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(54) Title: ORGANIC LIGHT EMITTING DIODE WITH TRANSPARENT METAL OXIDE ELECTRODE AND METHOD OF MAKING SAME

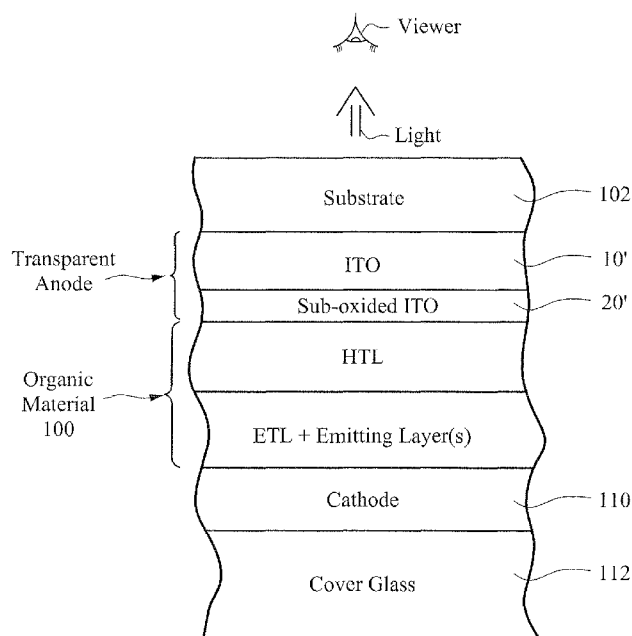


Fig. 3

(57) Abstract: A transparent electrode is provided for an organic light emitting diode (OLED) device. In certain embodiments, the electrode is made by sputter-depositing first and second transparent conductive oxide (TCO) layers of the same material (e.g., ITO), but with different stoichiometries, on a substrate. The first TCO layer is more oxidized than is the second TCO layer. The TCO layers of the electrode on the substrate may then be heat treated (HT) at high temperature(s) in order to increase the work function (WF) and/or increase visible transmission of the electrode. The electrode is provided in an OLED device.

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TITLE OF THE INVENTION

ORGANIC LIGHT EMITTING DIODE WITH TRANSPARENT METAL OXIDE ELECTRODE
AND METHOD OF MAKING SAME

[0001] Certain example embodiments relate to improved organic light emitting diode (OLED) devices, and/or methods of making the same. In particular, certain embodiments of this invention relate to a transparent electrode for an OLED device, and methods of making the same. In certain example embodiments, the electrode is made by sputter-depositing on a substrate first and second transparent conductive oxide (TCO) layers of the same material with different respective stoichiometries. The first TCO layer is located between the substrate and the second TCO layer. The first TCO layer is more oxidized than is the second TCO layer, while both are of the same material or substantially the same material. The TCO layers on the substrate may then be heat treated (HT) at high temperature(s) in order to increase its work function (WF) and/or increase visible transmission and electrical conductivity of the electrode to be used in an OLED.

BACKGROUND AND SUMMARY OF EXAMPLE EMBODIMENTS

[0002] An organic light emitting diode (OLED) is a light-emitting diode (LED) in which the emissive electroluminescent layer(s) is a film of or based mainly on organic compounds which emit light in response to an electric current. This layer of organic semiconductor material is situated between two electrodes in some cases. Generally, for example, at least one of these electrodes is transparent. OLEDs sometimes are used in television screens; computer monitors; small or portable system screens such as those found on mobile phones and PDAs; and/or the like. OLEDs may also sometimes be used in light sources for space illumination and in large-area light-emitting elements. OLED devices are described, for example, U.S. Patent Document Nos. 7,663,311; 7,663,312; 7,662,663; 7,659,661; 7,629,741; 7,601,436,

2011/0193477, and 2009/0295283, the entire contents of all of which are hereby incorporated herein by reference.

[0003] A typical OLED comprises at least two organic layers – e.g., electron and hole transport layers – that are embedded between two electrodes. One electrode typically is made of a reflective metal. The other electrode typically is a transparent conductive layer supported by a glass substrate. The one electrode generally is the cathode, and the other electrode generally is the anode. Indium tin oxide (ITO) often is used at the front portion of the OLED as the anode.

[0004] Fig. 1 is an example cross-sectional view of a typical OLED. The OLED includes glass substrate 102, transparent conductive anode layer 104, organic layer 100, cathode layer 110 and cover glass 112. The organic light emission layer 100 emits light, and light is generated by processes known from conventional OLEDs when electrons and holes injected into the organic layer 100 from different sides recombine. The organic layer 100 may include multiple layers. For example, in certain example instances the organic layer 100 may include a hole injection layer, a hole transport layer, a light-emitting layer, an electron transport layer, and an electron injection layer. An example shown in Fig. 1 illustrates the organic semiconductor layer 100 including a hole transport layer (HTL), and electron transport layer (ETL), and an emitting layer, where the ETL and emitting layer may or may not be present in one layer.

[0005] When a voltage is applied to the electrodes 104 and 110, the charges start moving in the device under the influence of the electric field. Electrons leave the cathode, and holes move from the anode in opposite direction. For example, the recombination of these charges leads to the creation of photons with frequencies given by an energy gap between LUMO and HOMO levels of the emitting molecules, so that the electrical power applied to the electrodes is transformed into light. Different materials and/or

dopants may be used to generate different colors, with the colors being combinable to achieve yet additional colors.

[0006] This disclosure relates to an improved electrode on the light-emitting side of the organic layer, for use in an OLED device or the like. For example, referring to the OLED in Fig. 1, this disclosure relates to an improved electrode 104 on the light emitting side of the organic layer 100 and a method of making the same.

[0007] In certain example embodiments of this invention, the electrode is made by depositing first and second successive transparent conductive oxide (TCO) layers of the same material (e.g., indium-tin-oxide; a/k/a ITO) with different respective stoichiometries. The first and second TCO layers are deposited (directly or indirectly) on a substrate (e.g., glass substrate), and may be deposited for example via sputtering at approximately room temperature. Sputter deposition without intentional heating of the substrate offers certain cost advantages due, primarily, to the lower capital, lower maintenance and higher deposition rates. At the same time, additional post-deposition heating of the TCO is usually used to optimize its optical and electrical performance. High temperatures of post-deposition heating allow better TCO properties. At ~350-500 C, however, the room temperature deposited ITO abruptly loses its conductivity when heated in air, unless its stoichiometry is substantially sub-oxidized (a lack of oxygen in the TCO composition). The properties of the sub-oxidized ITO, however, are not optimum after the heat treatment. To achieve the benefits of high-temperature post-deposition heat treatment while avoiding the conductivity loss, example embodiments of this invention introduce at least a double-layer TCO, where the second layer serves as a protection to the first layer optimized for the best TCO performance after the heat treatment. The first TCO layer is located between the substrate and the second TCO layer, and the first TCO layer is more oxidized as deposited than is the second TCO layer as deposited, while both are of the same material or substantially the same material. In certain example embodiments, as deposited, the first TCO layer

contains at least about 5% more oxygen, more preferably at least about 10% more oxygen, even more preferably at least about 20% more oxygen, and most preferable at least about 30% more oxygen, than does the second TCO layer. The TCO layers of the electrode on the substrate may then be heat treated (HT) at high temperature(s) in order to (a) activate the electrode for desired electrical and/or optical properties, (b) increase the work function (WF) of the electrode, and/or (c) increase visible transmission of the electrode.

[0008] In certain example embodiments of this invention, there is provided a method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising: sputter-depositing a first layer comprising indium tin oxide (ITO) on a glass substrate; sputter-depositing a second layer comprising ITO on the glass substrate over and directly contacting the first layer comprising ITO to form an electrode structure, so that the first layer comprising ITO is located between at least the substrate and the second layer comprising ITO in the electrode structure, wherein as sputter-deposited the first layer comprising ITO is more oxidized than is the second layer comprising ITO; and heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO at temperature(s) of at least about 400 degrees C in order to increase work function of ITO in the electrode structure and increase visible transmission of the electrode structure. As sputter-deposited, the first layer comprising ITO may contain at least 5% more oxygen, more preferably at least 10% more oxygen, still more preferably at least 20% more oxygen, and even more preferably at least 30% more oxygen (by mol %), than the second layer comprising ITO.

[0009] In certain embodiments of this invention, there is provided a method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising: sputter-depositing a first layer comprising metal oxide on a substrate; sputter-depositing a second layer comprising metal oxide on the substrate over and directly contacting the first layer comprising metal oxide to form an electrode structure, wherein the same

metal oxide is in both the first and second layers comprising metal oxide, but as sputter-deposited the first layer comprising metal oxide is more oxidized than is the second layer comprising metal oxide; and heat treating the electrode structure including the substrate and the first and second layers comprising metal oxide at temperature(s) of at least about 400 or 500 degrees C in order to increase work function of ITO in the electrode structure and increase visible transmission of the electrode structure. The substrate may comprise glass or quartz, and the metal oxide may be or comprise ITO, or alternatively the metal oxide may be another suitable metal oxide.

[0010] In certain embodiments of this invention, there is provided an organic light emitting diode (OLED) comprising: a transparent conductive electrode structure comprising first and second layers comprising the same metal oxide (e.g., ITO) on a substrate (e.g., glass or quartz substrate), the first layer comprising the metal oxide being located between the substrate and the second layer comprising the metal oxide, and wherein the second layer comprising the metal oxide directly contacts the first layer comprising the metal oxide; wherein the same metal oxide is in both the first and second layers comprising the metal oxide, and wherein the first layer comprising the metal oxide is more oxidized than is the second layer comprising the metal oxide; and an organic light emitting layer located between said transparent conductive electrode structure and another electrode, and wherein said transparent conductive electrode structure is on a light emitting side of the organic light emitting layer.

[0011] In certain embodiments of this invention, there is provided an organic light emitting diode (OLED) comprising: an organic light emitting layer located between a transparent conductive electrode structure and another electrode, and wherein said transparent conductive electrode structure is on a light emitting side of the organic light emitting layer; and wherein said transparent conductive electrode structure includes a film comprising a metal oxide (e.g., ITO), wherein said film comprising the metal oxide includes a first

portion and a second portion, the first portion being more oxidized than the second portion and being farther from the organic light emitting layer than the second portion. In certain example embodiments, the first portion may contain at least 5% (more preferably at least 10%, even more preferably at least 20% or 30%) more oxygen than the second portion. The film comprising the metal oxide may be oxidation graded, continuously or discontinuously, so as to be more oxidized farther from the organic light emitting layer.

[0012] These and other embodiments, features, aspect, and advantages may be combined in any suitable combination or sub-combination to produce yet further embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] These and other features and advantages may be better and more completely understood by reference to the following detailed description of exemplary illustrative embodiments in conjunction with the drawings, in which like reference numerals indicate like parts throughout the several views, of which:

[0014] FIGURE 1 is an example cross-sectional view of an OLED;

[0015] FIGURE 2 is a schematic diagram of a technique for making a transparent electrode for an OLED according to an example embodiment of this invention; and

[0016] FIGURE 3 is a cross-sectional view of an OLED, including the transparent electrode of FIGURE 2, according to an example embodiment of this invention.

DETAILED DESCRIPTION OF CERTAIN EXAMPLE EMBODIMENTS

[0017] Certain embodiments of this invention relate to a design and method of making a transparent electrode (contact) (e.g., of or including ITO) with an electrically active surface, which may be deposited at approximately

room temperature and which may be activated by post-deposition heat treatment (HT). A substantially sub-oxidized ITO layer 20 is initially deposited (e.g., via sputtering) over an optimized ITO layer 10. The protective sub-oxidized ITO layer 20 serves as an oxygen blocking layer to prevent the layer 10 from becoming overly oxidized during HT, thereby permitting the layer 10 to be exposed to high temperatures for improving electrical and optical properties without suffering undesirable defects.

[0018] ITO deposited at room temperature typically is thermally activated for optimal electrical and optical properties. If the activation temperature exceeds about 370 degrees C, the electrical conductivity tends to decrease due to formation of native defects caused by over-oxidation of the ITO. However, temperatures higher than 370 degrees C are needed for optimal ITO performance (e.g., to achieve desired conductivity, work function, and/or transparency). It is known to bake the ITO in a vacuum in an effort to prevent over-oxidation (excessive oxidation), or to try to protect the ITO with a dielectric layer to block oxygen. However, the simple baking in vacuum approach adds significantly to the cost and tends to slow down the manufacturing process, whereas simply protection by a dielectric layer introduces a non-conductive surface which can be problematic for applications such as OLEDs or electrochromic devices. A simple sub-oxidized ITO layer has been attempted, being oxidized to the same extent throughout the layer, but in this case optimal ITO properties could not be achieved. Thus, in certain embodiments of this invention, a substantially sub-oxidized ITO layer 20 is deposited from a metallic InSn target on top of an optimal ITO layer deposited using a ceramic ITO target which is optimized for post-deposition thermal activation. The stoichiometry and thickness of both ITO layers is optimized in such a way as to reach to desired optimum following HT. The most controllable ITO sputter deposition process can be achieved via a ceramic ITO target, which often does not permit deposition of a substantially sub-oxidized ITO layer. The stoichiometry of the ITO 10 closest to the substrate 102 is

optimized, via ceramic target sputtering, to ensure optimal ITO performance upon baking, while the top ITO layer 20 is more sub-oxidized to protect layer 10 during HT (e.g., to ensure effective oxygen properties so that the ITO layer 10 is not overly oxidized during the HT).

[0019] Referring generally to Figs. 2-3, in certain example embodiments of this invention there is provided a method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising: sputter-depositing a first layer 10 of or including indium tin oxide (ITO) on a glass substrate 102; sputter-depositing a second layer 20 of or including ITO on the transparent glass substrate 102 over and directly contacting the first layer 10 comprising ITO to form an electrode structure. The first layer 10 of or including ITO is located between at least the substrate 102 and the second layer 20 of or including ITO in the electrode structure. In certain example embodiments, as sputter-deposited (e.g., at approximately room temperature where the substrate 102 and layers 10, 20 are all at approximately room temperature, or alternatively at an elevated temperature such as from about 30-60 degrees C), the first layer 10 of or including ITO is more oxidized than is the second layer 20 of or including ITO. After the two layers 10 and 20 of or based on ITO are sputter-deposited on (directly or indirectly) the substrate, the layers on the substrate are heat treated (HT) 30 at temperature(s) of at least about 400 degrees C (more preferably at least about 500 degrees C, still more preferably at least about 550 degrees C and even more preferably at least about 600 degrees C) in order to increase work function of ITO 10 and/or 20 in the electrode structure and increase visible transmission of the electrode structure. In OLED application, a high work function (WF) is desired on the side of the ITO facing the viewer. The heat treatment may be performed for a time period sufficient to allow the bulk ITO to reach about 550 or 600 degrees C, for at least about 20 or 30 seconds, so as to achieve a desired increase in WF due to the HT in certain example embodiments. During heat treating, in certain example embodiments, the second ITO layer 20 is the uppermost and exposed

layer of the coating on substrate 102. Accordingly, by using the two layer 10, 20 approach, where the upper ITO layer 20 is sub-oxidized compared to the first ITO layer 10, the work function of the post-HT ITO electrode can be increased and the resulting electrode can be made to be more transparent and more conductive without suffering from significant defects.

[0020] While the substrate 102 may be of or including glass in preferred embodiments, it is also possible that the substrate may be of a different transparent material such as quartz in alternative embodiments.

[0021] As sputter-deposited and possibly after HT, the first layer 10 of or including ITO may contain at least 5% more oxygen (more preferably at least 10% more oxygen, still more preferably at least 20% more oxygen, and even more preferably at least 30% more oxygen, than the second layer 20 of or including ITO. The first layer 10 of or including ITO may be thicker (e.g., at least 50 nm thicker, most preferably at least about 100 nm thicker) than the second layer 20 of or including ITO.

[0022] In certain example embodiments, sputter-depositing of the first ITO layer 10 may be performed by sputtering a ceramic target of or including indium, tin and oxygen (e.g., with In/Sn molar ratio in the target and in the layer from 80/20 to 95/5), whereas sputter-depositing of the second ITO layer 20 may be performed by sputtering a metallic or substantially metallic target of or including indium and tin (e.g., InSn target) with a argon/oxygen gas ratio of from about 4:1 to 1:1. An example InSn target may have an In/Sn molar ratio of from 80/20 to 95/5. Thus, in certain embodiments, the first and second ITO layers 10 and 20 may be sputter-deposited using different types of targets in order to ensure that the second layer is less oxidized and to allow the oxidation values to be better controlled. Alternatively, the second ITO layer 20 may be sputter-deposited using a ceramic ITO target (e.g., with In/Sn molar ratio in the target and in the layer from 80/20 to 95/5), with the deposition being performed in a reduced atmosphere using a mixture of Ar and H₂ gas (e.g., from about 1-10%, more preferably about 5% H₂).

[0023] The first ITO layer 10 may be from about 50-500 nm thick, more preferably from about 100-200 nm thick (e.g., about 150 nm thick), and the second ITO layer 20 may be from about 20-500 nm thick, more preferably from about 20-95 nm thick (e.g., about 50 nm thick). While only two ITO layers are shown in Fig. 2, this invention is not so limited and more than two ITO layers may be provided. For example, there may be three or four ITO layers in certain example embodiments, where generally the layer(s) closer to the substrate 102 are more oxidized than are the layer(s) farther from the substrate 102.

[0024] While Fig. 2 illustrates ITO layer 10 and 20 as different “layers,” in certain example embodiments of this invention, they may be combined into a single oxidation graded layer that is oxidation graded, continuously or discontinuously, so that portion(s) closer to substrate 102 are more oxidized than are portions farther from substrate 102. The single layer in such graded embodiments may, for example, be deposited by varying gas flows around one or more targets (e.g., using more oxygen gas flow in the initial part of the sputter-depositing where the portion(s) closer to substrate 102 is formed, and then reducing the amount of oxygen gas in the sputtering chamber(s) later in the process when the portion(s) of the layer farther from substrate 102 is formed.

[0025] After the heat treating 30, the electrode structure (e.g., including the substrate 102 and the heat treated first and second ITO layers 10' and 20') may have a visible transmission of at least about 75%, more preferably of at least about 80%, and most preferably of at least about 82 or 84%. Moreover, after the heat treating, the heat treated electrode (e.g., layer 10' and/or layer 20') may have a specific resistivity of less than or equal to about 0.30 mOhms-cm, more preferably less than or equal to about 0.27 mOhms-cm.

[0026] After the heat treating 30, the electrode structure described above (e.g., including the heat treated first and second ITO layers 10' and 20', and optionally the substrate 102) is provided in an OLED device as shown in Fig. 3

so that an organic semiconductor film/layer 100, including an organic light emitting semiconductor layer, is located between the electrode structure and another electrode 110. For example, the organic film/layer 100 and cathode 110 may be formed on substrate 102 over the ITO electrode. The organic film/layer 100 emits light, and light is generated when electrons and holes injected into the organic film/layer 100 from different sides recombine. The organic film/layer 100 may include multiple layers, but always includes at least one light emitting layer. For example, in certain example embodiments, organic film/layer 100 may include a hole injection layer, a hole transport layer, a light-emitting layer, an electron transport layer, and an electron injection layer. An example shown in Fig. 3 illustrates the organic semiconductor film/layer 100 including a hole transport layer (HTL), and electron transport layer (ETL), and an emitting layer, where the ETL and emitting layer may or may not be present in one layer. When a voltage is applied to the electrodes 10', 20' and 110, the charges start moving in the device under the influence of the electric field. Electrons leave the cathode 110, and holes move from the anode 10', 20' in opposite direction, so that the electrical power applied to the electrodes is transformed into light. Fig. 3 illustrate that the electrode 110 is a cathode, and the transparent electrode made up of the ITO is the anode, however the "cathode" and "anode" may be reversed in certain example embodiments so that the cathode is transparent and made up of the ITO layers 10' and 20'.

[0027] In certain example embodiments, in one or more steps not shown, CRI matching layers, antireflective (AR) coatings, and/or the like may be provided in the OLED device. For example, an AR layer(s) may be provided either between the layer 10 and substrate 102, or on the major surface of substrate opposite the ITO 10, 20. In certain example embodiments, a layer of or including silicon nitride and/or silicon oxide may be provided between the substrate 102 and the ITO layer 10.

[0028] And although certain example embodiments have been described in connection with ITO being used as the metal oxide for the transparent electrode made up of 10' and 20', it will be appreciated that other conductive oxide materials may be used in place of ITO. Alternate materials may include, for example, zinc oxide, aluminum-doped zinc oxide (AZO), indium gallium zinc oxide (IGZO), etc.

[0029] These techniques similarly may be used in inorganic light emitting diodes (ILEDs), polymer light emitting diode (PLEDs), and/or other diode applications.

[0030] In certain example embodiments of this invention, there is provided a method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising: sputter-depositing a first layer comprising indium tin oxide (ITO) on a glass substrate; sputter-depositing a second layer comprising ITO on the glass substrate over and directly contacting the first layer comprising ITO to form an electrode structure, so that the first layer comprising ITO is located between at least the substrate and the second layer comprising ITO in the electrode structure, wherein as sputter-deposited the first layer comprising ITO is more oxidized than is the second layer comprising ITO; and heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO at temperature(s) of at least about 400 degrees C in order to increase work function of ITO in the electrode structure and increase visible transmission of the electrode structure.

[0031] In the method of the immediately preceding paragraph, the first and second layers comprising ITO may consist essentially of ITO.

[0032] In the method of any of the preceding two paragraphs, as sputter-deposited, the first layer comprising ITO may contain at least 5% more oxygen, more preferably at least 10% more oxygen, still more preferably at least 20% more oxygen, and even more preferably at least 30% more oxygen (by mol %), than the second layer comprising ITO.

[0033] In the method of any of the preceding three paragraphs, said heat treating may comprise heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO thereon at temperature(s) of at least about 500 degrees C, more preferably of at least about 550 or 600 degrees C.

[0034] In the method of any of the preceding four paragraphs, said sputter-depositing of the first layer comprising ITO and said sputter-depositing of the second layer comprising ITO may each comprise sputter-depositing at approximately room temperature.

[0035] In the method of any of the preceding five paragraphs, said first layer comprising ITO may be sputter-deposited on the glass substrate so as to directly contact the glass substrate.

[0036] In the method of any of the preceding six paragraphs, the first layer comprising ITO may be thicker (e.g., at least 50 nm thicker, most preferably at least about 100 nm thicker) than the second layer comprising ITO.

[0037] In the method of any of the preceding seven paragraphs, said sputter-depositing of the first layer comprising ITO may comprise sputtering a ceramic target comprising indium, tin and oxygen; and said sputter-depositing of the second layer comprising ITO may comprise sputtering a metal target comprising indium and tin.

[0038] In the method of any of the preceding eight paragraphs, the first layer comprising ITO may be from about 100-200 nm thick, and/or the second layer comprising ITO may be from about 20-95 nm thick.

[0039] In the method of any of the preceding nine paragraphs, after said heat treating, the electrode structure may have a visible transmission of at least about 80%.

[0040] In the method of any of the preceding ten paragraphs, after said heat treating, the electrode structure may be provided in an OLED device so that an organic light emitting semiconductor layer is located between said electrode structure and another electrode.

[0041] In certain embodiments of this invention, there is provided a method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising: sputter-depositing a first layer comprising metal oxide on a substrate; sputter-depositing a second layer comprising metal oxide on the substrate over and directly contacting the first layer comprising metal oxide to form an electrode structure, wherein the same metal oxide is in both the first and second layers comprising metal oxide, but as sputter-deposited the first layer comprising metal oxide is more oxidized than is the second layer comprising metal oxide; and heat treating the electrode structure including the substrate and the first and second layers comprising metal oxide at temperature(s) of at least about 400 or 500 degrees C in order to increase work function of ITO in the electrode structure and increase visible transmission of the electrode structure.

[0042] In the method of the immediately preceding paragraph, the substrate may comprise glass or quartz.

[0043] In the method of the immediately preceding paragraph, the metal oxide may be or comprise ITO.

[0044] In certain embodiments of this invention, there is provided an organic light emitting diode (OLED) comprising: a transparent conductive electrode structure comprising first and second layers comprising the same metal oxide on a substrate, the first layer comprising the metal oxide being located between the substrate and the second layer comprising the metal oxide, and wherein the second layer comprising the metal oxide directly contacts the first layer comprising the metal oxide; wherein the same metal oxide is in both the first and second layers comprising the metal oxide, and wherein the first layer comprising the metal oxide is more oxidized than is the second layer comprising the metal oxide; and an organic light emitting layer located between said transparent conductive electrode structure and another electrode, and wherein said transparent conductive electrode structure is on a light emitting side of the organic light emitting layer.

[0045] In the OLED of the immediately preceding paragraph, the substrate comprise glass or quartz.

[0046] In the OLED of any of the preceding two paragraphs, the metal oxide may be ITO.

[0047] In the OLED of any of the preceding three paragraphs, the first layer comprising the metal oxide may contain at least 5% (more preferably at least 10%, even more preferably at least 20%) more oxygen than the second layer comprising the metal oxide.

[0048] In certain embodiments of this invention, there is provided an organic light emitting diode (OLED) comprising: an organic light emitting layer located between a transparent conductive electrode structure and another electrode, and wherein said transparent conductive electrode structure is on a light emitting side of the organic light emitting layer; and wherein said transparent conductive electrode structure includes a film comprising a metal oxide (e.g., ITO), wherein said film comprising the metal oxide includes a first portion and a second portion, the first portion being more oxidized than the second portion and being farther from the organic light emitting layer than the second portion.

[0049] In the OLED of the immediately preceding paragraph, the first portion may contain at least 5% (more preferably at least 10%, even more preferably at least 20% or 30%) more oxygen than the second portion.

[0050] In the OLED of any of the preceding two paragraphs, the film comprising the metal oxide may be oxidation graded, continuously or discontinuously, so as to be more oxidized farther from the organic light emitting layer.

[0051] In the OLED of any of the preceding three paragraphs, the transparent conductive electrode structure may further comprises a glass substrate, wherein the first portion is located between the glass substrate and the second portion.

[0052] As used herein, the terms “on,” “supported by,” and the like should not be interpreted to mean that two elements are directly adjacent to one another unless explicitly stated. In other words, a first layer may be said to be “on” or “supported by” a second layer, even if there are one or more layers therebetween.

[0053] While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising:
 - sputter-depositing a first layer comprising indium tin oxide (ITO) on a glass substrate;
 - sputter-depositing a second layer comprising ITO on the glass substrate over and directly contacting the first layer comprising ITO to form an electrode structure, so that the first layer comprising ITO is located between at least the substrate and the second layer comprising ITO in the electrode structure, wherein as sputter-deposited the first layer comprising ITO is more oxidized than is the second layer comprising ITO; and
 - heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO at temperature(s) of at least about 400 degrees C in order to increase work function of ITO in the electrode structure and increase visible transmission of the electrode structure.
2. The method of claim 1, wherein the first and second layers comprising ITO consist essentially of ITO.
3. The method of any preceding claim, wherein, as sputter-deposited, the first layer comprising ITO contains at least 5% more oxygen than does the second layer comprising ITO.
4. The method of any preceding claim, wherein, as sputter-deposited, the first layer comprising ITO contains at least 10% more oxygen than does the second layer comprising ITO.

5. The method of any preceding claim, wherein, as sputter-deposited, the first layer comprising ITO contains at least 20% more oxygen than does the second layer comprising ITO.

6. The method of any preceding claim, wherein, as sputter-deposited, the first layer comprising ITO contains at least 30% more oxygen than does the second layer comprising ITO.

7. The method of any preceding claim, wherein said heat treating comprises heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO thereon at temperature(s) of at least about 500 degrees C.

8. The method of any preceding claim, wherein said heat treating comprises heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO thereon at temperature(s) of at least about 550 degrees C.

9. The method of any preceding claim, wherein said sputter-depositing of the first layer comprising ITO and said sputter-depositing of the second layer comprising ITO each comprises sputter-depositing at approximately room temperature.

10. The method of any preceding claim, wherein said first layer comprising ITO is sputter-deposited on the glass substrate so as to directly contact the glass substrate.

11. The method of any preceding claim, wherein the first layer comprising ITO is thicker than the second layer comprising ITO.

12. The method of any preceding claim, wherein the first layer comprising ITO is at least 50 nm thicker than the second layer comprising ITO.

13. The method of any preceding claim, wherein said sputter-depositing of the first layer comprising ITO comprises sputtering a ceramic target comprising indium, tin and oxygen; and said sputter-depositing of the second layer comprising ITO comprises sputtering a metal target comprising indium and tin.

14. The method of any preceding claim, wherein the first layer comprising ITO is from about 100-200 nm thick.

15. The method of any preceding claim, wherein the second layer comprising ITO is from about 20-95 nm thick.

16. The method of any preceding claim, wherein after said heat treating the electrode structure has a visible transmission of at least about 80%.

17. The method of any preceding claim, further comprising, after said heat treating, providing the electrode structure in an OLED device so that an organic light emitting semiconductor layer is located between said electrode structure and another electrode.

18. A method of making an organic light emitting diode (OLED) device, the method comprising:

sputter-depositing a first layer comprising indium tin oxide (ITO) on a glass substrate;

sputter-depositing a second layer comprising ITO on the glass substrate over the first layer comprising ITO to form an electrode structure, so that the first layer comprising ITO is located between at least the substrate and the

second layer comprising ITO in the electrode structure, wherein as sputter-deposited the first layer comprising ITO is more oxidized than is the second layer comprising ITO;

heat treating the electrode structure including the glass substrate and the first and second layers comprising ITO thereon at temperature(s) of at least about 500 degrees C to increase work function of the electrode structure; and

after said heat treating, providing the electrode structure in an OLED device so that an organic light emitting semiconductor layer of the OLED device is located between said electrode structure and another electrode.

19. The method of claim 18, where after said heat treating the electrode structure has a visible transmission of at least about 80%.

20. A method of making an electrode for use in an organic light emitting diode (OLED) device, the method comprising:

sputter-depositing a first layer comprising metal oxide on a substrate;

sputter-depositing a second layer comprising metal oxide on the substrate over and directly contacting the first layer comprising metal oxide to form an electrode structure, wherein the same metal oxide is in both the first and second layers comprising metal oxide, but as sputter-deposited the first layer comprising metal oxide is more oxidized than is the second layer comprising metal oxide; and

heat treating the electrode structure including the substrate and the first and second layers comprising metal oxide at temperature(s) of at least about 400 degrees C in order to increase work function of ITO in the electrode structure and increase visible transmission of the electrode structure.

21. The method of claim 20, wherein the substrate comprises glass.

22. The method of any of claims 20-21, wherein the metal oxide comprises ITO.

23. An organic light emitting diode (OLED) comprising:
a transparent conductive electrode structure comprising first and second layers comprising the same metal oxide on a substrate, the first layer comprising the metal oxide being located between the substrate and the second layer comprising the metal oxide, and wherein the second layer comprising the metal oxide directly contacts the first layer comprising the metal oxide;

wherein the same metal oxide is in both the first and second layers comprising the metal oxide, and wherein the first layer comprising the metal oxide is more oxidized than is the second layer comprising the metal oxide; and

an organic light emitting layer located between said transparent conductive electrode structure and another electrode, and wherein said transparent conductive electrode structure is on a light emitting side of the organic light emitting layer.

24. The OLED of claim 23, wherein the substrate comprises glass.

25. The OLED of any of claims 23-24, wherein the metal oxide comprises ITO.

26. The OLED of any of claims 23-25, wherein the first layer comprising the metal oxide contains at least 5% more oxygen than does the second layer comprising the metal oxide.

27. The OLED of any of claims 23-26, wherein the first layer comprising the metal oxide contains at least 10% more oxygen than does the second layer comprising the metal oxide.

28. An organic light emitting diode (OLED) comprising:
an organic light emitting layer located between a transparent conductive electrode structure and another electrode, and wherein said transparent conductive electrode structure is on a light emitting side of the organic light emitting layer; and

wherein said transparent conductive electrode structure includes a film comprising a metal oxide, wherein said film comprising the metal oxide includes a first portion and a second portion, the first portion being more oxidized than the second portion and being farther from the organic light emitting layer than the second portion.

29. The OLED of claim 28, wherein the first portion contains at least 5% more oxygen than does the second portion.

30. The OLED of any of claims 28-29, wherein the first portion contains at least 10% more oxygen than does the second portion.

31. The OLED of any of claims 28-30, wherein the film comprising the metal oxide is oxidation graded so as to be more oxidized farther from the organic light emitting layer.

32. The OLED of any of claims 28-31, wherein the transparent conductive electrode structure further comprises a glass substrate, wherein the first portion is located between the glass substrate and the second portion.

33. The OLED of claim any of claims 28-32, wherein the metal oxide is ITO.

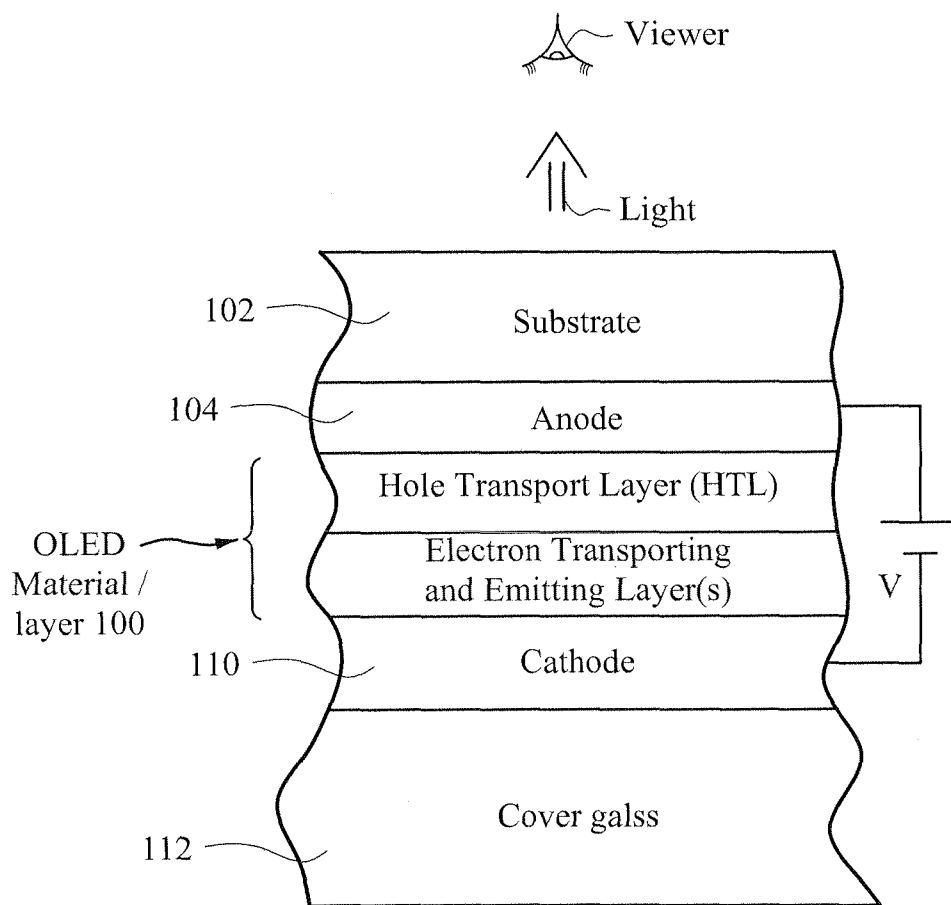


Fig. 1
(Prior Art)

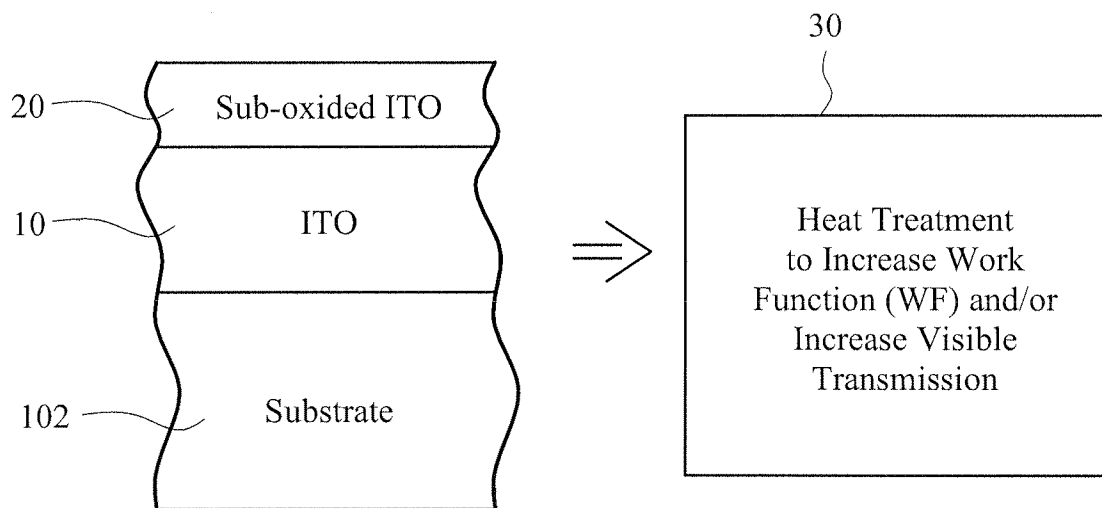


Fig. 2

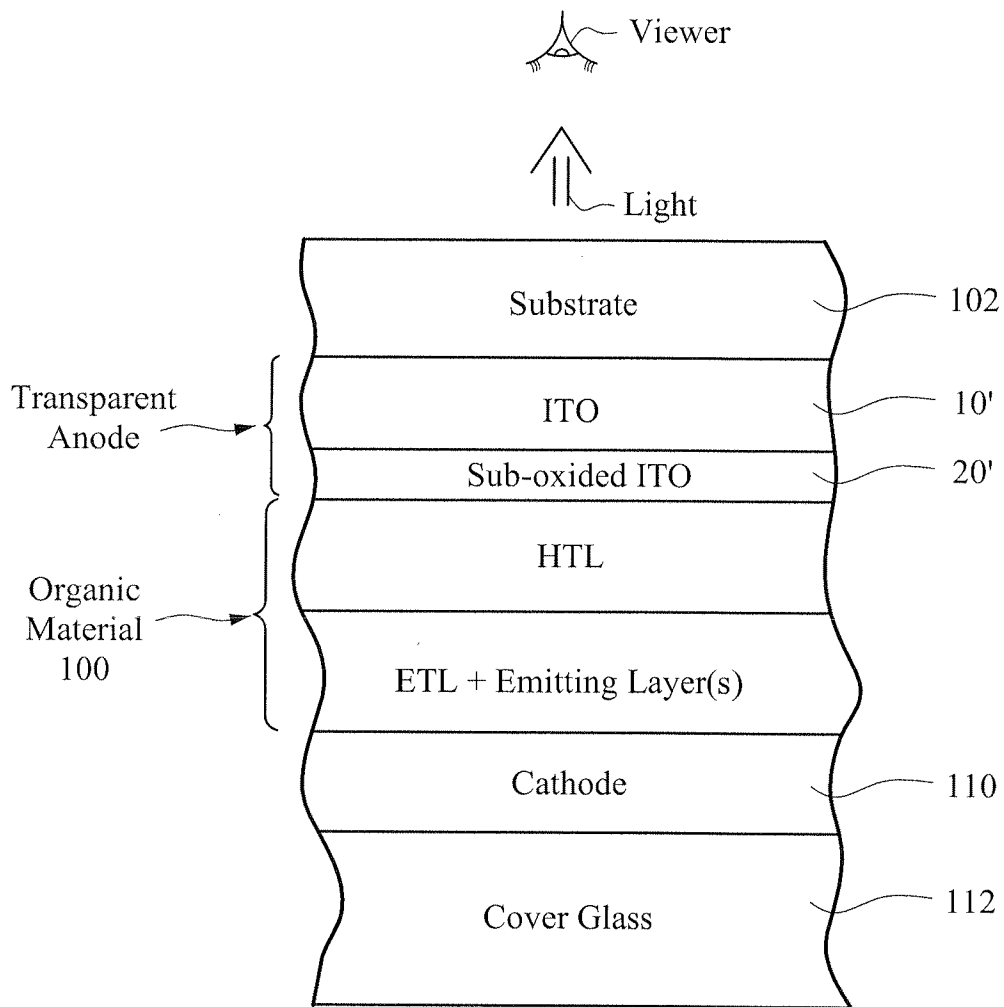


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No PCT/US2013/051925

A. CLASSIFICATION OF SUBJECT MATTER INV. H01L51/52 ADD.		
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) H01L C23C		
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 practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 952 779 A (ARAI MICHIO [JP] ET AL) 14 September 1999 (1999-09-14) column 2, line 9 - column 4, line 44; figure 2 column 7, lines 29-34 column 8, lines 45-58	23-27
X	----- US 6 259 202 B1 (STURM JAMES C [US] ET AL) 10 July 2001 (2001-07-10) column 5, line 40 - column 7, line 18; figures 1,5	28-33
A	----- US 2010/122900 A1 (KRASNOV ALEXEY [US]) 20 May 2010 (2010-05-20) paragraphs [0021] - [0032] -----	1-19
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		
<input checked="" type="checkbox"/> See patent family 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 application or patent 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	Date of mailing of the international search report	
16 September 2013	23/09/2013	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Boetticher, Harald	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 20-22

In claim 20 "to increase work function of ITO in the electrode structure" is obscure, because no ITO is claimed in the preceding passages of claim 20. Claim 20 shows "sputter-depositing a first layer comprising metal oxide" and "sputter-depositing a second layer comprising metal oxide on the substrate over and directly contacting the first layer comprising metal oxide to form an electrode structure", so the electrode structure does not show ITO. It is thus not apparent what is meant by "to increase work function of ITO in the electrode structure" in claim 20, making a complete meaningful search of the features of claim 20 impossible.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/051925

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 20-22
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2013/051925

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			US 2012064234 A1 15-03-2012
			US 2013059065 A1 07-03-2013
			WO 2010059311 A1 27-05-2010
