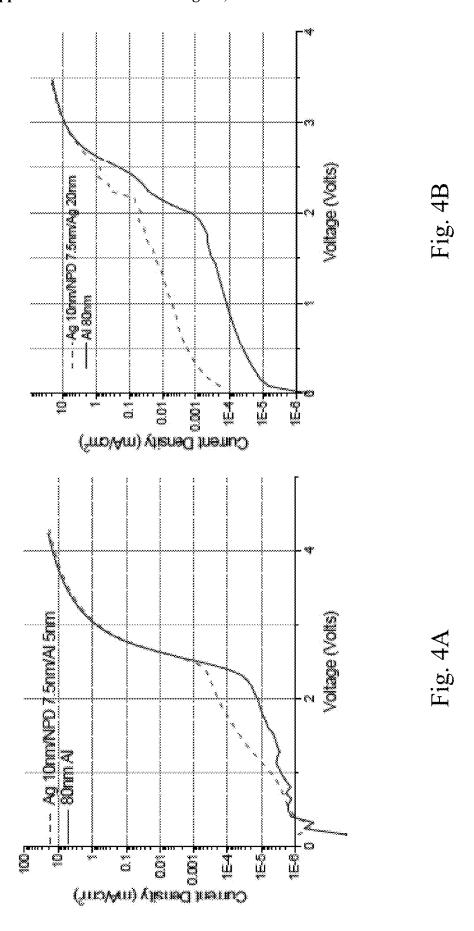


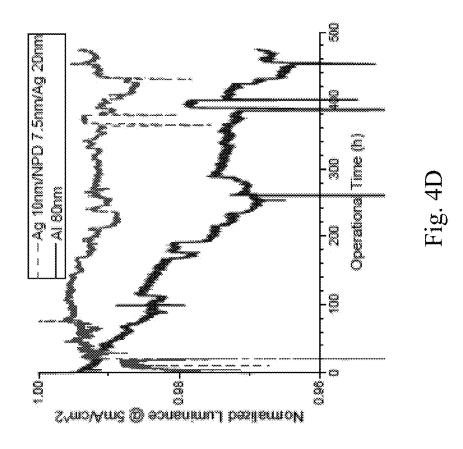
Fig. 2

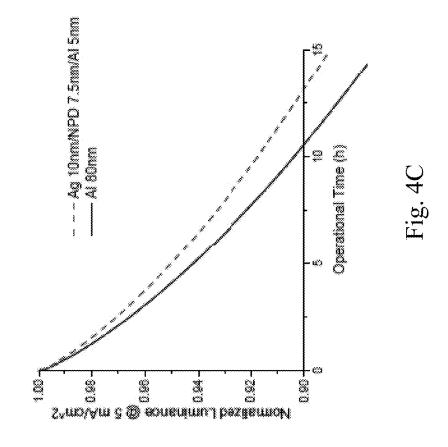


Ag 20nm
NPD 7.5nm
Ag 10nm
Al 1nm
Liq 2nm
Bpytp:Liq 15nm
Si2TrzPh 5nm
Pd308-P 5nm
TrisPCz 10nm
NPD 100nm
HATCN 10nm
ITO 100nm
Substrate

Fig. 3C







MULTILAYER CATHODE FOR ENHANCED STABILITY OF PLATINUM AND PALLADIUM BASED OLEDS

CROSS-REFERENCE TO RELATED APPLICATIONS

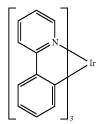
[0001] This application claims priority to U.S. provisional application No. 63/555,703 filed Feb. 20, 2024, incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] Opto-electronic devices that make use of organic materials are becoming increasingly desirable for a number of reasons. Many of the materials used to make such devices are relatively inexpensive, so organic opto-electronic devices have the potential for cost advantages over inorganic devices. In addition, the inherent properties of organic materials, such as their flexibility, may make them well suited for particular applications such as fabrication on a flexible substrate. Examples of organic opto-electronic devices include organic light emitting devices (OLEDs), organic phototransistors, organic photovoltaic cells, and organic photodetectors. For OLEDs, the organic materials may have performance advantages over conventional materials. For example, the wavelength at which an organic emissive layer emits light may generally be readily tuned with appropriate dopants.

[0003] OLEDs make use of thin organic films that emit light when voltage is applied across the device. OLEDs are becoming an increasingly interesting technology for use in applications such as flat panel displays, illumination, and backlighting. Several OLED materials and configurations are described in U.S. Pat. Nos. 5,844,363, 6,303,238, and 5,707,745, which are incorporated herein by reference in their entirety. One application for phosphorescent emissive molecules is a full color display. Industry standards for such a display call for pixels adapted to emit particular colors, referred to as "saturated" colors. In particular, these standards call for saturated red, green, and blue pixels. Color may be measured using CIE coordinates, which are well known to the art.

[0004] One example of a green emissive molecule is tris(2-phenylpyridine) iridium, denoted Ir(ppy)₃, which has the following structure:



[0005] In this, and later figures herein, we depict the dative bond from nitrogen to metal (here, Ir) as a straight line.

[0006] As used herein, the term "organic" includes polymeric materials as well as small molecule organic materials

meric materials as well as small molecule organic materials that may be used to fabricate organic opto-electronic devices. "Small molecule" refers to any organic material that is not a polymer, and "small molecules" may actually be

quite large. Small molecules may include repeat units in some circumstances. For example, using a long chain alkyl group as a substituent does not remove a molecule from the "small molecule" class. Small molecules may also be incorporated into polymers, for example as a pendent group on a polymer backbone or as a part of the backbone. Small molecules may also serve as the core moiety of a dendrimer, which consists of a series of chemical shells built on the core moiety. The core moiety of a dendrimer may be a fluorescent or phosphorescent small molecule emitter. A dendrimer may be a "small molecule," and it is believed that all dendrimers currently used in the field of OLEDs are small molecules.

[0007] As used herein, "top" means furthest away from the substrate, while "bottom" means closest to the substrate. Where a first layer is described as "disposed over" a second layer, the first layer is disposed further away from substrate. There may be other layers between the first and second layer, unless it is specified that the first layer is "in contact with" the second layer. For example, a cathode may be described as "disposed over" an anode, even though there are various organic layers in between.

[0008] As used herein, "solution processible" means capable of being dissolved, dispersed, or transported in and/or deposited from a liquid medium, either in solution or suspension form.

[0009] A ligand may be referred to as "photoactive" when it is believed that the ligand directly contributes to the photoactive properties of an emissive material. A ligand may be referred to as "ancillary" when it is believed that the ligand does not contribute to the photoactive properties of an emissive material, although an ancillary ligand may alter the properties of a photoactive ligand.

[0010] As used herein, and as would be generally understood by one skilled in the art, a first "Highest Occupied Molecular Orbital" (HOMO) or "Lowest Unoccupied Molecular Orbital" (LUMO) energy level is "greater than" or "higher than" a second HOMO or LUMO energy level if the first energy level is closer to the vacuum energy level. Since ionization potentials (IP) are measured as a negative energy relative to a vacuum level, a higher HOMO energy level corresponds to an IP having a smaller absolute value (an IP that is less negative). Similarly, a higher LUMO energy level corresponds to an electron affinity (EA) having a smaller absolute value (an EA that is less negative). On a conventional energy level diagram, with the vacuum level at the top, the LUMO energy level of a material is higher than the HOMO energy level of the same material. A "higher" HOMO or LUMO energy level appears closer to the top of such a diagram than a "lower" HOMO or LUMO energy

[0011] As used herein, and as would be generally understood by one skilled in the art, on a conventional energy level diagram, with the vacuum level at the top, a "shallower" energy level appears higher, or closer to the top, of such a diagram than a "deeper" energy level, which appears lower, or closer to the bottom.

[0012] As used herein, and as would be generally understood by one skilled in the art, a first work function is "greater than" or "higher than" a second work function if the first work function has a higher absolute value. Because work functions are generally measured as negative numbers relative to vacuum level, this means that a "higher" work function is more negative. On a conventional energy level diagram, with the vacuum level at the top, a "higher" work

function is illustrated as further away from the vacuum level in the downward direction. Thus, the definitions of HOMO and LUMO energy levels follow a different convention than work functions.

[0013] More details on OLEDs, and the definitions described above, can be found in U.S. Pat. No. 7,279,704, which is incorporated herein by reference in its entirety.

SUMMARY OF THE INVENTION

[0014] In one aspect, an organic optoelectronic device comprises an anode, an emitting layer positioned over the anode, and a multi-layer cathode positioned over the emitting layer, the multi-layer cathode comprising a first metal layer positioned over the emitting layer, an organic layer positioned over the first metal layer, and a second metal layer positioned over the organic layer.

[0015] In one embodiment, the first metal layer comprises silver. In one embodiment, the organic layer comprises a dielectric or hole transport material. In one embodiment, the second metal layer comprises silver or aluminum. In one embodiment, the first metal layer has a thickness between 5 nm and 20 nm. In one embodiment, the organic layer has a thickness between 5 nm and 30 nm. In one embodiment, the second metal layer has a thickness between 1 nm and 30 nm. In one embodiment, the emissive layer comprises platinum or palladium.

[0016] In one embodiment, a consumer product comprising an organic optoelectronic device disclosed herein is selected from the group consisting of a flat panel display, a curved display, a computer monitor, a medical monitor, a television, a billboard, a light for interior or exterior illumination and/or signaling, a heads-up display, a fully or partially transparent display, a flexible display, a rollable display, a foldable display, a stretchable display, a laser printer, a telephone, a cell phone, tablet, a phablet, a personal digital assistant (PDA), a wearable device, a laptop computer, a digital camera, a camcorder, a viewfinder, a microdisplay that is less than 2 inches diagonal, a 3-D display, a virtual reality or augmented reality display, a vehicle, a video walls comprising multiple displays tiled together, a theater or stadium screen, a light therapy device, and a sign.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The foregoing purposes and features, as well as other purposes and features, will become apparent with reference to the description and accompanying figures below, which are included to provide an understanding of the invention and constitute a part of the specification, in which like numerals represent like elements, and in which:

[0018] FIG. 1 shows an organic light emitting device; [0019] FIG. 2 shows an inverted organic light emitting device that does not have a separate electron transport layer;

[0020] FIG. 3A-FIG. 3C show cross-sectional views of devices disclosed herein; and

[0021] FIG. 4A-FIG. 4D are graphs of experimental data related to devices disclosed herein.

DETAILED DESCRIPTION

[0022] It is to be understood that the figures and descriptions of the present invention have been simplified to illustrate elements that are relevant for a clear understanding of the present invention, while eliminating, for the purpose of clarity, many other elements found in related systems and

methods. Those of ordinary skill in the art may recognize that other elements and/or steps are desirable and/or required in implementing the present invention. However, because such elements and steps are well known in the art, and because they do not facilitate a better understanding of the present invention, a discussion of such elements and steps is not provided herein. The disclosure herein is directed to all such variations and modifications to such elements and methods known to those skilled in the art.

[0023] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, exemplary methods and materials are described.

[0024] As used herein, each of the following terms has the meaning associated with it in this section.

[0025] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

[0026] "About" as used herein when referring to a measurable value such as an amount, a temporal duration, and the like, is meant to encompass variations of $\pm 20\%$, $\pm 10\%$, $\pm 5\%$, $\pm 1\%$, and $\pm 0.1\%$ from the specified value, as such variations are appropriate.

[0027] Throughout this disclosure, various aspects of the invention can be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed subranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 2.7, 3, 4, 5, 5.3, 6 and any whole and partial increments therebetween. This applies regardless of the breadth of the range.

[0028] The initial OLEDs used emissive molecules that emitted light from their singlet states ("fluorescence") as disclosed, for example, in U.S. Pat. No. 4,769,292, which is incorporated by reference in its entirety. Fluorescent emission generally occurs in a time frame of less than 10 nanoseconds.

[0029] More recently, OLEDs having emissive materials that emit light from triplet states ("phosphorescence") have been demonstrated. Baldo et al., "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices," Nature, vol. 395, 151-154, 1998; ("Baldo-I") and Baldo et al., "Very high-efficiency green organic light-emitting devices based on electrophosphorescence," Appl. Phys. Lett., vol. 75, No. 3, 4-6 (1999) ("Baldo-II"), which are incorporated by reference in their entireties. Phosphorescence is described in more detail in U.S. Pat. No. 7,279, 704 at cols. 5-6, which are incorporated by reference.

[0030] FIG. 1 shows an organic light emitting device 100. The figures are not necessarily drawn to scale. Device 100 may include a substrate 110, an anode 115, a hole injection layer 120, a hole transport layer 125, an electron blocking layer 130, an emissive layer 135, a hole blocking layer 140,

an electron transport layer 145, an electron injection layer 150, a protective layer 155, a cathode 160, and a barrier layer 170. Cathode 160 is a compound cathode having a first conductive layer 162 and a second conductive layer 164. Device 100 may be fabricated by depositing the layers described, in order. The properties and functions of these various layers, as well as example materials, are described in more detail in U.S. Pat. No. 7,279,704 at cols. 6-10, which are incorporated by reference.

[0031] More examples for each of these layers are available. For example, a flexible and transparent substrate-anode combination is disclosed in U.S. Pat. No. 5,844,363, which is incorporated by reference in its entirety. An example of a p-doped hole transport layer is m-MTDATA doped with F_{Δ} -TCNQ at a molar ratio of 50:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. Examples of emissive and host materials are disclosed in U.S. Pat. No. 6,303,238 to Thompson et al., which is incorporated by reference in its entirety. An example of an n-doped electron transport layer is BPhen doped with Li at a molar ratio of 1:1, as disclosed in U.S. Patent Application Publication No. 2003/0230980, which is incorporated by reference in its entirety. U.S. Pat. Nos. 5,703,436 and 5,707,745, which are incorporated by reference in their entireties, disclose examples of cathodes including compound cathodes having a thin layer of metal such as Mg:Ag with an overlying transparent, electricallyconductive, sputter-deposited ITO layer. The theory and use of blocking layers is described in more detail in U.S. Pat. No. 6,097,147 and U.S. Patent Application Publication No. 2003/0230980, which are incorporated by reference in their entireties. Examples of injection layers are provided in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety. A description of protective layers may be found in U.S. Patent Application Publication No. 2004/0174116, which is incorporated by reference in its entirety.

[0032] FIG. 2 shows an inverted OLED 200. The device includes a substrate 210, a cathode 215, an emissive layer 220, a hole transport layer 225, and an anode 230. Device 200 may be fabricated by depositing the layers described, in order. Because the most common OLED configuration has a cathode disposed over the anode, and device 200 has cathode 215 disposed under anode 230, device 200 may be referred to as an "inverted" OLED. Materials similar to those described with respect to device 100 may be used in the corresponding layers of device 200. FIG. 2 provides one example of how some layers may be omitted from the structure of device 100.

[0033] The simple layered structure illustrated in FIGS. 1 and 2 is provided by way of non-limiting example, and it is understood that embodiments of the disclosure may be used in connection with a wide variety of other structures. The specific materials and structures described are exemplary in nature, and other materials and structures may be used. Functional OLEDs may be achieved by combining the various layers described in different ways, or layers may be omitted entirely, based on design, performance, and cost factors. Other layers not specifically described may also be included. Materials other than those specifically described may be used. Although many of the examples provided herein describe various layers as comprising a single material, it is understood that combinations of materials, such as a mixture of host and dopant, or more generally a mixture,

may be used. Also, the layers may have various sublayers. The names given to the various layers herein are not intended to be strictly limiting. For example, in device 200, hole transport layer 225 transports holes and injects holes into emissive layer 220, and may be described as a hole transport layer or a hole injection layer. In one embodiment, an OLED may be described as having an "organic layer" disposed between a cathode and an anode. This organic layer may comprise a single layer, or may further comprise multiple layers of different organic materials as described, for example, with respect to FIGS. 1 and 2.

[0034] Structures and materials not specifically described may also be used, such as OLEDs comprised of polymeric materials (PLEDs) such as disclosed in U.S. Pat. No. 5,247, 190 to Friend et al., which is incorporated by reference in its entirety. By way of further example, OLEDs having a single organic layer may be used. OLEDs may be stacked, for example as described in U.S. Pat. No. 5,707,745 to Forrest et al, which is incorporated by reference in its entirety. The OLED structure may deviate from the simple layered structure illustrated in FIGS. 1 and 2. For example, the substrate may include an angled reflective surface to improve outcoupling, such as a mesa structure as described in U.S. Pat. No. 6,091,195 to Forrest et al., and/or a pit structure as described in U.S. Pat. No. 5,834,893 to Bulovic et al., which are incorporated by reference in their entireties.

[0035] Unless otherwise specified, any of the layers of the various embodiments may be deposited by any suitable method. For the organic layers, preferred methods include thermal evaporation, ink-jet, such as described in U.S. Pat. Nos. 6,013,982 and 6,087,196, which are incorporated by reference in their entireties, organic vapor phase deposition (OVPD), such as described in U.S. Pat. No. 6,337,102 to Forrest et al., which is incorporated by reference in its entirety, and deposition by organic vapor jet printing (OVJP), such as described in U.S. Pat. No. 7,431,968, which is incorporated by reference in its entirety. Other suitable deposition methods include spin coating and other solution based processes. Solution based processes are preferably carried out in nitrogen or an inert atmosphere. For the other layers, preferred methods include thermal evaporation. Preferred patterning methods include deposition through a mask, cold welding such as described in U.S. Pat. Nos. 6,294,398 and 6,468,819, which are incorporated by reference in their entireties, and patterning associated with some of the deposition methods such as ink-jet and OVJD. Other methods may also be used. The materials to be deposited may be modified to make them compatible with a particular deposition method. For example, substituents such as alkyl and aryl groups, branched or unbranched, and preferably containing at least 3 carbons, may be used in small molecules to enhance their ability to undergo solution processing. Substituents having 20 carbons or more may be used, and 3-20 carbons is a preferred range. Materials with asymmetric structures may have better solution processibility than those having symmetric structures, because asymmetric materials may have a lower tendency to recrystallize. Dendrimer substituents may be used to enhance the ability of small molecules to undergo solution processing.

[0036] Devices fabricated in accordance with embodiments of the present disclosure may further optionally comprise a barrier layer. One purpose of the barrier layer is to protect the electrodes and organic layers from damaging exposure to harmful species in the environment including

moisture, vapor and/or gases, etc. The barrier layer may be deposited over, under or next to a substrate, an electrode, or over any other parts of a device including an edge. The barrier layer may comprise a single layer, or multiple layers. The barrier layer may be formed by various known chemical vapor deposition techniques and may include compositions having a single phase as well as compositions having multiple phases. Any suitable material or combination of materials may be used for the barrier layer. The barrier layer may incorporate an inorganic or an organic compound or both. The preferred barrier layer comprises a mixture of a polymeric material and a non-polymeric material as described in U.S. Pat. No. 7,968,146, PCT Pat. Application Nos. PCT/US2007/023098 and PCT/US2009/042829, which are herein incorporated by reference in their entireties. To be considered a "mixture", the aforesaid polymeric and non-polymeric materials comprising the barrier layer should be deposited under the same reaction conditions and/or at the same time. The weight ratio of polymeric to non-polymeric material may be in the range of 95:5 to 5:95. The polymeric material and the non-polymeric material may be created from the same precursor material. In one example, the mixture of a polymeric material and a nonpolymeric material consists essentially of polymeric silicon and inorganic silicon.

[0037] Devices fabricated in accordance with embodiments of the disclosure can be incorporated into a wide variety of electronic component modules (or units) that can be incorporated into a variety of electronic products or intermediate components. Examples of such electronic products or intermediate components include display screens, lighting devices such as discrete light source devices or lighting panels, etc. that can be utilized by the end-user product manufacturers. Such electronic component modules can optionally include the driving electronics and/or power source(s). Devices fabricated in accordance with embodiments of the disclosure can be incorporated into a wide variety of consumer products that have one or more of the electronic component modules (or units) incorporated therein. A consumer product comprising an OLED that includes the compound of the present disclosure in the organic layer in the OLED is disclosed. Such consumer products would include any kind of products that include one or more light source(s) and/or one or more of some type of visual displays. Some examples of such consumer products include flat panel displays, curved displays, computer monitors, medical monitors, televisions, billboards, lights for interior or exterior illumination and/or signaling, headsup displays, fully or partially transparent displays, flexible displays, rollable displays, foldable displays, stretchable displays, laser printers, telephones, mobile phones, tablets, phablets, personal digital assistants (PDAs), wearable devices, laptop computers, digital cameras, camcorders, viewfinders, micro-displays (displays that are less than 2 inches diagonal), 3-D displays, virtual reality or augmented reality displays, vehicles, video walls comprising multiple displays tiled together, theaters or stadium screens, light therapy devices, and signs. Various control mechanisms may be used to control devices fabricated in accordance with the present disclosure, including passive matrix and active matrix. Many of the devices are intended for use in a temperature range comfortable to humans, such as 18 C to 30 C, and more preferably at room temperature (20-25 C),

but could be used outside this temperature range, for example, from -40 C to 80 C.

[0038] Although certain embodiments of the disclosure are discussed in relation to one particular device or type of device (for example OLEDs) it is understood that the disclosed improvements to light outcoupling properties of a substrate may be equally applied to other devices, including but not limited to PLEDs, OPVs, charge-coupled devices (CCDs), photosensors, or the like.

[0039] Although exemplary embodiments described herein may be presented as methods for producing particular circuits or devices, for example OLEDs, it is understood that the materials and structures described herein may have applications in devices other than OLEDs. For example, other optoelectronic devices such as organic solar cells and organic photodetectors may employ the materials and structures. More generally, organic devices, such as organic transistors, or other organic electronic circuits or components, may employ the materials and structures.

[0040] In some embodiments, the OLED has one or more characteristics selected from the group consisting of being flexible, being rollable, being foldable, being stretchable, and being curved. In some embodiments, the OLED is transparent or semi-transparent. In some embodiments, the OLED further comprises a layer comprising carbon nanotubes.

[0041] In some embodiments, at least one of the anode, the cathode, or a new layer disposed over the organic emissive layer functions as an enhancement layer. The enhancement layer comprises a plasmonic material exhibiting surface plasmon resonance that non-radiatively couples to the emitter material and transfers excited state energy from the emitter material to non-radiative mode of surface plasmon polariton. The enhancement layer is provided no more than a threshold distance away from the organic emissive layer, wherein the emitter material has a total non-radiative decay rate constant and a total radiative decay rate constant due to the presence of the enhancement layer and the threshold distance is where the total non-radiative decay rate constant is equal to the total radiative decay rate constant. In some embodiments, the OLED further comprises an outcoupling layer. In some embodiments, the outcoupling layer is disposed over the enhancement layer on the opposite side of the organic emissive layer. In some embodiments, the outcoupling layer is disposed on opposite side of the emissive layer from the enhancement layer but still outcouples energy from the surface plasmon mode of the enhancement layer. The outcoupling layer scatters the energy from the surface plasmon polaritons. In some embodiments this energy is scattered as photons to free space. In other embodiments, the energy is scattered from the surface plasmon mode into other modes of the device such as but not limited to the organic waveguide mode, the substrate mode, or another waveguiding mode. If energy is scattered to the non-free space mode of the OLED other outcoupling schemes could be incorporated to extract that energy to free space. In some embodiments, one or more intervening layer can be disposed between the enhancement layer and the outcoupling layer. The examples for interventing layer(s) can be dielectric materials, including organic, inorganic, perovskites, oxides, and may include stacks and/or mixtures of these materials.

[0042] The enhancement layer modifies the effective properties of the medium in which the emitter material resides resulting in any or all of the following: a decreased rate of

emission, a modification of emission line-shape, a change in emission intensity with angle, a change in the stability of the emitter material, a change in the efficiency of the OLED, and reduced efficiency roll-off of the OLED device. Placement of the enhancement layer on the cathode side, anode side, or on both sides results in OLED devices which take advantage of any of the above-mentioned effects. In addition to the specific functional layers mentioned herein and illustrated in the various OLED examples shown in the figures, the OLEDs according to the present disclosure may include any of the other functional layers often found in OLEDs.

[0043] The enhancement layer can be comprised of plasmonic materials, optically active metamaterials, or hyperbolic metamaterials. As used herein, a plasmonic material is a material in which the real part of the dielectric constant crosses zero in the visible or ultraviolet region of the electromagnetic spectrum. In some embodiments, the plasmonic material includes at least one metal. In such embodiments the metal may include at least one of Ag, Al, Au, Ir, Pt, Ni, Cu, W, Ta, Fe, Cr, Mg, Ga, Rh, Ti, Ru, Pd, In, Bi, Ca alloys or mixtures of these materials, and stacks of these materials. In general, a metamaterial is a medium composed of different materials where the medium as a whole acts differently than the sum of its material parts. In particular, we define optically active metamaterials as materials which have both negative permittivity and negative permeability. Hyperbolic metamaterials, on the other hand, are anisotropic media in which the permittivity or permeability are of different sign for different spatial directions. Optically active metamaterials and hyperbolic metamaterials are strictly distinguished from many other photonic structures such as Distributed Bragg Reflectors ("DBRs") in that the medium should appear uniform in the direction of propagation on the length scale of the wavelength of light. Using terminology that one skilled in the art can understand: the dielectric constant of the metamaterials in the direction of propagation can be described with the effective medium approximation. Plasmonic materials and metamaterials provide methods for controlling the propagation of light that can enhance OLED performance in a number of ways.

[0044] In some embodiments, the enhancement layer is provided as a planar layer. In other embodiments, the enhancement layer has wavelength-sized features that are arranged periodically, quasi-periodically, or randomly, or sub-wavelength-sized features that are arranged periodically, quasi-periodically, or randomly. In some embodiments, the wavelength-sized features and the sub-wavelength-sized features have sharp edges.

[0045] In some embodiments, the outcoupling layer has wavelength-sized features that are arranged periodically, quasi-periodically, or randomly, or sub-wavelength-sized features that are arranged periodically, quasi-periodically, or randomly. In some embodiments, the outcoupling layer may be composed of a plurality of nanoparticles and in other embodiments the outcoupling layer is composed of a plurality of nanoparticles disposed over a material. In these embodiments the outcoupling may be tunable by at least one of varying a size of the plurality of nanoparticles, varying a shape of the plurality of nanoparticles, changing a material of the plurality of nanoparticles, adjusting a thickness of the material, changing the refractive index of the material or an additional layer disposed on the plurality of nanoparticles, varying a thickness of the enhancement layer, and/or varying the material of the enhancement layer. The plurality of nanoparticles of the device may be formed from at least one of metal, dielectric material, semiconductor materials, an alloy of metal, a mixture of dielectric materials, a stack or layering of one or more materials, and/or a core of one type of material and that is coated with a shell of a different type of material. In some embodiments, the outcoupling layer is composed of at least metal nanoparticles wherein the metal is selected from the group consisting of Ag, Al, Au, Ir, Pt, Ni, Cu, W, Ta, Fe, Cr, Mg, Ga, Rh, Ti, Ru, Pd, In, Bi, Ca, alloys or mixtures of these materials, and stacks of these materials. The plurality of nanoparticles may have additional layer disposed over them. In some embodiments, the polarization of the emission can be tuned using the outcoupling layer. Varying the dimensionality and periodicity of the outcoupling layer can select a type of polarization that is preferentially outcoupled to air. In some embodiments the outcoupling layer also acts as an electrode of the device.

[0046] In this invention, multi-layer cathodes that enhance electroluminescent lifetime in OLEDs using platinum (II) and paladium (II) complexes as emitters have been designed. Devices using these invented cathodes are still able to maintain the same electrical properties as a device employing a conventional cathode. This class of electrodes could be found useful for full color displays and lighting applications. [0047] OLEDs have become prominent in the display industry due to their high color quality, efficiency, and relatively simple fabrication. Specifically, phosphorescent emissive materials have been of great interest due to their close to unity quantum yields. Colors like red and green have already demonstrated commercially viable lifetimes but there are still improvements that need to be made for blue. Although a significant amount of research has been conducted, stability of blue phosphorescence remains one of the key challenges in the OLED industry. Significant progress has been made in this regard using improved molecular design of emitters and materials used in the emissive layer. This disclosure presents a method for improving the stability of devices using a platinum or palladium-based emitter that allows for flexibility in design of the organic layers and does not influence device electrical properties.

[0048] With reference to FIG. 3B. the thickness and material selection of each layer comprising the cathode 310 is an important property for optimizing stability enhancement. In some embodiments, the metal layer 311 (Ag) adjacent to the Emissive Layer 314 has a thickness of 1-100 nm, 2-50 nm, 5-20 nm, 10-15 nm, or any suitable thickness. In some embodiments, the subsequent organic/dielectric layer 312 comprises an organic material, for example hole transporting material, having a thickness of 1-100 nm, 2-50 nm, 2-20 nm, or any suitable thickness. In some embodiments, the final external metal layer 313 has a thickness of 1-100 nm, 2-50 nm, 5-30 nm, or any suitable thickness depending on material selection. Using these thicknesses and structures allows for enhanced device stability to be achieved without influencing the current and voltage driving properties of the device. The exact device architecture that yielded experimental results is given in the figures provided.

[0049] FIG. 3A-FIG. 3C include cross sectional views of a conventional device structure (FIG. 3A), the disclosed device structure 300 (FIG. 3B), and an experimental structure that demonstrated enhanced performance for palladium emitter device (FIG. 3C).

[0050] FIG. 4A-FIG. 4D include driving characteristics for the conventional device and the disclosed device, using

a palladium emitter (FIG. 4A), a platinum emitter (FIG. 4B), and lifetime graphs for conventional device and the disclosed device using a palladium emitter (FIG. 4C), and a platinum emitter (FIG. 4D).

[0051] One aspect of the disclosed device is a multi-layer cathode 310, that demonstrates increased electroluminescent stability in OLEDs that use Platinum (II) and/or Paladium (II) based emitter molecules and does not influence the driving characteristics of the device. This configuration could be used in display and solid-state lighting applications to enhance the luminescent lifetime of the devices. Enhanced device lifetime makes the devices appealing for use in both display and solid-state lighting applications.

[0052] The invention of these cathodes could further improve the operational stability of device lifetimes without influencing the current and voltage driving characteristics of the device while still allowing for flexibility of material selection and thicknesses for the layers comprising the Emissive Layer stack.

[0053] Advantages include improved electroluminescent stability for OLEDs incorporating platinum (II) and/or palladium (II) based molecules as the emitter.

[0054] In some aspects, the present invention relates to a multi-layer cathode structure that demonstrates increased stability of organic light-emitting devices (OLEDs) using platinum or palladium-based emitters, without changing electrical properties when compared with conventional cathode structures.

[0055] In some aspects, the present invention relates to an organic light emitting diode (OLED) device comprising a stability enhancement electrode.

[0056] In one aspect, the present disclosure provides an organic light emitting diode (OLED) device having enhanced electroluminescent stability.

[0057] In one aspect, the present disclosure provides an organic light emitting diode (OLED) device 300, comprising a substrate 301 coated with a semi-transparent or transparent anode, an organic electroluminescent (EL) 314 layer comprising a hole injection layer (HIL) 303, a hole transporting layer (HTL) 304, an electron blocking layer (EBL) 305, an emissive layer (EML) 306, a hole blocking layer (HBL) 307, an electron transporting layer (ETL) 308, and/or electron injection layer(s) (EIL) 309, a multi-layer cathode (MLC) 310, wherein the MLC is a kind of organic electroluminescence device cathode, which is characterized in that it is comprised of three layers, wherein the first layer 311 is metal (for example, Ag), the second is an organic/dielectric/hole transport material (for example, NPD) 312, and the third layer 313 is metal (for example, Ag or Al).

[0058] In one embodiment, the metal layer 311 in contact with the EL layer 314 has a thickness between 2 and 20 nm and is comprised of a metal, for example Ag.

[0059] In one embodiment, the second layer (organic/dielectric) 312 in the electrode has a thickness between 5-30 nm and is comprised of a hole transport material, for example an organic material that functions as a hole transport material.

[0060] In one embodiment, the external metal layer 313 is 1-30 nm thick and can be comprised of either Ag or Al, wherein thickness and material selection are optimized to reach a peak stability enhancement.

[0061] FIG. 3A-FIG. 3C illustrate an exemplary crosssectional view of an enhanced stability OLED device disclosed herein. In some embodiments, the enhanced stability OLED device 300 includes a substrate 301; a metallic light transmissive electrode 302 which may in some embodiments comprise indium tin oxide (ITO); an organic electroluminescent layer stack 314 that comprises a hole injection layer (HIL) 303, a hole transporting layer (HTL) 304, an electron blocking layer (EBL) 305, an emissive layer (EML) 306, a hole blocking layer (HBL) 307, an electron transporting layer (ETL) 308, and/or an electron injection layer (EIL) 309; and a top multi-layer electrode 310 that comprises a first layer 311 of thin metal (for example Ag) that is semi-transparent, an organic and/or dielectric material layer 312 (for example NPD), and another metal layer 313 (for example Ag or Al).

Combination with Other Materials

[0062] The materials described herein as useful for a particular layer in an organic light emitting device may be used in combination with a wide variety of other materials present in the device. For example, emissive dopants disclosed herein may be used in conjunction with a wide variety of hosts, transport layers, blocking layers, injection layers, electrodes and other layers that may be present. The materials described or referred to below are non-limiting examples of materials that may be useful in combination with the compounds disclosed herein, and one of skill in the art can readily consult the literature to identify other materials that may be useful in combination.

[0063] Various materials may be used for the various emissive and non-emissive layers and arrangements disclosed herein. Examples of suitable materials are disclosed in U.S. Patent Application Publication No. 2017/0229663, which is incorporated by reference in its entirety.

Conductivity Dopants

[0064] A charge transport layer can be doped with conductivity dopants to substantially alter its density of charge carriers, which will in turn alter its conductivity. The conductivity is increased by generating charge carriers in the matrix material, and depending on the type of dopant, a change in the Fermi level of the semiconductor may also be achieved. Hole-transporting layer can be doped by p-type conductivity dopants and n-type conductivity dopants are used in the electron-transporting layer.

HIL/HTL

[0065] A hole injecting/transporting material to be used in the present disclosure is not particularly limited, and any compound may be used as long as the compound is typically used as a hole injecting/transporting material.

EBL

[0066] An electron blocking layer (EBL) may be used to reduce the number of electrons and/or excitons that leave the emissive layer. The presence of such a blocking layer in a device may result in substantially higher efficiencies, and or longer lifetime, as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED. In some embodiments, the EBL material has a higher LUMO (closer to the vacuum level) and/or higher triplet energy than the emitter closest to the EBL interface. In some embodiments, the EBL material has a higher LUMO (closer to the vacuum level) and or higher triplet energy than one or more of the hosts closest to the EBL interface. In one aspect, the compound

used in EBL contains the same molecule or the same functional groups used as one of the hosts described below.

Host

[0067] The light emitting layer of the organic EL device of the present disclosure preferably contains at least a metal complex as light emitting material, and may contain a host material using the metal complex as a dopant material. Examples of the host material are not particularly limited, and any metal complexes or organic compounds may be used as long as the triplet energy of the host is larger than that of the dopant. Any host material may be used with any dopant so long as the triplet criteria is satisfied.

HBL

[0068] A hole blocking layer (HBL) may be used to reduce the number of holes and/or excitons that leave the emissive layer. The presence of such a blocking layer in a device may result in substantially higher efficiencies and/or longer lifetime as compared to a similar device lacking a blocking layer. Also, a blocking layer may be used to confine emission to a desired region of an OLED. In some embodiments, the HBL material has a lower HOMO (further from the vacuum level) and or higher triplet energy than the emitter closest to the HBL interface. In some embodiments, the HBL material has a lower HOMO (further from the vacuum level) and or higher triplet energy than one or more of the hosts closest to the HBL interface.

ETL

[0069] An electron transport layer (ETL) may include a material capable of transporting electrons. The electron transport layer may be intrinsic (undoped), or doped. Doping may be used to enhance conductivity. Examples of the ETL material are not particularly limited, and any metal complexes or organic compounds may be used as long as they are typically used to transport electrons.

Charge Generation Layer (CGL)

[0070] In tandem or stacked OLEDs, the CGL plays an essential role in the performance, which is composed of an n-doped layer and a p-doped layer for injection of electrons and holes, respectively. Electrons and holes are supplied from the CGL and electrodes. The consumed electrons and holes in the CGL are refilled by the electrons and holes injected from the cathode and anode, respectively; then, the bipolar currents reach a steady state gradually. Typical CGL materials include n and p conductivity dopants used in the transport layers.

[0071] As previously disclosed, OLEDs and other similar devices may be fabricated using a variety of techniques and

devices. For example, in OVJP and similar techniques, one or more jets of material is directed at a substrate to form the various layers of the OLED.

[0072] The disclosures of each and every patent, patent application, and publication cited herein are hereby incorporated herein by reference in their entirety. While this invention has been disclosed with reference to specific embodiments, it is apparent that other embodiments and variations of this invention may be devised by others skilled in the art without departing from the true spirit and scope of the invention. The appended claims are intended to be construed to include all such embodiments and equivalent variations

What is claimed is:

- 1. An organic optoelectronic device, comprising: an anode:
- an emitting layer positioned over the anode; and
- a multi-layer cathode positioned over the emitting layer, the multi-layer cathode comprising:
 - a first metal layer positioned over the emitting layer; an organic layer positioned over the first metal layer; and
 - a second metal layer positioned over the organic layer.
- 2. The organic optoelectronic device of claim 1, wherein the first metal layer comprises silver.
- 3. The organic optoelectronic device of claim 1, wherein the organic layer comprises a dielectric or hole transport material.
- **4**. The organic optoelectronic device of claim **1**, wherein the second metal layer comprises silver or aluminum.
- 5. The organic optoelectronic device of claim 1, wherein the first metal layer has a thickness between 5 nm and 20 nm.
- 6. The organic optoelectronic device of claim 1, wherein the organic layer has a thickness between 5 nm and 30 nm.
- 7. The organic optoelectronic device of claim 1, wherein the second metal layer has a thickness between 1 nm and 30 nm
- **8**. The organic optoelectronic device of claim **1**, wherein the emissive layer comprises platinum or palladium.
- 9. A consumer product comprising the organic optoelectronic device of claim 1, wherein the consumer product is selected from the group consisting of a flat panel display, a curved display, a computer monitor, a medical monitor, a television, a billboard, a light for interior or exterior illumination and/or signaling, a heads-up display, a fully or partially transparent display, a flexible display, a rollable display, a foldable display, a stretchable display, a laser printer, a telephone, a cell phone, tablet, a phablet, a personal digital assistant (PDA), a wearable device, a laptop computer, a digital camera, a camcorder, a viewfinder, a microdisplay that is less than 2 inches diagonal, a 3-D display, a virtual reality or augmented reality display, a vehicle, a video walls comprising multiple displays tiled together, a theater or stadium screen, a light therapy device, and a sign.

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