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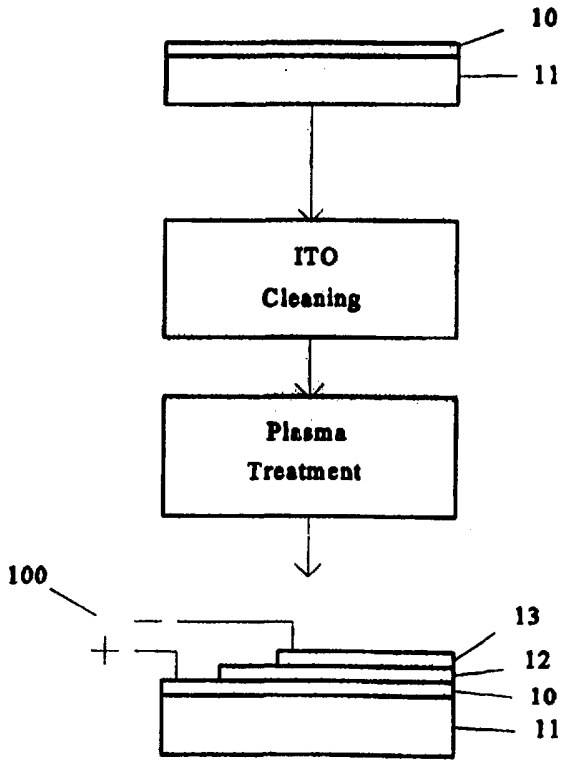
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(54) Title: PLASMA TREATMENT OF CONDUCTIVE LAYERS

(57) Abstract

A method for modifying the surface properties such as work function of semiconducting and conducting layers (10) by plasma treatment. Also disclosed are electrical devices such as organic light emitting devices (100) of enhanced performance owing to the use of plasma treatment-modified semiconducting or conducting layers.



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PLASMA TREATMENT OF CONDUCTIVE LAYERS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/019,657, filed June 12, 1996.

Field of the Invention

This invention relates to the field of organic optoelectronics, and more particularly to the enhancement of optoelectronic performance by the treatment of conductive layers used in optoelectronic devices.

Background of the Invention

Organic light emitting devices (OLEDs) make use of organic thin film materials which emit light when excited by electric current. These devices usually consist of a sandwich structure with organic thin films deposited onto a transparent substrate and covered by top metal cathode contacts. Between the transparent substrate and the organic thin films is a layer of transparent, conducting material which serves as an anode.

The organic thin films typically consist of an emission layer between a hole transporting layer and an electron transporting layer. When current is applied

between the cathode and anode, the emission layer provides a recombination site for electrons injected from the electron transporting layer and holes from the hole transporting layer. This recombination results in the emission of light having a characteristic wavelength depending on the organic materials used. Alternatively, single-layer organic or organic blend layers can be used instead of such multilayer organic thin film systems.

Because of its transparency, high conductivity and efficiency as a hole injector into organic materials, indium-tin-oxide ("ITO") is widely used as the anode material in OLEDs. Because the organic thin films are in direct contact with the ITO in OLEDs, the surface properties of ITO are expected to directly affect the characteristics of these devices. Consequently, ITO layers which are not properly cleaned or have other imperfections can result in poor device performance, such as shorting, unstable I-V characteristics, higher drive voltages and poor reliability.

To minimize the possibility of poor device performance due to the ITO layer, conventional ITO treatments usually include combinations of cleaning steps, such as sonification, boiling and rinsing in materials such as detergents, deionized ("DI") water and organic solvents, and degreasing in organic solvent vapor. Such cleaning techniques, however, are not often sufficiently reliable or reproducible, and consequently, irregular variations in device performance often occurs.

Summary of the Invention

The present invention provides a method for modifying the surface properties, such as chemical composition, work function, cleanliness and roughness, of semiconducting or conducting layers by plasma treatment. The present invention also provides for electrical devices of enhanced performance owing to the use of plasma treatment-modified semiconducting or conducting layers.

In one embodiment of the invention, a plasma treatment is used to modify at least one of the conductive layers used in an OLED. This device performance is greatly enhanced by the plasma treatment.

One advantage of the present invention is that it provides a reliable method for providing conductive layers of desired work function, cleanliness and performance.

Another advantage of the present invention is that it provides a reliable method for providing electrical devices, and particularly OLEDs, of enhanced performance.

Yet another advantage of the present invention is that it provides electrical devices, and particularly OLEDs, having enhanced performance.

Brief Description of the Drawings

Fig. 1 is a schematic flowchart showing the steps for fabricating an OLED in accordance with the present invention.

Fig. 2 shows I-V characteristics for OLEDs having plasma treated ITO layers.

Fig. 3 shows the brightness-current and brightness-voltage characteristics for OLEDs having plasma treated ITO layers.

Fig. 4 is a plot of OLED brightness as a function of time for plasma treated ITO compared to untreated ITO.

Fig. 5 shows compositional profiles for plasma treated ITO layers.

Detailed Description

The present invention makes use of a plasma treatment to modify the surface of conductive layers used in electrical devices such as OLEDs. By including such a plasma treatment to conductive layers, OLED performance is greatly enhanced in terms of qualities such as I-V characteristics, drive voltages, efficiency and reliability. The conductive layers in OLEDs are typically materials such as ITO, Pt, Al, Ag, Au, Mg, Mg/Ag, and Li/Al. ITO and Pt are the preferred materials for transparent and reflective anode conductive layers, respectively.

The present invention includes a method for making OLEDs of enhanced performance. As shown in Fig. 1, the first step in making OLED 100 is depositing conductive layer 10 onto substantially transparent substrate 11 to serve as an anode. Conductive layer 10 is substantially transparent and is preferably made of ITO. Substrate 11

can be made of any suitable transparent material, such as quartz, sapphire, plastic, or preferably glass. The preferred method of depositing the ITO layer 10 is by electron-beam evaporation or sputtering. After ITO layer 10 is deposited onto substrate 11, the ITO is cleaned by wet cleaning steps in detergents, water or solvents as is known in the art. Suitable detergents for cleaning ITO layer are known in the art, although TERGITOL™ (J.T. Baker Co.) is preferred. Suitable solvents include acetone, methanol and preferably trichloroethane ("TCA"). It is preferred that this step include cleaning by swabbing and sonification with TERGITOL, rinsing in DI water, degreasing by flushing in warm TCA, and finally rinsing in acetone and methanol.

After cleaning, ITO layer 10 is subjected to a plasma treatment. The gas used in the plasma treatment can be oxygen, hydrogen, argon, or gas mixtures containing these species, for example. Oxygen plasma, which tends to increase ITO work function, is the most preferred plasma for OLED applications. This step can be carried out in either a barrel-type plasma system or a parallel-type plasma system, as are known in the art. Power densities used during the plasma treatment range from 25 to 200 mW/cm^2. There is no intentional heating of the sample during the plasma treatment.

Organic layers 12 are deposited onto ITO layer 10 after the plasma treatment. The organic material chosen for deposition will depend on the color or combination of

colors desired for use. For example, if blue is the desired emission color, the emissive layer of OLED is made from any suitable blue light-emissive organic compound such as, for example, trivalent metal quinolate complexes, Schiff base divalent metal complexes, metal acetylacetonate complexes, metal bidentate ligand complexes, bisphosphonates, metal maleontriledithiolate complexes, molecular charge transfer complexes, aromatic and heterocyclic polymers and rare earth mixed chelates. The metal bidentate complexes have the formula MDL^4_2 wherein M is selected from trivalent metals of Groups 3-13 of the Periodic Table and Lanthanides. The preferred metal ions are Al^{+3}, Ga^{+3}, In^{+3} and Sc^{+3}. D is a bidentate ligand such as 2-picolylketones, 2-quinaldylkentones and 2-(o-phenoxy) pyridine ketones. The preferred groups for L^4 include acetylacetonate, compounds of the formula OR^3R wherein R^3 is selected from Si and C, and R is selected from hydrogen, substituted and unsubstituted alkyl, aryl and heterocyclic groups; 3,5-di(t-bu) phenol; 2,6-di(t-bu) phenol; 2,6-di(t-bu) cresol; and H_2Bpz_2. By way of example, the wavelength resulting from measurement of photoluminescence in the solid state of aluminum (picolymethylketone) bis [2,6-di(t-bu) phenoxide] is 420nm. The cresol derivative of this compound also measured 420nm. Aluminum (picolylmethyl-ketone) bis ($OsiPh_3$) and scandium (4-methoxy-picolyl-methylketone) bis (acetylacetonate) each measured 433nm, while aluminum [2-(O-phenoxy)pyridine] bis [2,6-di(t-bu) phenoxide] measured 450nm.

Examples of green emissive layer OLED materials include tin (iv) metal complexes, such as those having the formula $SnL^1_2L^2_2$ where L^1 is selected from salicylaldehydes, salicyclic acid or quinolates (e.g. 8-hydroxyquinoline). L^2 can be substituted and unsubstituted alkyl, aryl and heterocyclic groups. When L^1 is a quinolate and L^2 is a phenyl, for example, the tin (iv) metal complex will have an emission wavelength of 504nm.

Examples of red emissive layer OLED materials include divalent metal maleonitriledithiolate ("mnt") complexes, such as those described by C.E. Johnson et al. in "Luminescent Iridium(I), Rhodium(I), and Platinum(II) Dithiolate Complexes," 105 Journal of the American Chemical Society 1795 (1983). For example, the mnt [Pt $(Pph_3)_2$] has a characteristic wavelength emission of 652nm.

Additional OLED materials are known in the art (see, e.g., U.S. Patent No. 5,294,870 to Tang et al., entitled "Organic Electroluminescent Multicolor Image Display Device"; Hosokawa et al., "Highly efficient blue electroluminescence from a distyrylarylene emitting layer with a new dopant," 67 Applied Physics Letters 3853-55 (December 1995); Adachi et al., "Blue light-emitting organic electroluminescent devices," 56 Applied Physics Letters 799-801 (February 1990); Burrows et al., "Color-Tunable Organic Light Emitting Devices," 69 Applied Physics Letters 2959-61 (November 1996)). The entire disclosures of these references are hereby incorporated by reference. Distyrylarylene derivatives such as those described in

Hosokawa et al. are a preferred class of compounds. Other preferred OLEDs are described in the copending applications discussed below.

After the organic layers 12 are deposited, conductive layer 13 is deposited as a cathode layer to complete the OLED, as shown in Fig. 1.

The plasma treatment of semiconductive or conductive layers in accordance with the present invention does not degrade the bulk properties of these layers. Rather, the plasma treatment affects only the region at or near the layer surface, which in turn affects the performance characteristics of the electronic device. It is therefore concluded that changes in device performance are related to the treated semiconductor or conductor surface properties.

The mechanism by which the plasma treatment affects OLED performance is not presently known with certainty. While not wishing to be bound by theory, however, it is suspected that the influence of the plasma treatment on ITO surface work function has a significant effect on OLED performance. Other factors such as the removal of organic residue from the ITO surface and the reduction in surface roughness may also influence OLED performance.

The present invention is also applicable to so-called "top-emitting" OLEDs, in which emitted light is projected in a direction away from the substrate. In such devices, an anode layer is deposited onto a substrate, with either of the anode layer or the substrate being reflective. The organic layer(s) are then deposited over the anode, and a

substantially transparent cathode is deposited over the organic layer(s). The reflective anode is made of Pt, for example. In accordance with the present invention, the anode is subjected to a plasma treatment prior to the deposition of the organic layer(s). The plasma treatment has similar effects on the top-emitting device performance as it has on the non-inverted device, namely an enhancement in I-V characteristics, drive voltages, efficiency and reliability.

The present invention is also applicable to OLEDs in which the location of the anode and cathode about the organic layer(s) are reversed. In such devices, a plasma treatment is used to modify the surface characteristics of the cathode layer before depositing the organic layer(s).

The present invention is used to provide efficient, high brightness, monochromatic or multicolor, flat panel displays of any size. This widens the scope of this invention to include displays as small as a few millimeters to as large as the size of a building. The images created on such displays could be text or illustrations in full color, in any resolution depending on the size of the individual LED's. Display devices of the present invention are therefore appropriate for an extremely wide variety of applications including billboards and signs, computer monitors, telecommunications devices such as telephones, televisions, large area wall screens, theater screens and stadium screens. Embodiments of the present invention in which the emitted light is directed in a direction away

from the substrate are particularly useful for xerographic applications, as such embodiments allow for close positioning to print paper without the use of lenses.

Although the present invention is described with specific reference to OLEDs, it may also be useful for other applications in which the surface characteristics of semiconductor or conductor materials, such as chemical composition, work function, cleanliness and roughness, are modified by plasma treatment.

The subject invention as disclosed herein may be used in conjunction with co-pending applications: "High Reliability, High Efficiency, Integratable Organic Light Emitting Devices and Methods of Producing Same",Serial No. 08/774,119 (filed December 23, 1996); "Novel Materials for Multicolor LED's", Attorney Docket No. 10020/24 (filed May 2, 1997); "Electron Transporting and Light Emitting Layers Based on Organic Free Radicals", Serial No. 08/774,120 (filed December 23, 1996); "Multicolor Display Devices", Serial No. 08/772,333 (filed December 23, 1996); "Red-Emitting Organic Light Emitting Devices (LED's)", Serial No. 08/774,087 (filed December 23, 1996); "Driving Circuit For Stacked Organic Light Emitting Devices", Serial No. 08/792,050 (filed February 3, 1997); "High Efficiency Organic Light Emitting Device Structures", Serial No. 08/772,332 (filed December 23, 1996); "Vacuum Deposited, Non-Polymeric Flexible Organic Light Emitting Devices", Serial No. 08/789,319 (filed January 23, 1997); "Displays Having Mesa Pixel Configuration", Serial No. 08/794,595

(filed February 3, 1997); "Stacked Organic Light Emitting Devices", Serial No. 08/792,046 (filed February 3, 1997); "High Contrast Transparent Organic Light Emitting Device Display", Serial No. 08/821,380 (filed March 20, 1997); "Organic Light Emitting Devices Containing A Metal Complex of 5-Hydroxy-Quinoxaline as A Host Material", Serial No. 08/838,099 (filed April 14, 1997); "Light Emitting Devices Having High Brightness", Serial No. 08/844,353 (filed April 18, 1997); "Organic Semiconductor Laser", Attorney Docket No. 10020/23 (filed May 19, 1997); "Saturated Full Color Stacked Organic Light Emitting Devices", Attorney Docket No. 10020/22 (filed May 20, 1997); "An Organic Light Emitting Device Containing a Hole Injection Enhancement Layer", Attorney Docket No. 10020/13 (filed May 29, 1997); and "Patterning of Thin Films for the Fabrication of Organic Multi-Color Displays", Attorney Docket No. 10020/29 (filed concurrently herewith), each co-pending application being incorporated herein by reference in its entirety. The subject invention may also be used in conjunction with the subject matter of each of co-pending U.S. patent application Serial Nos. 08/354,674, 08/613,207, 08/632,322 and 08/693,359 and provisional patent application Serial Nos. 60/010,013, 60/024,001 and 60/025,501, each of which is also incorporated herein by reference in its entirety.

The present invention is further described in the following non-limiting examples.

Example 1

OLEDs having ITO layer anodes were fabricated according to the following method.

ITO coated glass substrates were purchased from Donnelly Applied Films Co. The 1.1mm thick polished glass was coated with a 200Å SiO_2 barrier layer and a 1400Å ITO film. ITO was sputtered from an In_2O_3-SnO_2 (90wt%-10wt%) oxide target in an Ar/O_2 ambient at an elevated temperature using a planar dc magnetron sputtering system. The ITO was annealed *in situ* during the deposition and no postdeposition annealing was performed.

Prior to their use, the ITO-coated glass substrates were cleaned by swabbing and sonification with detergent/DI water, rinsing in DI water, degreasing by flushing the ITO surface with convection flow in warm TCA, and finally rising in acetone and methanol. The substrates were then used as cleaned or treated by using a plasma before deposition of the organic layer. For the plasma treatment, the samples were exposed to plasmas of different gases in a parallel-plate type plasma reactor configured in the reactive ion etching mode. In this system, a rf power of 25W corresponds to a power density of about 50 mW/cm^2.

The surface roughness of the plasma treated ITO layers, as measured by atomic force microscopy, was found to be 2.2nm, 1.6nm and 1.7nm for the as-grown, oxygen plasma, and hydrogen plasma treated ITO samples, respectively.

The organic materials deposited onto the ITO-coated glass substrates were single-layer doped polymer devices in

which the hole-transport matrix polymer poly (N-vinylcarbazole) ("PVK") contained dispersed electron transport molecules, such as 2-(4-biphenyl)-5(4-tert-butyl-phenyl)-1,3,4-oxadiazole ("PBD") or tris (8-hydroxy quinolate) aluminum ("Alq"), and fluorescent dyes as efficient emission centers. PVK:PBD:coumarin 6 ("C6") (100:40:0.3 by weight) was used for green devices, and PVK:Alq:nile red (100:40:0.2 by weight) was used for orange-red devices. These layers were deposited by spin-coating onto the ITO-coated glass substrates. The organic film thickness was about 1050Å.

After the polymer layers were deposited, top metal cathode contacts consisting of 1200Å Mg:Ag alloy and 800Å Ag were deposited through a shadow mask with an array of 2mm x 2mm holes. All spin-coating, device processing, including direct loading into the evaporator for metallization, and device characteristics were carried out under a dry nitrogen atmosphere in a glove box.

Fig. 2 shows I-V characteristics for OLEDs having ITO layers which were treated with different plasmas. Fig. 3 shows the corresponding brightness-current and brightness-voltage characteristics, illustrating the effect of plasma treatments on OLED efficiency. All forward I-V curves have two regimes, a low current regime with a weaker voltage dependence and a high current regime with a steeper current rise with voltage. In all cases, the forward bias low current regime, referred to as "leakage," is symmetrical to its reverse bias counterpart. Light emission is observed

only in the high current regime, referred to as the "bipolar" regime.

As can be seen from Fig. 2, the various plasma treatments considerably affect the turn-on voltage of the bipolar current, the leakage current, and the quantum efficiency. Devices made on cleaned as-grown ITO had a turn-on voltage of about 12V and an external quantum efficiency at 2.5 mA/cm^2 of 0.28% photon/electron. The Ar plasma treatment reduced the turn-on voltage to 11V and increased efficiency to 0.35%. The oxygen plasma treatment dramatically reduced the turn-on voltage to 3V and increased efficiency to 1%. On the other hand, the hydrogen plasma treatment increased the turn-on voltage to 17V and reduced efficiency to 0.007%.

A further consequence of improved OLEDs which include oxygen-plasma treated ITO is an enhancement in reliability and maximum allowed current before catastrophic breakdown. As shown in Fig. 4, the lifetime of an OLED made with oxygen-plasma treated ITO was found to be at least two orders of magnitude longer than that of an OLED which included a cleaned as-grown ITO.

Example 2

OLEDs were prepared as described in Example 1. Composition profiles of the ITO surfaces were obtained via Auger electron spectroscopy depth profiling. As shown in Fig. 5, the as-grown ITO was Sn-rich and In-deficient near the surface as compared to the bulk. The Sn:In atomic

ratio near the surface was about 1:3, while it was about 1:10 in the bulk. The oxygen plasma treatment lowered the ITO surface Sn:In ratio to 1:6 and increased the surface oxygen concentration. The hydrogen plasma also reduced the Sn surface concentration, but substantially depleted the surface oxygen concentration. This is evidence for an electrochemical reduction-oxidation mechanism near the ITO surface in the reducing hydrogen plasma and the oxidizing oxygen plasma, respectively.

The improvement in device performance resulting from the oxygen plasma treatment, as described in Example 1, suggests that the surface chemical composition might play a role in increasing the hole injection ability at the ITO/organic layer interface. ITO is a heavily doped and degenerate *n*-type indium oxide with both Sn dopants and oxygen vacancies contributing to its conduction. The enhancement of hole injection may therefore be due to an increase in the work function of the ITO as the surface Sn:In ratio is decreased and the oxygen concentration is increased. Ultra-violet photoemission spectroscopy measurements on the oxygen-treated ITO surfaces showed an increase in the work function of about 100-300 meV over the cleaned as-grown ITO surfaces. Ultra-violet photoemission spectroscopy on the hydrogen-treated ITO surfaces showed a decrease in the work function of about 100 meV over the cleaned as-grown ITO surfaces. Furthermore, the effects of the plasma treatments appear to be reversible. That is, an oxygen treatment following a hydrogen treatment produced

results similar to those in which only an oxygen treatment was performed.

The present invention provides a reliable and effective method for modifying the surface properties such as work function of semiconducting or conducting layers by plasma treatment. When applied to OLEDs, this method results in significant enhancements in device performance which have not been previously known by the modification of conductive layers alone.

Those with skill in the art may recognize various modifications to the embodiments of the invention described and illustrated herein. Such modifications are meant to be covered by the spirit and the scope of the appended claims.

What is claimed is:

1. An electrical device comprising a semiconducting or conducting layer having a work function modified by plasma treatment.

2. The electrical device of claim 1 wherein said work function is increased.

3. The electrical device of claim 1 wherein said work function is decreased.

4. The electrical device of claim 1 wherein said plasma treatment is with an oxygen-containing specie.

5. The electrical device of claim 1 wherein said plasma treatment is with a hydrogen-containing specie.

6. The electrical device of claim 1 wherein said layer is a substantially transparent conductor.

7. The electrical device of claim 6 wherein said substantially transparent conductor is indium-tin oxide.

8. The electrical device of claim 7 wherein said plasma treatment is an oxygen plasma treatment.

9. The electrical device of claim 7 wherein said indium-tin oxide layer has an increased oxygen concentration at or near its surface.

10. The electrical device of claim 1 wherein said layer is platinum.

11. An organic light emitting device comprising:

a plasma treated contact layer;

an organic layer over said plasma treated contact layer; and

a second contact layer over said organic layer.

12. The organic light emitting device of claim 11 wherein said plasma treated contact layer has a work function that is increased relative to said plasma treated contact layer without plasma treatment.

13. The organic light emitting device of claim 11 wherein said plasma treated contact layer has a work function that is decreased relative to said plasma treated contact layer without plasma treatment.

14. The organic light emitting device of claim 11 wherein said plasma treated contact layer is the product of a plasma treatment with an oxygen-containing specie.

15. The organic light emitting device of claim 11 wherein

said plasma treated contact layer is the product of a plasma treatment with a hydrogen-containing specie.

16. The organic light emitting device of claim 11 wherein said plasma treated contact layer is a substantially transparent conductor.

17. The organic light emitting device of claim 16 wherein said substantially transparent conductor is indium-tin oxide.

18. The organic light emitting device of claim 17 wherein said plasma treated contact layer is the product of a plasma treatment with an oxygen-containing specie.

19. The organic light emitting device of claim 17 wherein said indium-tin oxide layer has an increased oxygen concentration at or near its surface.

20. The organic light emitting device of claim 11 wherein said layer is platinum.

21. A method of modifying the work function of a conductor or semiconductor surface comprising:

selecting plasma treatment appropriate to modify said work function; and

subjecting said conductor or semiconductor to said plasma treatment.

22. The method of claim 21 wherein said work function is increased by said plasma treatment.

23. The method of claim 21 wherein said work function is decreased by said plasma treatment.

24. The method of claim 21 wherein said plasma treatment is with an oxygen-containing specie.

25. The method of claim 21 wherein said plasma treatment is with a hydrogen-containing specie.

26. The method of claim 21 wherein said conductor is a substantially transparent conductor.

27. The method of claim 26 wherein said substantially transparent conductor is indium-tin oxide.

28. The method of claim 27 wherein said plasma treatment is with an oxygen-containing specie.

29. The method of claim 27 wherein said indium-tin oxide layer has an increased oxygen concentration at or near its surface.

30. The method of claim 21 wherein said conductor is platinum.

31. A method of making an organic light emitting device comprising:

providing a first contact layer;

treating said first contact layer with a plasma;

placing an organic layer over said contact layer; and

placing a second contact layer over said organic layer.

32. The method of claim 31 wherein said step of plasma treatment provides a first contact layer having a work function that is increased relative to said first contact layer without plasma treatment.

33. The method of claim 31 wherein said step of plasma treatment provides a first contact layer having a work function that is decreased relative to said first contact layer without plasma treatment.

34. The method of claim 31 wherein said plasma treatment is with an oxygen-containing specie.

35. The method of claim 31 wherein said plasma treatment is with a hydrogen-containing specie.

36. The method of claim 31 wherein said first contact layer is a substantially transparent conductor.

37. The method of claim 36 wherein said substantially transparent conductor is indium-tin oxide.

38. The method of claim 37 wherein said plasma treatment is with an oxygen-containing specie.

39. The method of claim 37 wherein said indium-tin oxide layer has an increased oxygen concentration at or near its surface.

40. The method of claim 31 wherein said first contact layer is platinum.

41. The electrical device of claim 4, wherein said work function is increased by about 100 to about 300 meV.

42. The of electrical device claim 1, wherein said plasma treatment is conducted at a power density ranging from about 25 to about 200 mW/cm^2.

43. The organic light emitting device of claim 14, wherein said work function is increased by about 100 to about 300 meV.

44. The organic light emitting device of claim 11, wherein said plasma treated contact layer is subjected to a plasma treatment conducted at a power density ranging from about 25 to about 200 mW/cm^2.

45. The method of claim 24, wherein said work function is increased by about 100 to about 300 meV.

46. The method of claim 21, wherein said plasma treatment is conducted at a power density ranging from about 25 to about 200 mW/cm^2.

47. The method of claim 34, wherein said work function is increased by about 100 to about 300 meV.

48. The method of claim 31, wherein said step of plasma treatment is conducted at a power density ranging from about 25 to about 200 mW/cm^2.

49. An article incorporating the electronic device of claim 1, said article selected from the group consisting of a computer, a television, a billboard, a sign, a vehicle, a printer, a telecommunications device, a telephone, and a copier.

50. An article incorporating the organic light emitting device of claim 11, said article selected from the group consisting of a computer, a television, a billboard, a sign, a vehicle, a printer, a telecommunications device, a telephone, and a copier.

51. The method of claim 5, wherein said work function is decreased by about 100 meV.

52. The method of claim 15, wherein said work function is decreased by about 100 meV.

53. The method of claim 25, wherein said work function is decreased by about 100 meV.

54. The method of claim 35, wherein said work function is decreased by about 100 meV.

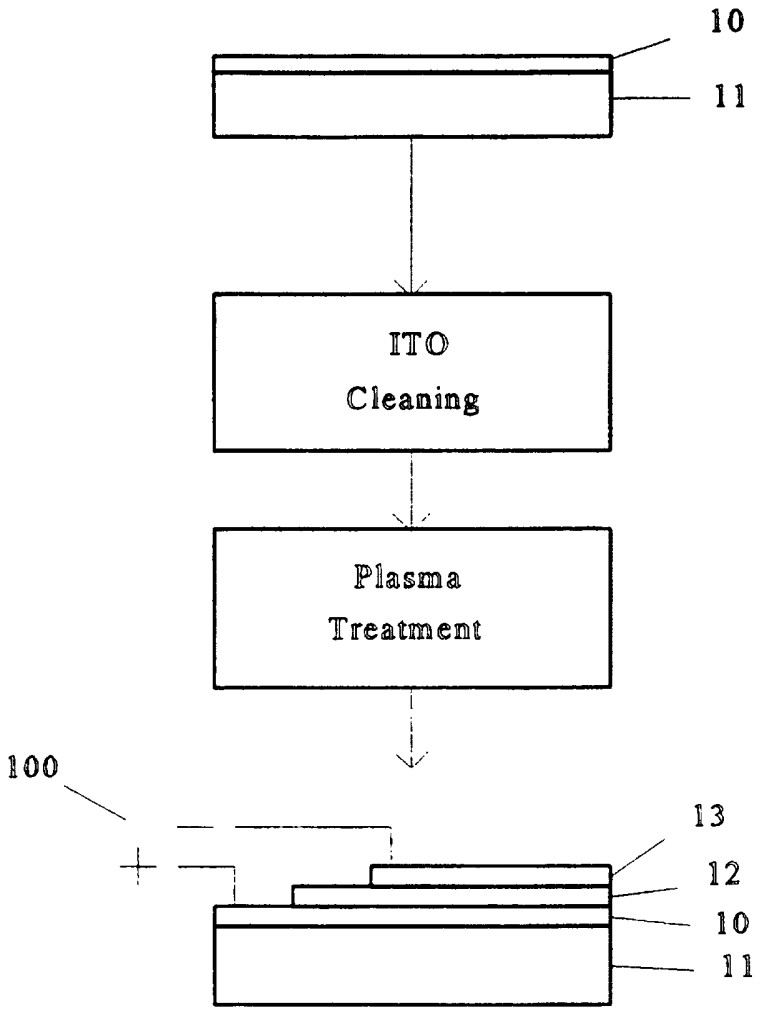


Fig. 1

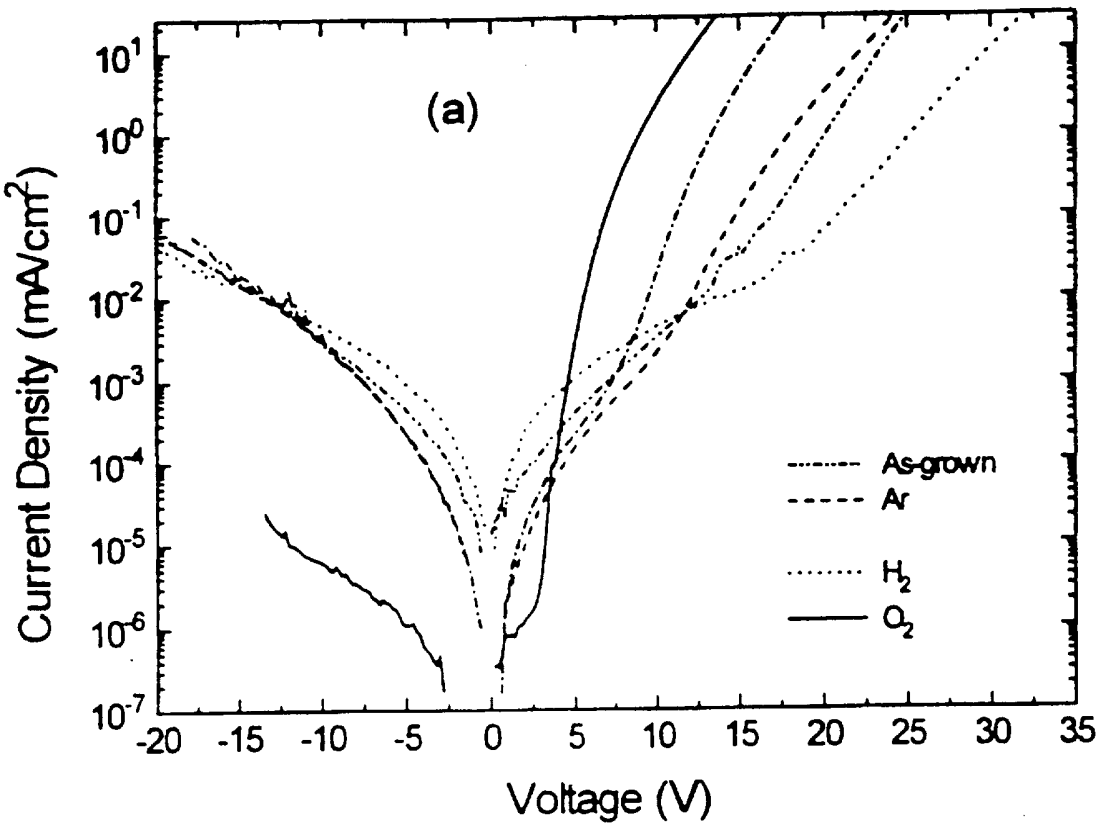

(a)
Current Density (mA/cm²)
Voltage (V)
As-grown
Ar
H2
O2
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
-20
-15
-10
-5
0
5
10
15
20
25
30
35

Fig. 2

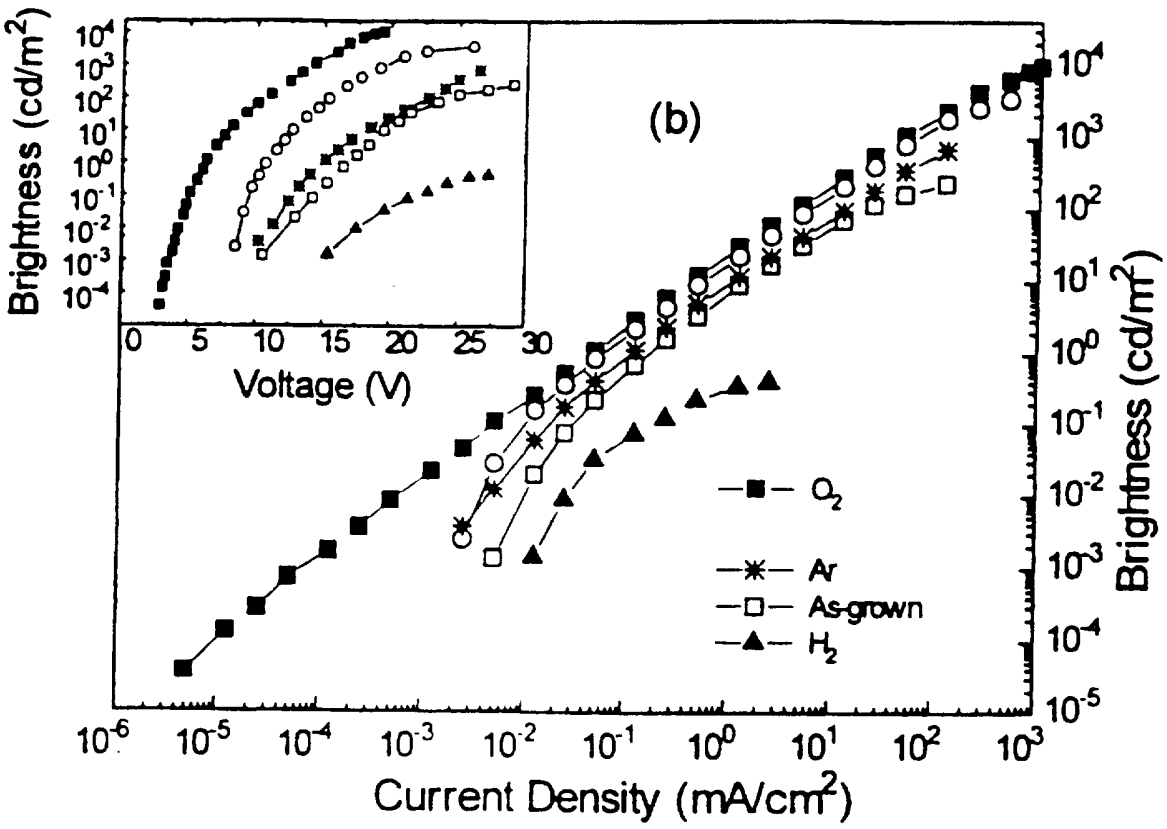

Brightness (cd/m²)
Voltage (V)
(b)
O₂
Ar
As-grown
H₂
Current Density (mA/cm²)
Brightness (cd/m²)

Fig. 3

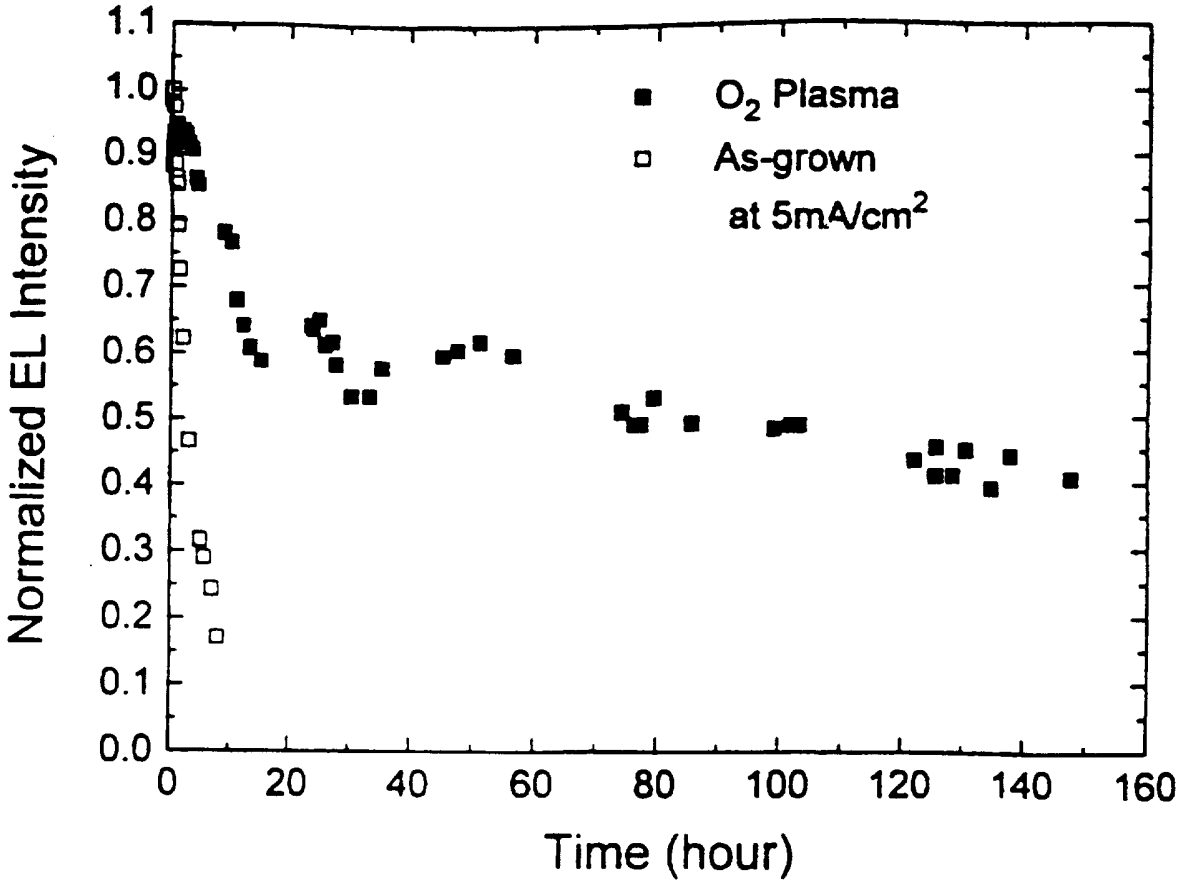

Normalized EL Intensity
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
20
40
60
80
100
120
140
160
Time (hour)
O2 Plasma
As-grown
at 5mA/cm2

Fig. 4

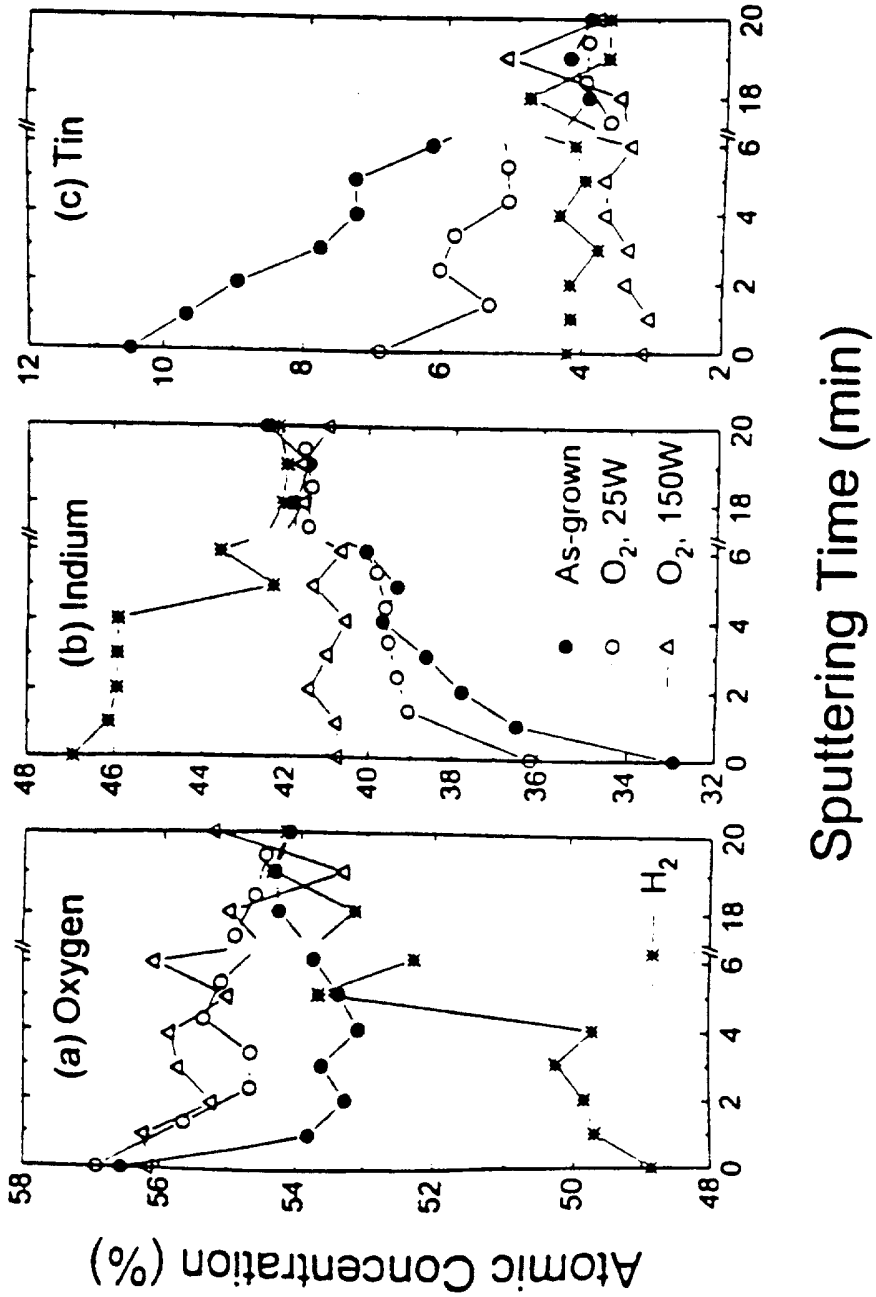

(a) Oxygen
(b) Indium
(c) Tin
As-grown
O_2, 25W
O_2, 150W
H_2
Atomic Concentration (%)
Sputtering Time (min)

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/10252

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :H01J 01/62, 63/04
US CL :313/504, 506, 509
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)

U.S. : 313/504, 505, 506, 507, 508, 509, 510, 511, 512; 437/4, 40, 41, 100, 101, 108, 109; 136/258, 163

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,281,546 A (POSSIN et al.) 25 January 1994, col 2, line 44-col 3, line 6	1-10, 21-30
Y	US 5,419,783 A (NOGUCHI et al.) 30 May 1995, col 2, line 45-col 6, line 23	1-10, 21-30
A	US 4,431,683 A (SASAKI et al.) 14 February 1984, see abstract and entire document	1-10, 21-30
A	US 4,859,617 A (NOMOTO et al.) 22 August 1989, see abstract and entire document	1-10, 21-30
A	US 5,273,920 A (KWASNICK et al.) 28 December 1993, see abstract and entire document	1-10, 21-30

☐ Further documents are listed in the continuation of Box C. ☐ 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

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"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
29 SEPTEMBER 1997

Date of mailing of the international search report
31 OCT 1997

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