



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b>  <b>H01L 51/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/36665</b>  <b>(43) International Publication Date:</b> 22 June 2000 (22.06.00)		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <b>(21) International Application Number:</b> PCT/US99/29853   <b>(22) International Filing Date:</b> 15 December 1999 (15.12.99)   <b>(30) Priority Data:</b>  <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>09/212,779</div> <div>16 December 1998 (16.12.98)</div> <div>US</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>09/427,138</div> <div>25 October 1999 (25.10.99)</div> <div>US</div> </div>   <b>(71) Applicant:</b> BATTELLE MEMORIAL INSTITUTE [US/US];            Pacific Northwest Division, Intellectual Property Services,            P.O. Box 999, Richland, WA 99352 (US).   <b>(72) Inventors:</b> GRAFF, Gordon, L.; 3750 Westlake Drive, West            Richland, WA 99353 (US). GROSS, Mark, E.; 50 Deseret            Drive, Pasco, WA 99301 (US). AFFINITO, John, D.; 2718            Kyle Road, Kennewick, WA 99338 (US). SHI, Ming-Kun;            2500 George Washington Way, Richland, WA 99352 (US).            HALL, Michael, G.; 4125 Ironton Drive, West Richland,            WA 99353 (US). MAST, Eric, S.; 634 Chesnut Avenue,            Richland, WA 99352 (US).   <b>(74) Agent:</b> MAY, Stephen, R.; Battelle Memorial Institute, Pacific            Northwest Division, Intellectual Property Services, P.O. Box            999, MSIN: K1-53, Richland, WA 99352 (US).         </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <b>(81) Designated States:</b> JP, KR, European patent (AT, BE, CH, CY,            DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT,            SE).   <b>Published</b>  <i>With international search report.</i> </td> </tr> </table>			<b>(21) International Application Number:</b> PCT/US99/29853  <b>(22) International Filing Date:</b> 15 December 1999 (15.12.99)  <b>(30) Priority Data:</b> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>09/212,779</div> <div>16 December 1998 (16.12.98)</div> <div>US</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>09/427,138</div> <div>25 October 1999 (25.10.99)</div> <div>US</div> </div> <b>(71) Applicant:</b> BATTELLE MEMORIAL INSTITUTE [US/US]; Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).  <b>(72) Inventors:</b> GRAFF, Gordon, L.; 3750 Westlake Drive, West Richland, WA 99353 (US). GROSS, Mark, E.; 50 Deseret Drive, Pasco, WA 99301 (US). AFFINITO, John, D.; 2718 Kyle Road, Kennewick, WA 99338 (US). SHI, Ming-Kun; 2500 George Washington Way, Richland, WA 99352 (US). HALL, Michael, G.; 4125 Ironton Drive, West Richland, WA 99353 (US). MAST, Eric, S.; 634 Chesnut Avenue, Richland, WA 99352 (US).  <b>(74) Agent:</b> MAY, Stephen, R.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).	<b>(81) Designated States:</b> JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(21) International Application Number:</b> PCT/US99/29853  <b>(22) International Filing Date:</b> 15 December 1999 (15.12.99)  <b>(30) Priority Data:</b> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>09/212,779</div> <div>16 December 1998 (16.12.98)</div> <div>US</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div>09/427,138</div> <div>25 October 1999 (25.10.99)</div> <div>US</div> </div> <b>(71) Applicant:</b> BATTELLE MEMORIAL INSTITUTE [US/US]; Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US).  <b>(72) Inventors:</b> GRAFF, Gordon, L.; 3750 Westlake Drive, West Richland, WA 99353 (US). GROSS, Mark, E.; 50 Deseret Drive, Pasco, WA 99301 (US). AFFINITO, John, D.; 2718 Kyle Road, Kennewick, WA 99338 (US). SHI, Ming-Kun; 2500 George Washington Way, Richland, WA 99352 (US). HALL, Michael, G.; 4125 Ironton Drive, West Richland, WA 99353 (US). MAST, Eric, S.; 634 Chesnut Avenue, Richland, WA 99352 (US).  <b>(74) Agent:</b> MAY, Stephen, R.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).	<b>(81) Designated States:</b> JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>			
<b>(54) Title:</b> ENVIRONMENTAL BARRIER MATERIAL FOR ORGANIC LIGHT EMITTING DEVICE AND METHOD OF MAKING				
<b>(57) Abstract</b>  <p>An encapsulated organic light emitting device. The device includes a first barrier stack (110) comprising at least one first barrier layer (140) and at least one first polymer layer (150, 160). There is an organic light emitting layer stack (120) adjacent to the first barrier stack. A second barrier stack (130) is adjacent to the organic light emitting layer stack. The second barrier stack has at least one second barrier layer (170) and at least one second polymer layer (180, 190). A method of making the encapsulated organic light emitting device is also provided.</p>				

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## ENVIRONMENTAL BARRIER MATERIAL FOR ORGANIC LIGHT EMITTING DEVICE AND METHOD OF MAKING

5

### BACKGROUND OF THE INVENTION

The present invention relates to organic light emitting devices (OLEDs), and more particularly to OLEDs encapsulated in barrier stacks.

10 There is a need for versatile visual displays for electronic products of many different types. Light emitting diodes (LEDs) and liquid crystal displays (LCDs) have found many useful applications, but they are not adequate for all situations. OLEDs are a relatively new type of visual display which has shown great promise. An OLED basically includes an organic electroluminescent  
15 substance placed between two electrodes. When an electric potential is applied across the electrodes, the electroluminescent substance emits visible light. Typically, one of the electrodes is transparent, allowing the light to shine through. U.S. Patent Nos. 5,629,389 (Roitman et al.), 5,747,182 (Friend et al.), 5,844,363 (Gu et al.), 5,872,355 (Hueschen), 5,902,688 (Antoniadis et al.), and 5,948,552  
20 (Antoniadis et al.), which are incorporated herein by reference, disclose various OLED structures.

The use of OLEDs in flat panel displays and other information display formats is limited by the poor environmental stability of the devices. G.Gustafson, Y.Cao, G.M.Treacy, F.Klavetter, N.Colaneri, and A.J.Heeger,  
25 Nature, Vol. 35, 11 June 1992, pages 477-479. Humidity and oxygen significantly reduce the useful life of most OLEDs. As a result, these devices are typically fabricated on glass substrates with glass covers laminated on top of the OLED and with the edges sealed to exclude water and oxygen from the active layers. U.S. Patent No. 5,872,355 discloses the use of a polymer such as saran  
30 to seal the device. The water vapor permeation rates (WVTR) required to provide sufficient lifetime for OLEDs is calculated to be approximately  $10^{-6}$  g/m<sup>2</sup>/day. The best polymer films (such as saran) have WVTR values that are 5 orders of magnitude too high to be considered for OLED encapsulation.

Furthermore, saran cannot be deposited using flash evaporation, condensation, and in situ polymerization within a vacuum chamber.

Thus, there is a need for an improved lightweight, barrier construction which can be used to encapsulate the OLED and prevent the deterioration caused by permeation of oxygen and water vapor and for a method of making such an encapsulated OLED.

## SUMMARY OF THE INVENTION

These needs are met by the present invention, which is an encapsulated organic light emitting device (OLED). The device includes a first barrier stack comprising at least one first barrier layer and at least one first polymer layer. There is an organic light emitting layer stack adjacent to the first barrier stack. A second barrier stack is adjacent to the organic light emitting layer stack. The second barrier stack has at least one second barrier layer and at least one second polymer layer. The device optionally includes at least one first intermediate barrier stack located between the substrate and the first barrier stack, and/or at least one second intermediate barrier stack located between the organic light emitting layer stack and either the first or second barrier stacks. The first and second intermediate barrier stacks include at least one polymer layer and at least one barrier layer.

Preferably, either one or both of the first and second barrier layers of the first and second barrier stacks is substantially transparent. At least one of the first and second barrier layers preferably comprises a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof. The metal oxides are preferably selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof, the metal nitrides are preferably selected from aluminum nitride, silicon nitride, and combinations thereof, the metal carbide is preferably silicon carbide, and the metal oxynitride is preferably silicon oxynitride.

The encapsulated OLED can also include a substrate adjacent to the first barrier stack on a side opposite to the organic light emitting layer stack. The

substrate can be either a flexible substrate or a rigid substrate. It is preferably a flexible substrate material, which can be polymers, metals, paper, fabric, and combinations thereof. The rigid substrate is preferably glass, metal, or silicon. If a rigid substrate is used, it can be removed prior to use if desired.

5       The polymer layers of the first and second barrier stacks and the polymer layers in the first and second intermediate barrier stacks are preferably acrylate-containing polymers (as used herein, the term acrylate-containing polymer includes acrylate-containing polymers, methacrylate-containing polymers, and combinations thereof). The polymer layers in the first and/or the second barrier  
10       stacks can be the same or different.

      The organic light emitting layer stack preferably comprises a first electrode, an electroluminescent layer, and a second electrode. The electroluminescent layer preferably includes a hole transporting layer, and an electron transporting layer, as is known in the art and shown in the patents  
15       whose disclosures have been specifically incorporated herein.

      The invention also involves a method of making the encapsulated organic light emitting device. The method includes forming a first barrier stack comprising at least one first barrier layer and at least one first polymer layer, forming an organic light emitting layer stack, forming a second barrier stack  
20       comprising at least one second barrier layer and at least one second polymer layer, and combining the first barrier stack, the organic light emitting layer stack, and the second barrier stack to form the encapsulated organic light emitting device. Intermediate barrier stacks can optionally be formed. The layers are preferably formed by vacuum deposition.

25       The organic light emitting layer stack can be combined with the first barrier stack and/or the second barrier stack by laminating them together. Alternatively, they can be combined simultaneously with forming by depositing one layer on the other.

      In an alternative embodiment, the invention involves an encapsulated  
30       organic light emitting device having a substrate, an organic light emitting layer stack adjacent to the substrate, and a barrier stack comprising at least one barrier layer and at least one polymer layer, the barrier stack adjacent to the

organic light emitting layer stack. The invention also involves methods of making the encapsulated organic light emitting device. One method includes providing a substrate having an organic light emitting layer stack thereon, and laminating a barrier stack comprising at least one barrier layer and at least one polymer layer over the organic light emitting layer stack to encapsulate the organic light emitting barrier layer stack. The barrier stack is preferably laminated (edge sealed) using an adhesive, but other methods can be used including heat.

Another method involves vacuum depositing the barrier stack on a substrate having an organic light emitting layer stack thereon. Still another method involves providing a substrate with an organic light emitting layer stack thereon, vacuum depositing at least one barrier layer on the organic light emitting layer stack, and depositing at least one first polymer layer on the at least one barrier layer. At least one second polymer layer can be deposited on the organic light emitting layer stack before the barrier layer is deposited.

Accordingly, it is an object of the present invention to provide an encapsulated OLED, and to provide a method of making such a device.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-section of one embodiment of the encapsulated OLED of the present invention.

Fig. 2 is a cross-section of an alternate embodiment of the encapsulated OLED of the present invention.

Fig. 3 is a cross-section of an embodiment of an encapsulated OLED of the present invention.

## DESCRIPTION OF THE INVENTION

One embodiment of the present invention is an encapsulated OLED as shown in Fig. 1. The encapsulated OLED 100 includes substrate 105, a first barrier stack 110, an organic light emitting layer stack 120, and a second barrier stack 130. The first barrier stack 110 has a first barrier layer 140 and two

polymer layers 150, 160. The second encapsulation layer 130 includes a second barrier layer 170 and two polymer layers 180, 190.

Although the Figures show barrier stacks with a single polymer layer on both sides of a single barrier layer, the barrier stacks can have one or more polymer layers and one or more barrier layers. There could be one polymer layer and one barrier layer, there could be multiple polymer layers on one side of one or more barrier layers, or there could be one or more polymer layers on both sides of one or more barrier layers. The important feature is that the barrier stack have at least one polymer layer and at least one barrier layer.

The organic light emitting layer stack 120 includes a first electrode layer 200, an electroluminescent layer 210, and a second electrode 220. The electroluminescent layer 210 can include a hole transport layer 230, and an electron transport layer 235. The exact form and composition of the organic light emitting layer stack is not critical. The organic light emitting layer stack includes first and second electrode layers on opposite sides of one or more active layers. The electrode layers are connected to a power source. At least one of the electrodes is transparent. The electroluminescent layer may be multiple layers as shown, or a single layer. The electroluminescent layer typically includes a hole injection layer, a hole transport layer, an electron transport layer, and an emissive layer, and combinations thereof. Additional layers may also be present, including dielectric layers. The organic light emitting layer stack can be made using known techniques, such as those described in U.S. Patent Nos. 5,629,389 (Roitman et al.), 5,844,363 (Gu et al.), 5,872,355 (Hueschen), 5,902,688 (Antoniadis et al.), and 5,948,552 (Antoniadis et al.), which have been incorporated herein by reference.

The present invention is compatible with organic light emitting layer stacks made with light emitting polymers and small molecules.

In the alternate embodiment shown in Fig. 2, the encapsulated OLED 300 also includes a first intermediate barrier stack 240 and a second intermediate barrier stack 270. The first intermediate barrier stack is located between the substrate 105 and the first barrier stack 110, and it includes a polymer layer 250 and a barrier layer 260. The second intermediate barrier stack 270 includes a

polymer layer 280 and a barrier layer 290. The second intermediate barrier stack 270 is located between the organic light emitting layer stack 120 and the second barrier stack 130. Alternatively, the second intermediate layer could be located between the first barrier layer and the organic light emitting layer stack.

5 In addition, there could be multiple first intermediate barrier stacks on top of one another to provide enhanced barrier protection. Similarly, there could be multiple second intermediate barrier stacks on top of one another. The order of the barrier and polymer layers in the intermediate barrier stacks is not critical. It depends on where the intermediate barrier stack is located and what layers are  
10 next to them.

The encapsulated OLED can be made by forming the first barrier stack 110, the organic light emitting layer stack 120, and the second barrier stack 130. The stacks are combined to form the encapsulated OLED.

Preferably, the stacks are combined by forming them using vacuum  
15 deposition. In this method, one layer is vacuum deposited on the previous layer, thereby combining the layers simultaneously with forming them. Alternatively, the organic light emitting layer stack can be combined with the first and second barrier stacks by laminating it between the first and second barrier stacks and sealing it along the edges with adhesive, glue, or the like, or by heating. The first  
20 and second barrier stacks include at least one barrier layer and at least one polymer layer. If a polymer/barrier/polymer structure is desired, it can be preferably formed as follows. These barrier stacks can be formed by depositing a layer of polymer, for example an acrylate-containing polymer, onto a substrate or previous layer. Preferably, an acrylate-containing monomer, oligomer or resin  
25 (as used herein, the term acrylate-containing monomer, oligomer, or resin includes acrylate-containing monomers, oligomers, and resins, methacrylate-containing monomers, oligomers, and resins, and combinations thereof) is deposited and then polymerized *in situ* to form the polymer layer. The acrylate-containing polymer layer is then coated with a barrier layer. Another polymer  
30 layer is deposited onto the barrier layer. U.S. Patent Nos. 5,440,446 and 5,725,909, which are incorporated herein by reference, describe methods of depositing thin film, barrier stacks.



The barrier stacks are preferably vacuum deposited. Vacuum deposition includes flash evaporation of acrylate-containing monomer, oligomer, or resin with *in situ* polymerization under vacuum, plasma deposition and polymerization of acrylate-containing monomers, oligomer, or resin, as well as vacuum  
5 deposition of the barrier layers by sputtering, chemical vapor deposition, plasma enhanced chemical vapor deposition, evaporation, sublimation, electron cyclotron resonance-plasma enhanced vapor deposition (ECR-PECVD), and combinations thereof.

It is critical to protect the integrity of the barrier layer to avoid the formation  
10 of defects and/or microcracks in the deposited layer. The encapsulated OLED is preferably manufactured so that the barrier layers are not directly contacted by any equipment, such as rollers in a web coating system, to avoid defects that may be caused by abrasion over a roll or roller. This can be accomplished by designing the deposition system such that a set of layers of  
15 polymer/barrier/polymer are deposited prior to contacting or touching any handling equipment.

The substrate can be flexible or rigid. The flexible substrate may be any flexible material, including, but not limited to, polymers, for example polyethylene terephthalate (PET), polyethylene naphthalate (PEN), or high temperature  
20 polymers such as polyether sulfone (PES), polyimides, or Transphan™ (a high Tg cyclic olefin polymer available from Lofo High Tech Film, GMBH of Weil am Rhein, Germany), metal, paper, fabric, and combinations thereof. The rigid substrate is preferably glass, metal, or silicon. If a flexible, encapsulated OLED is desired and a rigid substrate was used during manufacture, the rigid substrate  
25 is preferably removed prior to use.

The polymer layers of the first and second barrier stacks and the polymer layers of the first and second intermediate barrier stacks are preferably acrylate-containing monomer, oligomer or resin, and combinations thereof. The polymer layers of the first and second barrier stacks and first and second intermediate  
30 stacks can be the same or they can be different. In addition, the polymer layers within the each barrier stack can be the same or different.

The barrier layers in the barrier stacks and the intermediate barrier stacks may be any barrier material. The barrier materials in the first and second barrier stacks and first and second intermediate barrier stacks can be the same or different. In addition, multiple layers of the same or different barrier layers can be used in a stack. Preferred transparent barrier materials include, but are not limited to, metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof. The metal oxides are preferably selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof, the metal nitrides are preferably selected from aluminum nitride, silicon nitride, and combinations thereof, the metal carbide is preferably silicon carbide, and the metal oxynitride is preferably silicon oxynitride.

Since only one side of the device must be transparent, only one of the barrier layers must be transparent. In this situation, the barrier layer on the opposite side could be an opaque barrier material, including, but not limited to, metal, ceramic or polymer.

An alternate encapsulated OLED is shown in Fig. 3. The encapsulated OLED 400 has a substrate 105 on which is fabricated an organic light emitting layer stack 120. A barrier stack 130 is deposited conformally over the organic light emitting layer stack 120, encapsulating it. The polymer layers in the barrier stack can be deposited in vacuum or by using atmospheric processes such as spin coating and/or spraying. A preferred method of forming the barrier stack is flash evaporating acrylate-containing monomers, oligomers or resins, condensing on the OLED layer stack, and polymerizing in-situ in a vacuum chamber. The barrier layer is then deposited on the polymer layer using conventional vacuum processes such as evaporation, sputtering, CVD, PECVD or ECR-PECVD. A second polymer layer is then deposited on the barrier layer using the process described above.

Alternatively, the OLED device could also be encapsulated by laminating a lid structure, containing the barrier stack, to the substrate over the organic light emitting layer structure. The lamination can be performed using either adhesive, or glue, or the like, or by heating. The encapsulated OLED could also include an

intermediate barrier stack 270 as shown. If the substrate is transparent, then the barrier material could be opaque, or vice versa, as discussed above.

A single pass, roll-to-roll, vacuum deposition of a three layer combination on a PET substrate, i.e., PET substrate/polymer layer/barrier layer/polymer layer, can be more than five orders of magnitude less permeable to oxygen and water vapor than a single oxide layer on PET alone. See J.D.Affinito, M.E.Gross, C.A.Coronado, G.L.Graff, E.N.Greenwell, and P.M.Martin, Polymer-Oxide Transparent Barrier Layers Produced Using PML Process, 39<sup>th</sup> Annual Technical Conference Proceedings of the Society of Vacuum Coaters, Vacuum Web Coating Session, 1996, pages 392-397; J.D.Affinito, S.Eufinger, M.E.Gross, G.L.Graff, and P.M.Martin, PML/Oxide/PML Barrier Layer Performance Differences Arising From Use of UV or Electron Beam Polymerization of the PML Layers, Thin Solid Films, Vol.308, 1997, pages 19-25. This is in spite of the fact that the effect on the permeation rate of the polymer multilayers (PML) layers alone, without the barrier layer (oxide, metal, nitride, oxynitride) layer, is barely measurable. It is believed that the improvement in barrier properties is due to two factors. First, permeation rates in the roll-to-roll coated oxide-only layers were found to be conductance limited by defects in the oxide layer that arose during deposition and when the coated substrate was wound up over system idlers/rollers. Asperities (high points) in the underlying substrate are replicated in the deposited inorganic barrier layer. These features are subject to mechanical damage during web handling/take-up, and can lead to the formation of defects in the deposited film. These defects seriously limit the ultimate barrier performance of the films. In the single pass, polymer/barrier/polymer process, the first acrylic layer planarizes the substrate and provides an ideal surface for subsequent deposition of the inorganic barrier thin film. The second polymer layer provides a robust "protective" film that minimizes damage to the barrier layer and also planarizes the structure for subsequent barrier layer (or organic light emitting layer stack) deposition. The intermediate polymer layers also decouple defects that exist in adjacent inorganic barrier layers, thus creating a tortuous path for gas diffusion. The permeability of the barrier stacks used in the present invention is shown below.

Table 1

Sample	Oxygen Permeation Rate (cc/m <sup>2</sup> /day)		Water vapor Permeation (g/m <sup>2</sup> /day) <sup>+</sup>
	23°C*	38°C <sup>+</sup>	38°C <sup>+</sup>
1-barrier stack	<0.005	<0.005	0.46
2- barrier stacks	<0.005	<0.005	<0.005
5-barrier stacks	<0.005	<0.005	<0.005

\* 38°C, 90% RH, 100% O<sub>2</sub>

+ 38°C, 100% RH

NOTE: Permeation rates of <0.005 are below the detection limits of current instrumentation (Mocon OxTran 2/20L).

As can be seen from the data in Table 1, the barrier stacks used in the present invention provide exceptional environmental protection, which was previously unavailable with polymers.

We have also compared the performance of OLED devices (fabricated on glass and silicon) before and after encapsulation using the barrier stacks of the present invention. After encapsulation, the current density-versus-voltage and brightness-versus-current density characteristics were identical (within experimental error) to the measured behavior of the pristine (unencapsulated) devices. This shows that the barrier stacks and deposition methods are compatible with OLED device manufacturing.

Thus, the present invention provides a barrier stack with the exceptional barrier properties necessary for hermetic sealing of an OLED. It permits the production of an encapsulated OLED.

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the compositions and methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

What is claimed is:

1. An encapsulated organic light emitting device comprising:  
5 a first barrier stack comprising at least one first barrier layer and at least one first polymer layer;  
an organic light emitting layer stack adjacent to the first barrier stack; and  
a second barrier stack comprising at least one second barrier layer and at least one second polymer layer, the second barrier stack adjacent to the organic  
10 light emitting layer stack.
2. The encapsulated organic light emitting device of claim 1 further comprising a substrate adjacent to the first barrier stack on a side opposite to the organic light emitting layer stack.  
15
3. The encapsulated organic light emitting device of claim 2 further comprising at least one first intermediate barrier stack located between the substrate and the first barrier stack, the first intermediate barrier stack comprising at least one third polymer layer and at least one third barrier layer.  
20
4. The encapsulated organic light emitting device of claim 1 further comprising at least one second intermediate barrier stack located between the organic light emitting layer stack and either the first or second barrier stacks, the second intermediate barrier stack comprising at least one fourth polymer layer  
25 and at least one fourth barrier layer.
5. The encapsulated organic light emitting device of claim 1 wherein the at least one first barrier layer is substantially transparent.
- 30 6. The encapsulated organic light emitting device of claim 1 wherein the at least one second barrier layer is substantially transparent.

7. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one first and second barrier layers comprise a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof.

5

8. The encapsulated organic light emitting device of claim 7 wherein the metal oxides are selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof.

10

9. The encapsulated organic light emitting device of claim 7 wherein the metal nitrides are selected from aluminum nitride, silicon nitride, and combinations thereof.

10. The encapsulated organic light emitting device of claim 1 wherein the at least one first barrier layer is substantially opaque.

15

11. The encapsulated organic light emitting device of claim 1 wherein the at least one second barrier layer is substantially opaque.

12. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one first and second barrier layers is selected from opaque metals, opaque polymers, and opaque ceramics.

20

13. The encapsulated organic light emitting device of claim 2 wherein the substrate comprises a flexible substrate material.

25

14. The encapsulated organic light emitting device of claim 13 wherein the flexible substrate material is selected from polymers, metals, paper, fabric, and combinations thereof.

30

15. The encapsulated organic light emitting device of claim 2 wherein the substrate comprises a rigid substrate material.

16. The encapsulated organic light emitting device of claim 15 wherein the rigid substrate material is selected from glass, metal, and silicon.

17. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one first polymer layers comprises an acrylate-containing polymer.

18. The encapsulated organic light emitting device of claim 1 wherein at least one of the at least one second polymer layers comprises an acrylate-containing polymer.

19. The encapsulated organic light emitting device of claim 3 wherein at least one of the at least one third polymer layers comprises an acrylate-containing polymer.

20. The encapsulated organic light emitting device of claim 4 wherein at least one of the at least one fourth polymer layers comprises an acrylate-containing polymer.

21. The encapsulated organic light emitting device of claim 1 wherein the organic light emitting layer stack comprises a first electrode, an electroluminescent layer, and a second electrode.

22. The encapsulated organic light emitting device of claim 21 wherein the electroluminescent layer comprises a hole transporting layer, and an electron transporting layer.

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

forming a first barrier stack comprising at least one first barrier layer and at least one first polymer layer;

forming an organic light emitting layer stack;

forming a second barrier stack comprising at least one second barrier layer and at least one second polymer layer; and

combining the first barrier stack, the organic light emitting layer stack adjacent to the first barrier stack, and the second barrier stack adjacent to the organic light emitting layer stack to form the encapsulated organic light emitting device.

24. The method of claim 23 further comprising providing a substrate and forming the first barrier stack on the substrate.

25. The method of claim 24 further comprising placing at least one first intermediate barrier stack comprising at least one third polymer layer and at least one third barrier layer between the substrate and the first barrier stack.

26. The method of claim 23 further comprising placing at least one second intermediate barrier stack comprising at least one fourth polymer layer and at least one fourth barrier layer between the organic light emitting layer stack and either the first or second barrier stacks.

27. The method of claim 23 wherein the organic light emitting layer stack is combined with the first barrier stack by laminating the organic light emitting layer stack to the first barrier stack.

28. The method of claim 23 wherein the organic light emitting layer stack is combined with the first barrier stack simultaneously with forming by depositing the organic light emitting layer stack on the first barrier stack.

29. The method of claim 23 wherein the second barrier stack is combined with the organic light emitting layer stack by laminating the second barrier stack over the organic light emitting layer stack.



30. The method of claim 23 wherein the second barrier stack is combined with the organic light emitting layer stack simultaneously with forming by depositing the second barrier stack on the organic light emitting layer stack.

5 31. The method of claim 24 wherein the substrate comprises a flexible material.

32. The method of claim 24 wherein the substrate comprises a rigid material.

10

33. The method of claim 24 wherein the substrate is removed from the encapsulated organic light emitting device.

15 34. The method of claim 23 wherein the first barrier stack is formed by vacuum deposition.

35. The method of claim 23 wherein the organic light emitting layer stack is formed by vacuum deposition.

20 36. The method of claim 23 wherein the second barrier stack is formed by vacuum deposition.

37. The method of claim 23 wherein at least one of the at least one first and second barrier layers is substantially transparent.

25

38. The method of claim 23 wherein at least one of the first and second barrier layers comprises a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof.

30 39. The method of claim 38 wherein the metal oxides are selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof.

40. The method of claim 38 wherein the metal nitrides are selected from aluminum nitride, silicon nitride, and combinations thereof.

41. The method of claim 23 wherein at least one of the at least one first  
5 and second barrier layers is substantially opaque.

42. The method of claim 23 wherein at least one of the at least one first  
and second barrier layers is selected from opaque metals, opaque polymers, and  
opaque ceramics.

10 43. The method of claim 31 wherein the flexible substrate material is  
selected from polymers, metals, paper, fabric, and combinations thereof.

44. The method of claim 32 wherein the rigid substrate material is  
15 selected from glass, metal, and silicon.

45. The method of claim 23 wherein at least one of the at least one first  
and second pairs of polymer layers comprises an acrylate-containing polymer.

20 46. The method of claim 25 wherein the third polymer layer comprises  
an acrylate-containing polymer.

47. The method of claim 26 wherein the fourth polymer layer comprises  
an acrylate-containing polymer.

25 48. An encapsulated organic light emitting device comprising:  
a first intermediate barrier stack comprising at least one polymer layer and  
at least one barrier layer ;  
a first barrier stack comprising at least one first barrier layer and at least  
30 one first polymer layer adjacent to the first intermediate barrier stack;  
an organic light emitting layer stack adjacent to the first barrier stack;

a second intermediate barrier stack comprising at least one polymer layer and at least one barrier layer, the second intermediate barrier stack adjacent to the organic light emitting layer stack; and

5 a second barrier stack comprising at least one second barrier layer and at least one second polymer layer, the second barrier stack adjacent to the second intermediate barrier stack.

49. The encapsulated organic light emitting device of claim 48 further comprising a substrate adjacent to the first intermediate barrier stack on a side  
10 opposite to the first barrier stack.

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

forming a first intermediate barrier stack comprising at least one polymer  
15 layer and at least one barrier layer;

forming a first barrier stack comprising at least one first barrier layer and at least one first polymer layer adjacent to the first intermediate barrier stack;

forming an organic light emitting layer stack adjacent to the first barrier  
stack;

20 forming a second intermediate barrier stack comprising at least one polymer layer and at least one barrier layer adjacent to the organic light emitting layer stack; and

forming a second barrier stack comprising at least one second barrier  
layer and at least one second polymer layer adjacent to the second intermediate  
25 barrier stack; and

combining the first intermediate barrier stack, the first barrier stack, the organic light emitting layer stack, the second intermediate barrier stack, and the second barrier stack to form the encapsulated organic light emitting device.

30 51. The method of claim 50 wherein the first intermediate barrier stack is formed by vacuum deposition.

52. The method of claim 50 wherein the first barrier stack is formed by vacuum deposition.

53. The method of claim 50 wherein the organic light emitting layer  
5 stack is formed by vacuum deposition.

54. The method of claim 50 wherein the second intermediate barrier stack is formed by vacuum deposition.

10 55. The method of claim 50 wherein the second barrier stack is formed by vacuum deposition.

56. An encapsulated organic light emitting device comprising:  
a substrate;  
15 an organic light emitting layer stack adjacent to the substrate;  
a barrier stack comprising at least one barrier layer and at least one polymer layer, the barrier stack adjacent to the organic light emitting layer stack.

57. The encapsulated organic light emitting device of claim 56 further  
20 comprising an intermediate barrier stack located between the organic light emitting layer stack and the barrier stack, the intermediate barrier stack comprising at least one polymer layer and at least one barrier layer.

58. The encapsulated organic light emitting device of claim 56 wherein  
25 the at least one barrier stack is substantially transparent.

59. The encapsulated organic light emitting device of claim 56 wherein the at least one barrier layer comprises a material selected from metal oxides, metal nitrides, metal carbides, metal oxynitrides, and combinations thereof.

30

60. The encapsulated organic light emitting device of claim 59 wherein the metal oxides are selected from silica, alumina, titania, indium oxide, tin oxide, indium tin oxide, and combinations thereof.

5 61. The encapsulated organic light emitting device of claim 59 wherein the metal nitrides are selected from aluminum nitride, silicon nitride, and combinations thereof.

10 62. The encapsulated organic light emitting device of claim 56 wherein the at least one barrier layer is substantially opaque.

63. The encapsulated organic light emitting device of claim 56 wherein the at least one barrier layer is selected from opaque metals, opaque polymers, and opaque ceramics.

15 64. The encapsulated organic light emitting device of claim 56 wherein at least one of the at least one polymer layers comprises an acrylate-containing polymer.

20 65. The encapsulated organic light emitting device of claim 56 wherein the substrate comprises a rigid substrate material.

66. The encapsulated organic light emitting device of claim 65 wherein the rigid substrate material is selected from glass, metal, and silicon.

25 67. The encapsulated organic light emitting device of claim 56 wherein the substrate comprises a flexible substrate material.

30 68. The encapsulated organic light emitting device of claim 67 wherein the flexible substrate material is selected from polymers, metals, paper, fabric, and combinations thereof.

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

providing a substrate having an organic light emitting layer stack thereon; and

5 vacuum depositing a barrier stack comprising at least one barrier layer and at least one polymer layer over the organic light emitting layer stack to encapsulate the organic light emitting layer stack.

70. The method of claim 69 further comprising depositing an  
10 intermediate barrier layer stack comprising at least one polymer layer and at least one barrier layer on the organic light emitting layer stack prior to vacuum depositing the barrier stack.

71. A method of making an encapsulated organic light emitting device  
15 comprising:

providing a substrate having an organic light emitting layer stack thereon;

vacuum depositing at least one barrier layer over the organic light emitting layer stack;

20 depositing at least one first polymer layer over the at least one barrier layer.

72. The method of claim 71 further comprising depositing at least one  
second polymer layer over the organic light emitting layer stack prior to vacuum  
25 depositing the at least one barrier layer.

73. The method of claim 71 further comprising depositing an  
intermediate barrier layer stack comprising at least one polymer layer and at  
least one barrier layer on the organic light emitting layer stack prior to depositing  
30 the at least one barrier layer.

74. The method of claim 71 wherein at least one of the at least one first polymer layers is deposited using a process at atmospheric pressure.

5 75. The method of claim 74 wherein the process at atmospheric pressure is selected from spin coating and spraying.

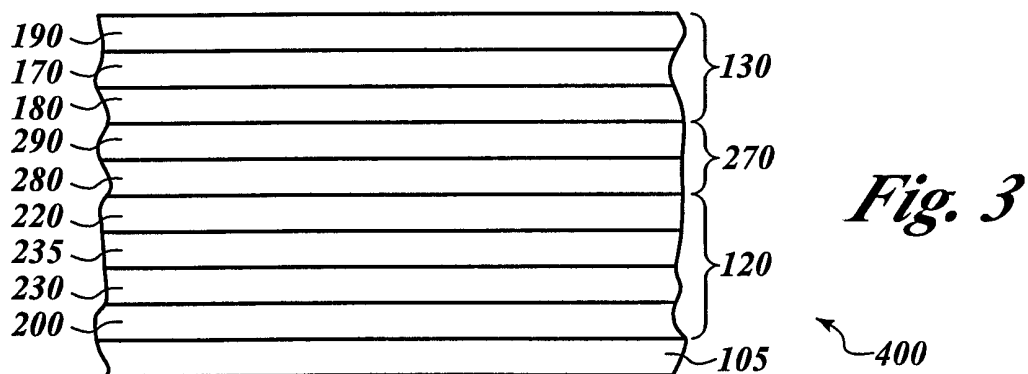
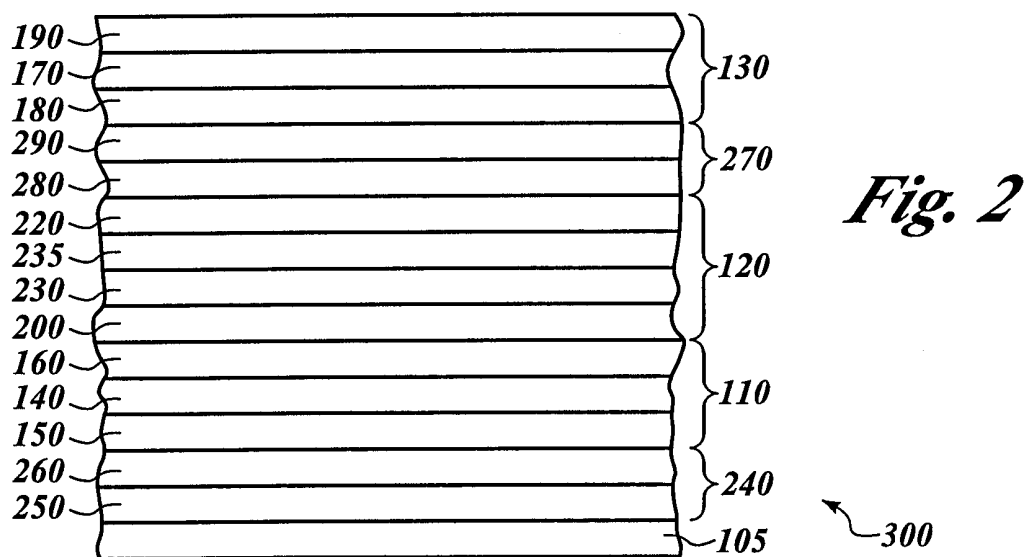
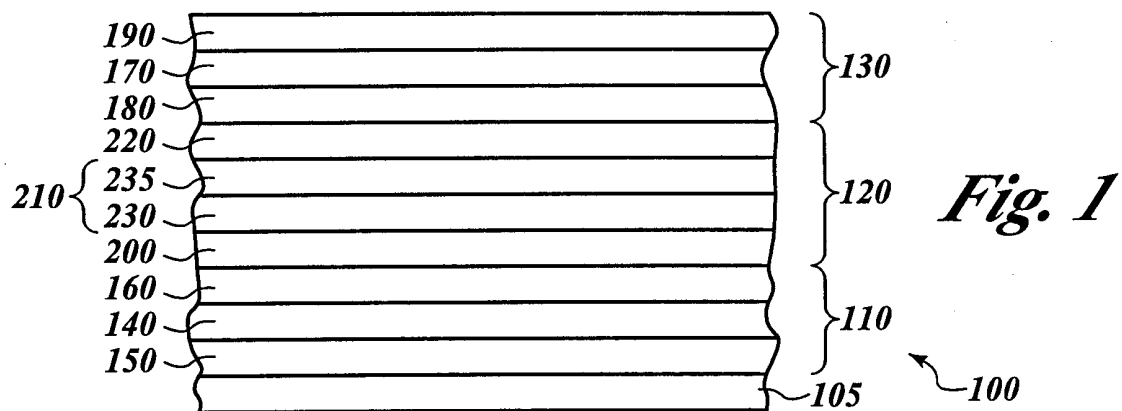
76. The process of 71 wherein at least one of the at least one first polymer layers is deposited using a vacuum process.

10 77. The method of claim 72 wherein at least one of the at least one second polymer layers is deposited using a process at atmospheric pressure.

78. A method of making an encapsulated organic light emitting device comprising:  
15 providing a substrate having an organic light emitting layer stack thereon; and  
laminating a barrier stack comprising at least one barrier layer and at least one polymer layer over the organic light emitting layer stack to encapsulate the organic light emitting layer stack.

20 79. The method of claim 78 wherein the barrier stack is laminated using an adhesive.

80. The method of claim 78 wherein the barrier stack is laminated  
25 using heat.





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/29853

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L51/20

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L H05B

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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 757 126 A (HARVEY III THOMAS B ET AL) 26 May 1998 (1998-05-26)	1-5, 7-9, 11-14, 21-26, 28, 30, 31, 34, 35, 37-43, 48-53, 56, 57, 62, 63, 67, 68
Y	the whole document	1-9, 11-14, 21-31, 34, 35, 37-43, 48-53, 56-63,
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### ° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 February 2000

Date of mailing of the international search report

03/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

De Laere, A

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/29853

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A		67, 68, 78-80 10, 17-20, 36, 45-47, 54, 55, 64, 69-77
X	DE 196 03 746 A (BOSCH GMBH ROBERT) 24 April 1997 (1997-04-24)	56, 58-63, 67, 68, 78-80
Y	the whole document	1-9, 11-14, 21-31, 34, 35, 37-43, 48-53, 56-63, 67, 68, 78-80
A		10, 36, 55, 69, 71, 72, 74-77
A	AFFINITO J D ET AL: "PML/oxide/PML barrier layer performance differences arising from use of UV or electron beam polymerization of the PML layers" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 308-309, no. 1-4, 31 October 1997 (1997-10-31), pages 19-25, XP004110238 ISSN: 0040-6090 cited in the application	1, 5, 7, 8, 13, 14, 17, 23, 24, 31, 34, 37-39, 43, 48-50, 52, 56, 58-60, 64, 67-69, 71, 72, 76, 78
	the whole document	

-/--

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/29853

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 547 508 A (AFFINITO JOHN D) 20 August 1996 (1996-08-20)</p> <p>abstract column 3, line 65 -column 4, line 11 ---</p>	<p>1, 5, 7, 8, 10, 12-14, 23, 24, 31, 33, 34, 37-39, 41-43, 48-50, 52, 56, 58-60, 62, 63, 67-69, 71, 72, 76, 78</p>
E	<p>EP 0 977 469 A (HEWLETT PACKARD CO) 2 February 2000 (2000-02-02)</p> <p>the whole document -----</p>	<p>1, 2, 5-9, 13, 14, 17, 18, 21-24, 28, 30, 31, 34-40, 43, 45, 56, 58-61, 64, 67-69, 71, 72, 76</p>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/29853

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5757126 A	26-05-1998	US 5686360 A EP 0777280 A JP 9161967 A	11-11-1997 04-06-1997 20-06-1997
DE 19603746 A	24-04-1997	WO 9716053 A	01-05-1997
US 5547508 A	20-08-1996	US 5395644 A US 5260095 A AT 170779 T CA 2142895 A DE 69320971 D DE 69320971 T EP 0655954 A JP 8503099 T WO 9404285 A	07-03-1995 09-11-1993 15-09-1998 03-03-1994 15-10-1998 27-05-1999 07-06-1995 02-04-1996 03-03-1995
EP 0977469 A	02-02-2000	NONE	