# ORGANIC LIGHT EMITTING DIODE (OLED)

## Technical Field

The present invention relates to Organic Light Emitting Diodes (OLEDs) and, in particular, to an OLED which is adapted to inhibit the formation and growth of non-emissive areas known as "dark spots".

The invention is particularly suitable for OLEDs used in flat panel displays, and will be described hereinafter with reference to this application. However, it will be appreciated that the invention is not limited to this particular field of use.

## Background Art

A typical OLED consists of two electrodes with one or more polymer layers disposed between the electrodes. As shown in Figure 1, these devices commonly include the following layers, arranged in the following order:

(i) a substrate 2 often made from plastic or glass;

(ii) an anode 3 disposed on the substrate and commonly made from a transparent conductive material, which may be an organic material or an inorganic oxide such as Indium Tin Oxide (ITO);

(iii) a hole transport layer 5 disposed on the anode;

(iv) an electroluminescence (EL) layer 6 disposed on the hole transport layer; and

(v) a cathode 8 disposed on the EL layer, the cathode being made from a first layer 9 of Calcium or Magnesium and a second layer 10 of Silver or Aluminium.

The anode 3 is biased positively with respect to the cathode. In use, the electrons and holes are injected into the EL layer 6, where they migrate in the electric field until they recombine to produce a photon. The total organic layer thickness is usually around 50 -150nm, and the bias is about 2-20V. The

anode 3 is typically transparent and the work functions of the cathode materials are chosen to match the energy levels of the polymer HOMO for the anode and LUMO for the cathode. Hence, the materials most widely used for OLED cathodes are calcium, magnesium and aluminium and lithium alloys.

In recent times considerable improvements have been made in the materials and device architecture of OLEDs, which has resulted in devices with luminance values exceeding 100 000 cd/$m^2$ and external quantum efficiencies in excess of 4%. These new generation devices have been found to be useful in large area illuminators and flat panel displays.

Although remarkably stable electroluminescent (EL) devices have been demonstrated operating in inert environments, the lifetimes of such devices have been limited by the formation and growth of non-emissive areas known as "dark spots".

A number of factors contribute to the formation and growth of dark spots. One such factor is cathode defects such as pinholes. These pinholes are often formed during resistive-heating evaporation. The oxidised cathode reduces the electron injection efficiency of the device and a higher driving bias is therefore needed. This significantly increases the chance of local shorting. Although sputtering is one of the methods commonly used in the semiconductor industry for the deposition of cathodes, this technique has, until now, not been suitable for OLEDs. This is because OLEDs are extremely sensitive and are damaged by the radiation, charging, heating and ion bombardment involved in the sputtering process. Although sputtering produces cathodes with few or no pinholes, it has not been used on OLEDs because of the damage caused by the technique.

Another factor in dark spot formation and growth is the evolution of oxygen and moisture in the OLED materials and its permeation through the device during operation. The diffusion of moisture and oxygen through the layers of the OLED is a significant cause of the growth of dark spots on the cathode. Magnesium and Calcium are often used as cathode materials in OLED devices because of their low work function. However, Calcium and Magnesium are very sensitive to oxygen and water vapour. The dark spot and

defect growths are due to the oxygen and moisture produced within the OLED materials which then permeates through the various layers and substrates and reacts with the electrodes.

An additional factor in dark spot growth is the migration of the electrode materials during electrical stress. This metal migration causes peaks of electrical shorts and strong electrical fields in various parts of the OLED.

A further factor which contributes to the formation of dark spots is local heating. This heating is often caused by high currents. It expedites material failure, increases the possibility of inter-diffusion of the organic layers and leads to dark spot growth.

A further problem faced by prior art OLEDs is that they do not have very good polymer stability. One of the more significant degradation mechanisms in conjugated polymers has been found to be photo-oxidation. Such photo-oxidation induces the chain scission of the vinyl double bond on the polymer backbone thereby reducing the conjugation length by the formation of carbonyl groups, resulting in lower photoluminescence efficiencies.

In recent times it has been found that the performance of OLEDs is enhanced not only by the proper selection of organic materials but also by the efficient carrier injection of electrodes and the controlled electron-hole recombination within a well-defined zone. Research that has focussed on increasing the charge injection and carrier confinement have led to significant improvements in device performance.

Figure 2 shows an advanced form of such prior art OLEDs which consists of a multi-layer, high efficiency, structure. In addition to the layers labelled with common numerals to those of Figure 1, the advanced prior art OLED also includes an electron injecting layer 15 and a dielectric layer 14.

The electron injecting layer 15 is disposed between the EL layer 6 and the cathode 8 and serves to efficiently control hole and electron injection.

The dielectric layer 14 is disposed between the anode 3 and the hole transport layer 5. If the thickness of the dielectric layer is within tunnelling thickness, the effective barrier to electron injection is lowered and the injection

of holes to the emitting layer is reduced. As a result, this lowering of the effective barrier to carrier injection leads to more balanced injection of electrons and holes and the quantum efficiency of the OLED increases.

This more advanced prior art OLED device therefore exhibits superior luminescence and efficiency. However, because these advanced OLEDs also exhibit dark spot formation and growth they therefore have a relatively short lifespan.

There is therefore a need for an improved OLED which is adapted to inhibit the formation and growth of dark spots.

Disclosure of Invention

In a first aspect, the present invention provides an organic light emitting diode (OLED) comprising:

(a) an anode disposed on a substrate;

(b) a cathode;

(c) an electroluminescent (EL) layer disposed between said anode and said cathode;

(d) a hole transport layer disposed between said anode and said EL layer; and

(e) at least one oxygen/moisture barrier disposed between one or more of:

(i) said anode and said hole transport layer;

(ii) said hole transport layer and said EL layer; and

(iii) said EL layer and said cathode;

said barrier being adapted to at least one of:

(A) resist permeation by oxygen;

(B) resist permeation by moisture; and

(C) inhibit metal migration.

Preferably, the OLED further comprises an encapsulation layer at least partially encapsulating the OLED, said encapsulation layer being adapted to resist permeation by oxygen and/or moisture.

In one form, the OLED further comprises a dielectric layer disposed between said anode and said hole transport layer and wherein said at least one barrier is disposed between one or more of:

(i) said anode and said dielectric layer; and

(ii) said dielectric layer and said hole transport layer.

In another form, the OLED further comprises an electron injecting layer disposed between said EL layer and said cathode and wherein said at least one barrier is disposed between one or more of:

(i) said EL layer and said electron injecting layer; and

(ii) said electron injecting layer and said cathode.

Preferably, the barrier is an organic barrier which is at least partially made from a polymer and has a thickness in the range of 1 to 20 nm. More preferably, the barrier is deposited by any conventional coating technique including:

(i) spin coating;

(ii) vacuum deposition; or

(iii) chemical vapour deposition.

Preferably, the encapsulation layer is an organic encapsulation layer which is at least partially made from a polymer and has a thickness in the range of 1nm to 30μm. More preferably, the encapsulation layer is deposited by any conventional coating technique including:

(i) spin coating;

(ii) vacuum deposition; or

(iii) chemical vapour deposition.

Preferably, the polymer is selected from:

(i) polyimides;

(ii) teflon; and

(iii) parylene.

In a second aspect, the present invention provides an organic light emitting diode (OLED) adapted to inhibit the growth of non-emissive areas comprising:

(a) an anode disposed on a substrate;

(b) a cathode;

(c) an electroluminescent (EL) layer disposed between said anode and said cathode;

(d) a hole transport layer disposed between said anode and said EL layer; and

(e) at least one oxygen/moisture barrier disposed between one or more of:

(i) said anode and said hole transport layer;

(ii) said hole transport layer and said EL layer; and

(iii) said EL layer and said cathode;

said barrier being adapted to at least one of:

(A) resist permeation by oxygen;

(B) resist permeation by moisture; and

(C) inhibit metal migration.

Preferably, the OLED further comprises an encapsulation layer at least partially encapsulating the OLED, said encapsulation layer being adapted to resist permeation by oxygen and/or moisture.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be

understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

In order that the present invention may be more clearly understood, preferred forms will be described with reference to the following drawings and examples.

Brief Description of the Drawings

Figure 1 is a schematic cross-sectional view of a simple prior art OLED;

Figure 2 is a schematic cross-sectional view of an advanced prior art OLED;

Figure 3 is a schematic cross-sectional view of a first preferred embodiment of the present invention;

Figure 4 is a simplified schematic cross-sectional view of the first preferred embodiment of the present invention clearly showing the encapsulation layer;

Figure 5 is a schematic cross-sectional view of a second preferred embodiment of the OLED of the present invention; and

Figure 6 is a schematic cross-sectional view of a third preferred embodiment of the OLED of the present invention.

The Preferred Embodiments

Referring to the drawings, Figure 3 shows a schematic cross-sectional view of a first preferred embodiment of the OLED of the present invention. As seen in that Figure, the OLED 1 includes a number of layers disposed on a substrate 2. In this embodiment, the layers are arranged in the following order: an anode 3, a first oxygen/moisture barrier 4, a hole transport layer 5, and electrolumincescent (EL) layer 6, a second oxygen/moisture barrier 7 and a cathode 8. In this embodiment the cathode 8 includes a calcium cathode layer 9 and a silver/aluminium cathode layer 10. All of these layers are at least partially encapsulated by an encapsulation layer 11.

The first oxygen/moisture barrier 4 is adapted to resist permeation by oxygen and moisture and is also designed to inhibit metal migration. In this preferred embodiment the barrier 4 is an organic barrier made from a polymer selected from polyimides, teflon and parylene. It is between 1 and 20 nm thick and is deposited on the anode using any conventional coating process such as spin coating, vacuum deposition or chemical vapour deposition (CVD).

Although, in this preferred embodiment, the first oxygen/moisture barrier is disposed between the anode 3 and the hole transport layer 5, effective results have also been achieved when it is disposed between the hole transport layer 5 and the EL layer 6.

This first oxygen/moisture barrier 4 has a moisture barrier property in the range of 0.1g/m$^2$/day to 50g/m$^2$/day at 39°@ 95% RH. It is transparent in the visible wavelength range and is resistant to metal ion migration under electrical fields.

Because this barrier is adapted to resist permeation by oxygen and/or moisture it is able to prevent oxygen diffusion from the anode 3 to the hole transport layer 5 and the EL layer 6. It also acts as a thermal barrier film and is able to effectively reduce the heat transfer from the anode to the EL layer during operation of the OLED 1. This barrier 4 is preferably free of pinholes and other defects so that it provides a smooth morphology to allow the effective deposition of the hole transport layer 5.

This barrier 4 is also able to reduce the strong electric field produced at anode spikes and serves to increase the carrier injection efficiency by reducing the barrier height through the potential drop across the layers.

The second oxygen/moisture barrier 7 has substantially the same composition and properties as the first oxygen/moisture barrier 4, but it is disposed between the EL layer 6 and the cathode 8.

In its preferred form, this second barrier 7 is also adapted to resist permeation by oxygen and/or moisture and is therefore able to prevent oxygen and moisture from diffusing to the EL layer 6 and reacting with the cathode.

This second barrier 7 should also be free of pinholes and other defects so that it can provide a smooth morphology for deposition of the cathode 8.

As discussed earlier, the preferred method of depositing a cathode on an OLED is by the process known as "sputtering". However, this technique tends to damage the EL layer thereby reducing the EL efficiency of the device. In this preferred embodiment, since the second oxygen/moisture barrier 7 is deposited on the EL layer 6 it protects the EL layer, allowing the cathode 8 to be deposited by sputtering without damaging the EL layer. In this way, the second barrier 7 is able to protect the EL layer 6 from ion bombardment, radiation and metal migration. By depositing the cathode using sputtering techniques the cathode can be produced with few or no pinholes.

Turning to Figure 4 there is shown a simplified schematic cross-sectional view of the preferred embodiment of the OLED of the present invention clearly showing the encapsulation layer 11. In that Figure, the OLED 1 is shown disposed on a substrate 2 and encapsulated by the encapsulation layer 11. A pair of epoxy seals 12 extend between the substrate 2 and a cover substrate 13 to enclose the OLED 1. The encapsulation layer 11 shown in both Figure 3 and Figure 4 is adapted to resist permeation by oxygen and/or moisture. In this preferred embodiment, it is an organic encapsulation layer 11 made at least partially from a polymer selected from polyimides, teflon and parylene. Of these polymers, the parylene series has produced the best results because it can be deposited at room temperature and it does not alter the electronic

parameters of the OLED. It also has excellent step coverage and therefore provides conformal coverage of the OLED 1. The encapsulation layer 11 is preferably deposited by any conventional coating process such as spin coating, vacuum deposition or CVD and is deposited to a thickness ranging between 1nm and 30 μm.

Because of the excellent oxygen and moisture barrier properties of the encapsulation layer, it is able to exhibit a moisture absorbency of less than 0.1% by weight. The layer 11 provides an excellent barrier to moisture permeation and therefore protects the OLED 1 once it has been encapsulated. This encapsulation layer 11 allows the OLED 1 to be hermetically sealed thereby reducing the chance that the OLED will be oxidised as a result of the permeation of moisture and oxygen.

In this, and the following preferred embodiments, the substrate 2 is also adapted to resist permeation by oxygen and/or moisture and is at least partially made from a rigid or flexible material such as plastic or glass.

In addition, the cathode (and the anode in a multi-layer OLED architecture) is at least partially made from a cathode material which includes organic metals, inorganic metals, organic metal oxides and inorganic metal oxides. The cathode (and the anode in a multi-layer OLED architecture) is preferably deposited on the OLED by the technique known as sputtering so that it has few or no pinholes.

Turning now to Figure 5 there is shown a second preferred embodiment of the OLED of the present invention. This embodiment shows the first and second oxygen/moisture barriers 4, 7 and the encapsulation layer 11 used in a more advanced OLED.

The numbering used in this figure is the same as that used to describe the first preferred embodiment shown in Figure 3. This second preferred embodiment has two additional layers, namely a dielectric layer 14 disposed between the anode 3 and the hole transport layer 5, and an electron injecting layer 15 disposed between the EL layer 6 and the cathode 8. In this preferred embodiment, the first oxygen/moisture barrier 4 is disposed between the anode

3 and the dielectric layer 14. The second oxygen/moisture barrier 7 is disposed between the EL layer 6 and the electron injecting layer 15.

The third preferred embodiment shown in Figure 6 is similar to the second preferred embodiment, except that the first oxygen/moisture barrier 4 is disposed between the dielectric layer 14 and the hole transport layer 5, and the second oxygen/moisture barrier 7 is disposed between the electron injecting layer 15 and the cathode 8. Alternative embodiments with combinations of these and other arrangements of the first and second oxygen/moisture barriers 4, 7 are also envisaged. Further embodiments including more than 2 oxygen/moisture barriers are also envisaged.

In these preferred embodiments, the thickness of the dielectric layer is within tunnelling range. Furthermore, the dielectric layer is adapted to lower the effective barrier height for electron injection and is therefore able to enhance the luminescence quantum efficiency of the OLED.

It will be appreciated from the foregoing discussion that by interposing a number of oxygen/moisture barriers within the OLED and applying an encapsulation layer around the OLED, the formation and growth of dark spots is significantly reduced. The result is an OLED with significantly improved performance and lifespan which may be used in any number of applications, including the commercial production of flat panel displays.

The inventors have found that, by using the barriers and encapsulation layers described above, the number of dark spots formed in an OLED have been reduced by a factor of 100.

The present invention therefore addresses the causes of dark spot formation and growth. The problem of cathode defects such as pinholes is addressed by the second oxygen/moisture barrier acting as a protective layer over the EL layer, allowing the calcium electrode to be deposited by sputtering without damaging the EL layer.

The problem of oxygen and moisture diffusion through the layers of the OLED is addressed by the first and second oxygen/moisture barriers. They act to reduce the diffusion of oxygen and moisture from the underlying layers to cathode, thereby reducing the gaseous evolution caused by moisture reacting with the Ca electrode.

The barriers also address the problem of metal migration. They reduce the migration of metal, thereby reducing the likelihood that sharp spikes will form, inhibiting the deterioration of the polymer and limiting the occurrence of short circuits.

The problem of excessive heat build up is addressed because the barriers act as thermal barrier films to effectively reduce the heat transfer from the anode to the EL layer during the operation of the OLED.

The barriers also provide a smoother surface for the deposition of subsequent layers, thereby enhancing the quality of the OLED.

Furthermore, the encapsulation layer serves to protect the device from intrinsic and external ingress of moisture and oxygen.

An additional advantage of the barriers is that they increase the quantum efficiency of the device by more accurately matching the energy work functions of the metals in the device with the LUMO or HOMO of the polymers in the device.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

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CLAIMS:

1. An organic light emitting diode (OLED) comprising:

(a) an anode disposed on a substrate;

(b) a cathode;

(c) an electroluminescent (EL) layer disposed between said anode and said cathode;

(d) a hole transport layer disposed between said anode and said EL layer; and

(e) at least one oxygen/moisture barrier disposed between one or more of:

(i) said anode and said hole transport layer;

(ii) said hole transport layer and said EL layer; and

(iii) said EL layer and said cathode;

said barrier being adapted to at least one of:

(A) resist permeation by oxygen;

(B) resist permeation by moisture; and

(C) inhibit metal migration.

2. An OLED according to claim 1 further comprising an encapsulation layer at least partially encapsulating the OLED, said encapsulation layer being adapted to resist permeation by oxygen and/or moisture.

3. An OLED according to claim 1 or claim 2 further comprising a dielectric layer disposed between said anode and said hole transport layer and wherein said at least one barrier is disposed between one or more of:

(i) said anode and said dielectric layer; and

(ii) said dielectric layer and said hole transport layer.

4. An OLED according to any one of the preceding claims further comprising an electron injecting layer disposed between said EL layer and said cathode and wherein said at least one barrier is disposed between one or more of:

(i) said EL layer and said electron injecting layer; and

(ii) said electron injecting layer and said cathode.

5. An OLED according to any one of the preceding claims wherein said barrier is an organic barrier.

6. An OLED according to claim 5 wherein said organic barrier is at least partially made from a polymer.

7. An OLED according to any one of the preceding claims wherein the thickness of said barrier lies in the range of 1 to 20 nm.

8. An OLED according to any one of the preceding claims wherein said barrier is deposited by any conventional coating technique including:

(i) spin coating;

(ii) vacuum deposition; or

(iii) chemical vapour deposition.

9. An OLED according to any one of claims 2 to 8 wherein said encapsulation layer is an organic encapsulation layer.

10. An OLED according to claim 9 wherein said organic encapsulation layer is at least partially made from a polymer.

11. An OLED according to any one of the preceding claims wherein the thickness of said encapsulation layer lies in the range of 1nm to 30μm.

12. An OLED according to any one of the preceding claims wherein said encapsulation layer is deposited by any conventional coating technique including:

(i) spin coating;

(ii) vacuum deposition; or

(iii) chemical vapour deposition.

13. An OLED according to any one of claims 6 to 12 wherein said polymer is selected from:

(i) polyimides;

(ii) teflon; and

(iii) parylene.

14. An OLED according to any one of the preceding claims wherein said substrate is adapted to resist permeation by oxygen and/or moisture and is at least partially made from a rigid or flexible material including plastic or glass.

15. An OLED according to any one of claims 3 to 14 wherein the thickness of said dielectric layer is within tunnelling range.

16. An OLED according to claim 15 wherein said dielectric layer is adapted to lower the effective barrier height for electron injection and thereby enhance the luminescence quantum efficiency of the OLED.

17. An OLED according to any one of the preceding claims wherein said cathode and/or said anode is at least partially made from one or more of the following cathode materials:

(i) organic metals;

(ii) inorganic metals;

(iii) organic metal oxides; and

(iv) inorganic metal oxides.

18. An OLED according to claim 17 wherein said cathode materials are at least partially made by sputtering.

19. An OLED according to claim 18 wherein said cathode materials have few or no pinholes.

20. An OLED according to claim 18 or claim 19 wherein at least one of said barriers is a protective barrier disposed between said EL layer and said cathode and being adapted to protect said EL layer from damage due to the effects of the sputtering process.

21. An OLED according to claim 20 wherein said protective barrier is adapted to protect said EL layer from damage due to one or both of:

(i) ion bombardment;

(ii) radiation; and

(iii) metal migration.

22. An organic light emitting diode (OLED) adapted to inhibit the growth of non-emissive areas comprising:

(a) an anode disposed on a substrate;

(b) a cathode;

(c) an electroluminescent (EL) layer disposed between said anode and said cathode;

(d) a hole transport layer disposed between said anode and said EL layer; and

(e) at least one oxygen/moisture barrier disposed between one or more of:

(i) said anode and said hole transport layer;

(ii) said hole transport layer and said EL layer; and

(iii) said EL layer and said cathode;

said barrier being adapted to at least one of:

(A) resist permeation by oxygen;

(B) resist permeation by moisture; and

(C) inhibit metal migration.

23. An OLED according to claim 22 further comprising an encapsulation layer at least partially encapsulating the OLED, said encapsulation layer being adapted to resist permeation by oxygen and/or moisture.