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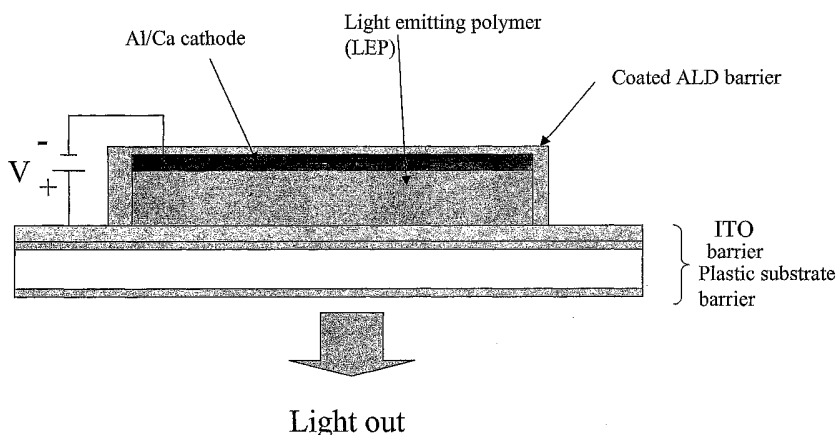
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[Continued on next page]

(54) Title: BARRIER FILMS FOR PLASTIC SUBSTRATES FABRICATED BY ATOMIC LAYER DEPOSITION

### LEP with barrier-substrate and barrier-top-coat



(57) Abstract: Gas permeation barriers can be deposited on plastic or glass substrates by atomic layer deposition (ALD). The use of the ALD coatings can reduce permeation by many orders of magnitude at thicknesses of tens of nanometers with low concentrations of coating defects. These thin coatings preserve the flexibility and transparency of the plastic substrate. Such articles are useful in container, electrical and electronic applications.

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The present invention is further an article comprising:

- a) A substrate made of a material selected from the group consisting of plastic and glass;
- b) an adhesion layer coated; and
- 5 c) a gas permeation barrier deposited by atomic layer deposition.

Another embodiment of the present invention is an article comprising:

- a) a substrate made of a material selected from the group consisting of plastic and glass;
- 10 b) an organic semiconductor, and
- c) a gas permeation barrier deposited by atomic layer deposition.

A yet further embodiment of the present invention is an article comprising:

- 15 a) A substrate made of a material selected from the group consisting of plastic and glass,
- b) A liquid crystal polymer, and
- c) a gas permeation barrier deposited by atomic layer

deposition

20 The invention further describes an embodiment that is an enclosed container.

Another embodiment of the present invention is an electrical or electronic device.

25 Yet another embodiment of the present invention is a light-emitting polymer device.

Yet another embodiment of the present invention is liquid crystalline polymer device.

The invention further describes an organic light emitting diode.

Another embodiment of the present invention is a transistor.

30 Yet another embodiment of the present invention is a circuit comprising a light emitting polymer device.

A still further article is an organic photovoltaic cell.

35 A second article taught herein comprises a plurality of layers, each layer comprising one article, as described above, wherein the articles are in contact with each other. In one embodiment of this second article of the articles above are in contact with each other by lamination means.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a light-emitting polymer device with a barrier substrate and a barrier top coat.

Figure 2 shows a light-emitting polymer device with a barrier substrate and a barrier capping layer.

Figure 3 shows an organic transistor with a barrier substrate and a barrier capping layer.

Figure 4 shows an organic transistor with a barrier substrate and a barrier capping layer.

Figure 5 shows the measured optical transmission through 0.002 inch thick polyethylene naphthalate (PEN) coated with 25 nm of  $\text{Al}_2\text{O}_3$  barrier film.

### DETAILED DESCRIPTION

The permeation of  $\text{O}_2$  and  $\text{H}_2\text{O}$  vapor through polymer films is facile. To reduce permeability for packaging applications, polymers are coated with a thin inorganic film. Al-coated polyester is common. Optically transparent barriers, predominantly  $\text{SiO}_x$  or  $\text{AlO}_y$ , made either by physical vapor deposition (PVD) or chemical vapor deposition (CVD), are also used in packaging. The latter films are commercially available and are known in the industry as "glass-coated" barrier films. They provide an improvement for atmospheric gas permeation of about 10x, reducing transmission rates to about 1.0 cc  $\text{O}_2/\text{m}^2/\text{day}$  and 1.0 ml  $\text{H}_2\text{O}/\text{m}^2/\text{day}$  through polyester film (M. Izu, B. Dotter, and S. R. Ovshinsky, J. *Photopolymer Science and Technology.*, vol. 8 1995 pp 195-204). While this modest improvement is a reasonable compromise between performance and cost for many high-volume packaging applications, this performance falls far short of packaging requirements in electronics. Electronic packaging usually requires at least an order of magnitude longer desired lifetime than, for example, beverage containing. As an example, flexible displays based on organic light emitting polymers (OLEDs), fabricated on flexible polyester substrates need an estimated barrier improvement of  $10^5$ - $10^6$ x for exclusion of atmospheric gases since gases can seriously degrade both the light-emitting polymer and the water-sensitive metal cathode which can frequently be Ca or Ba.

Because of their inherent free volume fraction, the intrinsic permeability of polymers is, in general, too high by a factor  $10^4$ - $10^6$  to achieve the level of protection needed in electronic applications, such as

flexible OLED displays. Only inorganic materials, with essentially zero permeability, can provide adequate barrier protection. Ideally, a defect-free, continuous thin-film coating of an inorganic should be impermeable to atmospheric gases. However, the practical reality is that thin films have defects, such as pinholes, either from the coating process or from substrate imperfections which compromise barrier properties. Even grain boundaries in films can present a pathway for facile permeation. For the best barrier properties, films should be deposited in a clean environment on clean, defect-free substrates. The film structure should be amorphous. The deposition process should be non-directional, (i.e. CVD is preferred over PVD) and the growth mechanism to achieve a featureless microstructure would ideally be layer-by-layer to avoid columnar growth with granular microstructure.

Atomic layer deposition (ALD) is a film growth method that satisfies many of these criteria for low permeation. A description of the atomic layer deposition process can be found in "Atomic Layer Epitaxy," by Tuomo Suntola in *Thin Solid Films*, vol. 216 (1992) pp. 84-89. As its name implies, films grown by ALD form by a layer by layer process. In general, a vapor of film precursor is absorbed on a substrate in a vacuum chamber. The vapor is then pumped from the chamber, leaving a thin layer of absorbed precursor, usually essentially a monolayer, on the substrate. A reactant is then introduced into the chamber under thermal conditions, which promote reaction with the absorbed precursor to form a layer of the desired material. The reaction products are pumped from the chamber. Subsequent layers of material can be formed by again exposing the substrate to the precursor vapor and repeating the deposition process. ALD is in contrast to growth by common CVD and PVD methods where growth is initiated and proceeds at finite numbers of nucleation sites on the substrate surface. The latter technique can lead to a columnar microstructures with boundaries between columns along which gas permeation can be facile. ALD can produce very thin films with extremely low gas permeability, making such films attractive as barrier layers for packaging sensitive electronic devices and components built on plastic substrates.

This invention describes barrier layers formed by ALD on plastic substrates and useful for preventing the passage of atmospheric gases. The substrates of this invention include the general class of polymeric

materials, such as described by but not limited to those in *Polymer Materials*, (Wiley, New York, 1989) by Christopher Hall or *Polymer Permeability*, (Elsevier, London, 1985) by J. Comyn. Common examples include polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), which are commercially available as film base by the roll. The materials formed by ALD, suitable for barriers, include oxides and nitrides of Groups IVB, VB, VIB, IIIA, and IVA of the Periodic Table and combinations thereof. Of particular interest in this group are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Si<sub>3</sub>N<sub>4</sub>. One advantage of the oxides in this group is optical transparency which is attractive for electronic displays and photovoltaic cells where visible light must either exit or enter the device. The nitrides of Si and Al are also transparent in the visible spectrum.

The precursors used in the ALD process to form these barrier materials can be selected from precursors known to those skilled in the art and tabulated in published references such as M. Leskela and M. Ritala, "ALD precursor chemistry: Evolution and future challenges," in *Journal de Physique IV*, vol. 9, pp 837-852 (1999) and references therein.

The preferred range of substrate temperature for synthesizing these barrier coatings by ALD is 50°C-250°C. Too high temperature (>250°C) is incompatible with processing of temperature-sensitive plastic substrates, either because of chemical degradation of the plastic substrate or disruption of the ALD coating because of large dimensional changes of the substrate.

The preferred thickness range for barrier films is 2 nm-100 nm. A more preferred range is 2-50 nm. Thinner layers will be more tolerant to flexing without causing the film to crack. This is extremely important for polymer substrates where flexibility is a desired property. Film cracking will compromise barrier properties. Thin barrier films also increase transparency in the cases of electronic devices where input or output of light is important. There may be a minimum thickness corresponding to continuous film coverage, for which all of the imperfections of the substrate are covered by the barrier film. For a nearly defect-free substrate, the threshold thickness for good barrier properties was estimated to be at least 2 nm, but may be as thick as 10 nm.

Some oxide and nitride barrier layers coated by ALD may require a "starting" or "adhesion layer" to promote adhesion to the plastic substrate or the article requiring protection. The preferred thickness of the adhesion

layer is in the range of 1 nm -100 nm.. The choice of the materials for the adhesion layer will be from the same group of barrier materials. Aluminum oxide and silicon oxide are preferred for the adhesion layer, which may also be deposited by ALD, although other methods such as chemical and physical vapor deposition or other deposition methods known in the art may also be suitable.

The basic building block of the barrier structure is either: (A) a single barrier layer with or without an adhesion layer, coated by ALD on a plastic or glass substrate, or (B) a barrier layer with or without an adhesion layer, coated by ALD on each side of a plastic substrate. This basic structure can then be combined in any number of combinations by laminating this building block to itself to form multiple, independent barrier layers. It is known in the art of barrier coatings that multiple layers, physically separate, can improve the overall barrier properties by much more than a simple multiplicative factor, corresponding the number of layers. This is demonstrated, for example, in *J. Phys. Chem. B* 1997, vol. 101, pp 2259-2266, "Activated rate theory treatment of oxygen and water transport through silicon oxide/poly(ethylene terephthalate) composite barrier structures," by Y. G. Tropsha and N. G. Harvey. This follows because the path for diffusing gas molecules is tortuous through multiple barrier layers that are separated. The effective diffusion path is much larger than the sum of the thickness of the individual layers.

Another barrier configuration involves directly coating the electronic or electro-optical device, requiring protection. In this regard, ALD is particularly attractive because it forms a highly conformal coating. Therefore devices with complex topographies can be fully coated and protected.

## EXAMPLES

### Example 1

Figure 1 shows a schematic representation of a light-emitting polymer device. For simplicity, the light emitting polymer device is shown as the light-emitting polymer (LEP) sandwiched between two electrodes. In practice, a hole-conducting and/or electron-conducting layer can be inserted between the appropriate electrode and the LEP layer to increase device efficiency. The anode is a layer of indium-tin oxide and the cathode is a Ca/Al layer composite. With a voltage applied between the electrodes, holes injected at the anode and electrons injected at the

cathode combine to form excitons which decay radioactively, emitting light from the LEP. The LEP is typically a photosensitive polymer such as polyphenylene vinylene (PPV) or its derivatives. The cathode is frequently Ba or Ca and is extremely reactive with atmospheric gases, especially water vapor. Because of the use of these sensitive materials, the device packaging needs to exclude atmospheric gases in order to achieve reasonable device lifetimes. In Figure 1, the package is comprised of a barrier-substrate which can be plastic or glass on which the LEP device is deposited and then a top coated barrier film. The substrate is comprised of a polyester film, polyethylene naphthalate (PEN) which is 0.004 inch thick. Each side of the PEN film is coated with a 50 nm thick film of  $\text{Al}_2\text{O}_3$ , which is deposited by atomic layer deposition, using trimethylaluminum as the precursor for aluminum and ozone ( $\text{O}_3$ ) as the oxidant. The substrate temperature during deposition is  $150^\circ\text{C}$ . In the ALD process, the PEN substrate is placed in a vacuum chamber equipped with a mechanical pump. The chamber is evacuated. The trimethylaluminum precursor is admitted to the chamber at a pressure of 500 millitorr for approximately 2 seconds. The chamber is then purged with argon for approximately 2 seconds. The oxidant, ozone, is then admitted to the chamber at approximately 500 millitorr for approximately 2 seconds. Finally, the oxidant is purged with argon for approximately 2 seconds. This deposition process is repeated approximately 50 times to obtain a coating approximately 100 nanometers in thickness. The  $\text{Al}_2\text{O}_3$  layer is optically transparent in the visible. The coated substrate may be flexed without loss of the coating. One of the  $\text{Al}_2\text{O}_3$  barriers is coated with indium-tin oxide transparent conductor by rf magnetron sputtering from a 10% (by weight) Sn-doped indium oxide target. The ITO film thickness is 150 nm. The LEP is spin coated on the ITO electrode, after which a cathode of 5 nm Ca with about  $1\ \mu\text{m}$  of Al are thermally evaporated from Ca and Al metal sources, respectively. This LEP device is then coated with a 50 nm-thick, top barrier layer film of  $\text{Al}_2\text{O}_3$ , deposited by atomic layer deposition, again using trimethylaluminum as the precursor for aluminum and ozone ( $\text{O}_3$ ) as the oxidant. The resulting structure is now impervious to atmospheric gases.

### 35 Example 2

Another version of a packaging scheme is shown in Figure 2. The top-coated barrier is replaced by an identical substrate barrier structure

(Al<sub>2</sub>O<sub>3</sub>/PEN/Al<sub>2</sub>O<sub>3</sub>) without an ITO electrode as described in the Example 1 above. This capping barrier structure is sealed to the substrate barrier using a layer of epoxy.

### Example 3

5           Figure 3 illustrates a protection strategy with ALD barrier coatings for an organic transistor. The transistor shown is a bottom gate structure with the organic semiconductor as the final or top layer. Because most organic semiconductors are air sensitive and prolonged exposure degrades their properties, protection strategies are necessary. In Figure 3  
10 the package is comprised of a barrier-substrate on which the transistor is deposited and then sealed to an identical capping barrier structure. The substrate is comprised of a polyester film, polyethylene naphthalate (PEN), 0.004 inch thick. Each side of the PEN film is coated with a 50 nm thick film of Al<sub>2</sub>O<sub>3</sub>, which is deposited by atomic layer deposition, using  
15 trimethylaluminum as the precursor for aluminum and ozone (O<sub>3</sub>) as the oxidant. The substrate temperature during deposition is 150°C. In the ALD process, the PEN substrate is placed in a vacuum chamber equipped with a mechanical pump. The chamber is evacuated. The trimethylaluminum precursor is admitted to the chamber at a pressure of  
20 500 millitorr for approximately 2 seconds. The chamber is then purged with argon for approximately 2 seconds. The oxidant, ozone, is then admitted to the chamber at approximately 500 millitorr for approximately 2 seconds. Finally, the oxidant is purged with argon for approximately 2 seconds. This deposition process is repeated approximately 50 times to  
25 obtain a coating approximately 100 nanometers in thickness. A gate electrode of 100 nm thick Pd metal is ion-beam sputtered through a shadow mask on to the barrier film of Al<sub>2</sub>O<sub>3</sub>. A gate dielectric of 250 nm Si<sub>3</sub>N<sub>4</sub> is then deposited by plasma-enhanced chemical vapor deposition, also through a mask to allow contact to the metal gate. This is followed by  
30 patterning of 100 nm-thick Pd source and drain electrodes, ion beam sputtered on the gate dielectric. Finally the top organic semiconductor, e.g. pentacene, is thermally evaporated through a shadow mask that allows contact to source-drain electrodes. The entire transistor is capped with an Al<sub>2</sub>O<sub>3</sub>/PEN/Al<sub>2</sub>O<sub>3</sub> barrier-structure, sealed to substrate barrier with an  
35 epoxy sealant.

Example 4

In Figure 4, the capping barrier of Example 3 can be replaced by a single layer of 50 nm-thick  $\text{Al}_2\text{O}_3$ , deposited by atomic layer deposition, using trimethylaluminum as the precursor for aluminum and ozone ( $\text{O}_3$ ) as the oxidant. Both packaging structures for the organic transistor device are impervious to atmospheric gases. The plastic substrate with barrier coatings can also be replaced by an impermeable glass substrate. The barrier capping layer is comprised of an initial adhesion layer of silicon nitride deposited by plasma-enhanced chemical vapor deposition at room temperature, followed by a 50 nm-thick  $\text{Al}_2\text{O}_3$  barrier, deposited by atomic layer deposition, as described in Example 3.

Example 5

A substrate film of polyethylene terephthalate (PEN), 0.002 inches thick, was coated by atomic layer deposition at 120° C with  $\text{Al}_2\text{O}_3$  about 25 nm thick on one side of the PEN substrate. Prior to evaluating its permeability properties the coated PEN substrate was flexed at least once to a radius of at least 1.5 inches to remove the coated  $\text{Al}_2\text{O}_3$ -coated PEN substrate from the rigid silicon carrier wafer, to which it was attached with Kapton® tape during ALD deposition. The oxygen transport rate with 50% relative humidity was measured with a commercial instrument (MOCON Ox-Tran 2/20) through the film with  $\text{Al}_2\text{O}_3$  deposited by ALD. After 80 hours of measurement time, within the measurement sensitivity (.005 cc- $\text{O}_2$  /m<sup>2</sup>/day), no oxygen transport (<0.005 cc/m<sup>2</sup>/day) through the barrier film was detected, in spite of the severe prior flexing. For comparison, we measured oxygen transport of about 10 cc- $\text{O}_2$ /m<sup>2</sup>/day through an uncoated PEN substrate. Figure 5 shows that the optical transmission for this  $\text{Al}_2\text{O}_3$ -coated PEN barrier and uncoated PEN is the same (>80% transmittance above 400 nm) verifying the transparency of the thin  $\text{Al}_2\text{O}_3$  barrier coating.

CLAIMS

What is claimed is:

1. An article comprising:
  - a) a substrate made of a material selected from the group consisting of plastic and glass, and
  - b) a gas permeation barrier deposited on said substrate by atomic layer deposition.
2. An article comprising:
  - a) a substrate made of a material selected from the group consisting of plastic and glass,
  - b) an adhesion layer coated, and
  - c) a gas permeation barrier deposited on said substrate by atomic layer deposition.
3. An article comprising:
  - a) a substrate made of a material selected from the group consisting of plastic and glass,
  - b) an organic semiconductor, and
  - c) a gas permeation barrier deposited by atomic layer deposition.
4. An article comprising:
  - a) a substrate made of a material selected from the group consisting of plastic and glass,
  - b) a liquid crystal polymer, and
  - c) a gas permeation barrier deposited by atomic layer deposition
5. The article of any one of Claims 1, 2, 3 or 4 where the article is an enclosed container.
6. The article of any one of Claims 1, 2, 3 or 4 where the article is an electrical or electronic device.
7. The article of any one of Claims 1, 2, 3 or 4 where the article is a light-emitting polymer device.
8. The article of any one of Claims 1, 2, 3 or 4 where the article is an organic light emitting diode.
9. The article of any one of Claims 1, 2, 3 or 4 where the article is a transistor.
10. The article of any one of Claims 1, 2, 3 or 4 where the article is a circuit comprising a light emitting polymer device.

11. The article of any one of Claims 1, 2, 3 or 4 where the article is a circuit comprising a transistor.

12. The article of any one of Claims 1, 2, 3 or 4 wherein the article is an organic photovoltaic cell.

5 13. The article of any one of Claims 1, 2, 3 or 4 wherein the a gas permeation barrier deposited by atomic layer deposition is deposited on a top side and a bottom side of the polymer.

10 14. A second article comprising a plurality of layers, each layer comprising one article, as described in any one of Claims 1, 2, 3 or 4, wherein articles are in contact to each other.

15 15. The second article of claim 11 wherein the articles of any one of Claims 1, 2, 3 or 4 are in contact with each other by lamination means.

16. The article of any one of Claims 1, 2, 3 or 4 wherein the article is a liquid crystal display.

15

# LEP with barrier-substrate and barrier-top-coat

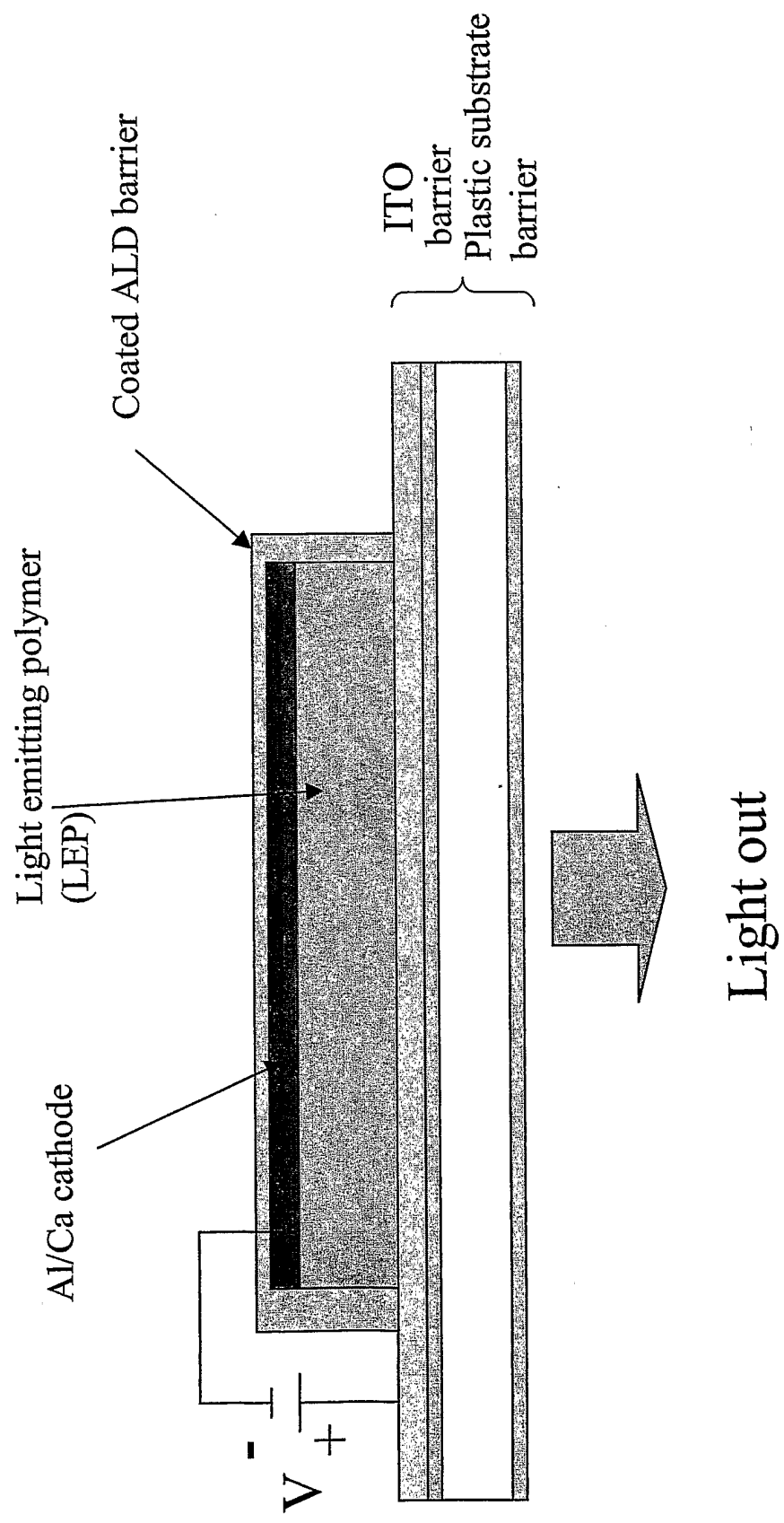


FIG. 1

# LEP with barrier-substrate and barrier-capping layer

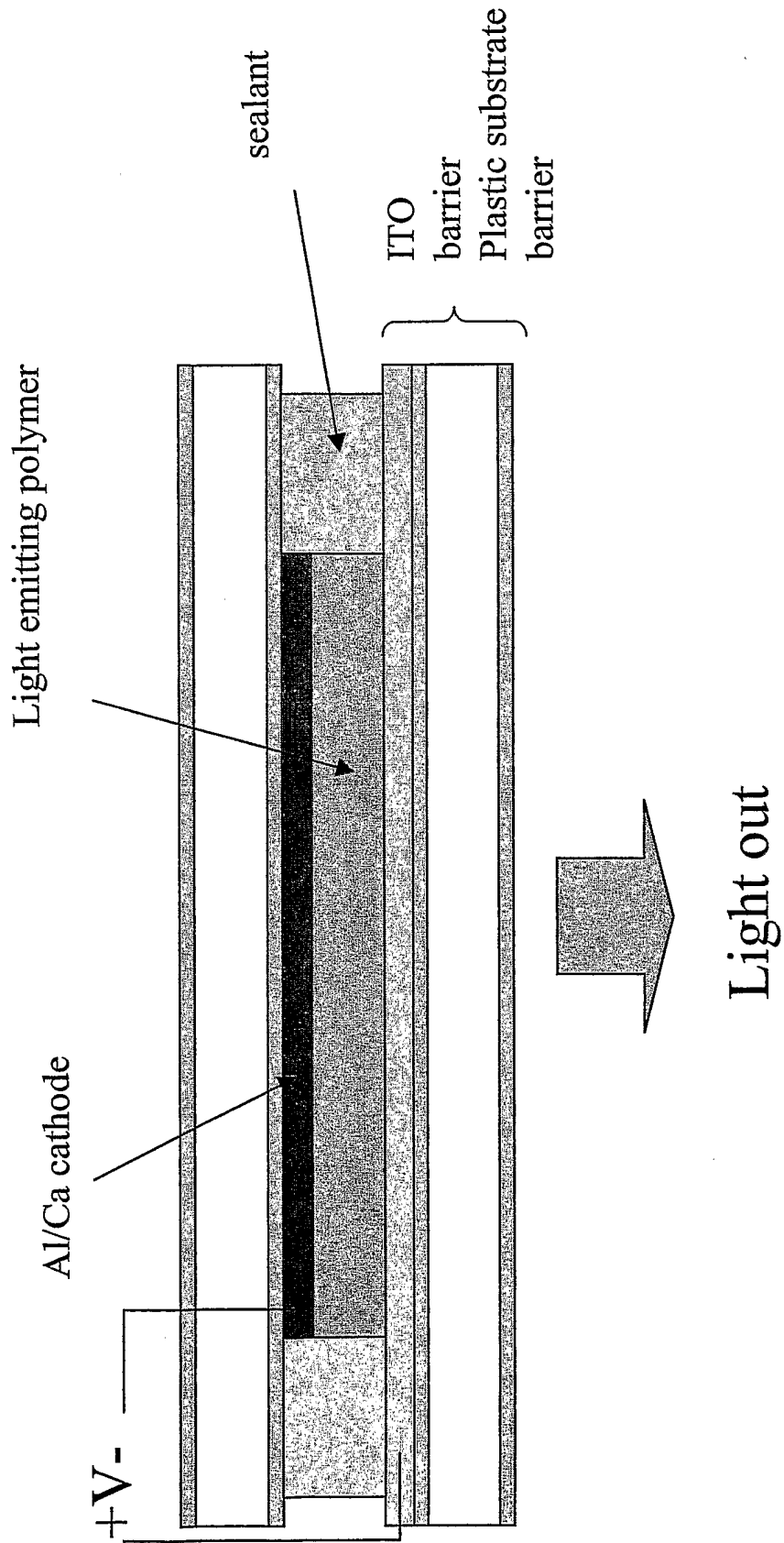


FIG. 2

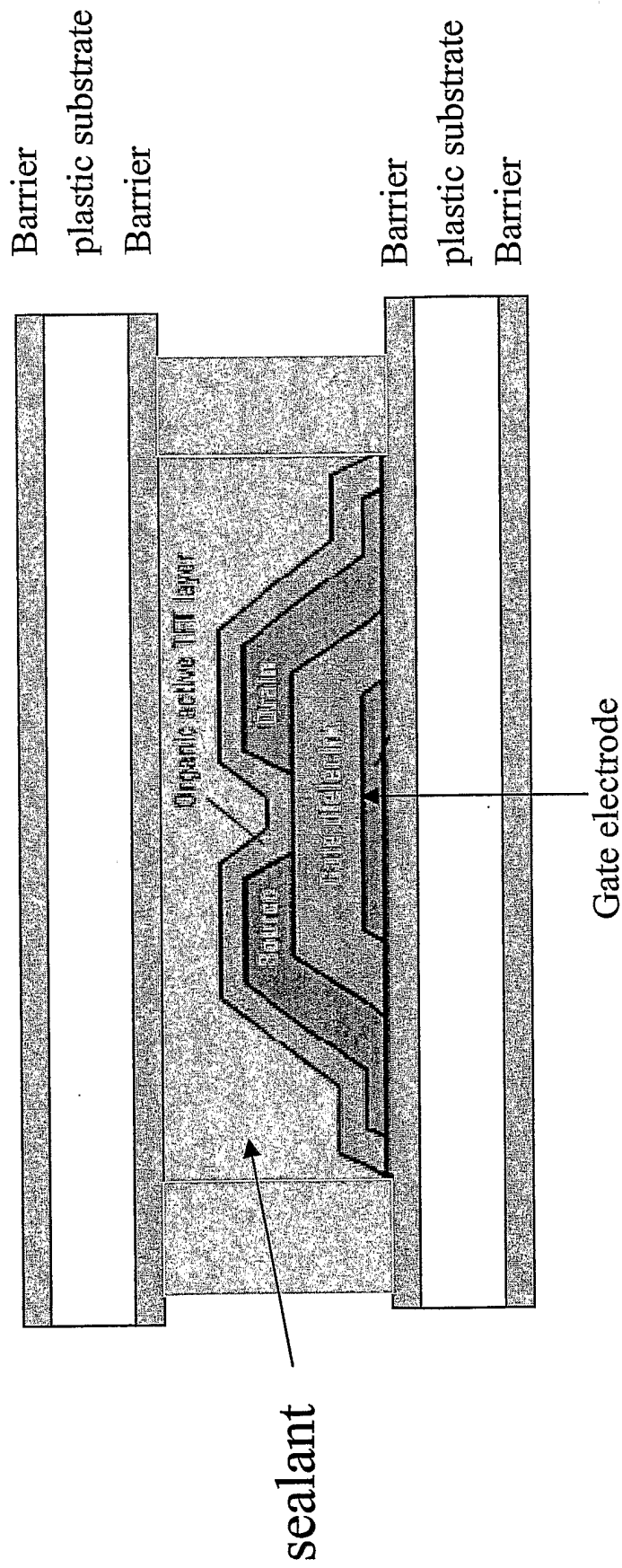


FIG. 3

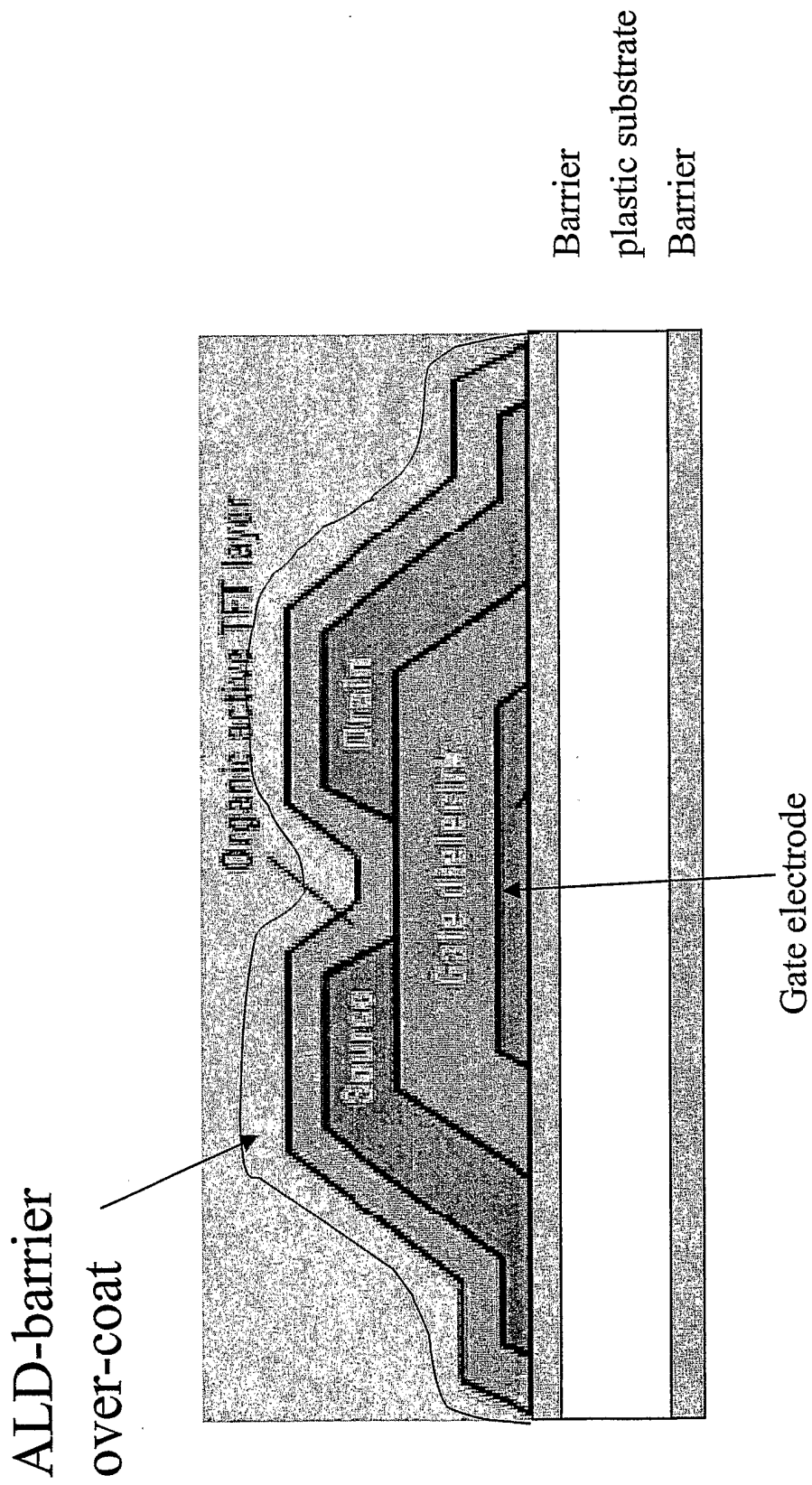


FIG. 4

Figure 5. Optical Transmission of Un-coated PEN and PEN with 25 nm thick ALD  $Al_2O_3$  barrier film

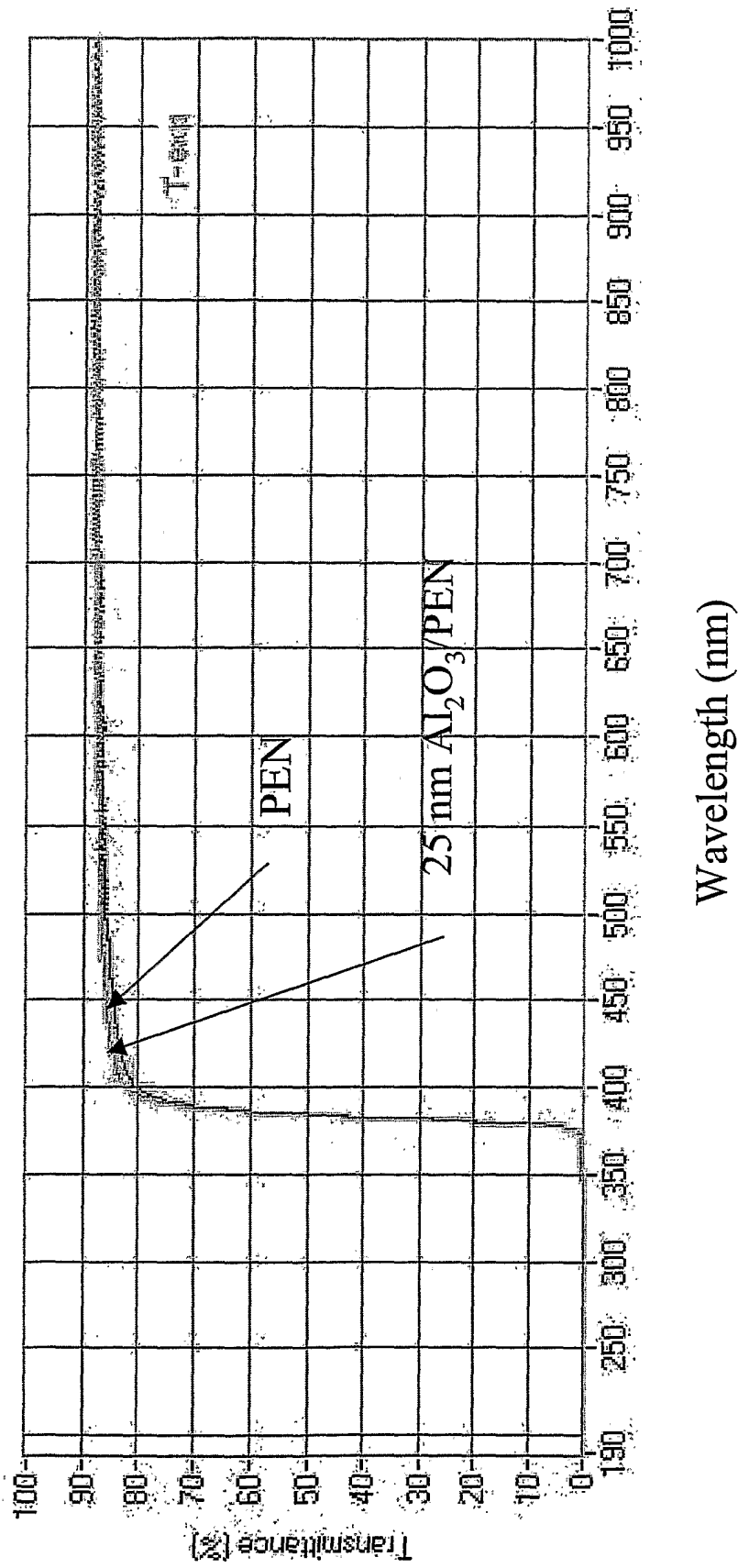


FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No  
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 H01L51/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01L G02F		
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) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01/82390 A (EMAGIN CORP) 1 November 2001 (2001-11-01) page 1, lines 13-19 page 2, lines 9-21 page 3, lines 3-8, 13-24 page 4, lines 2-7, 11-14, 20-23 page 5, lines 2-9, 15-21 page 6, lines 1-4 page 8, lines 13-25 page 9, lines 1-3 page 10, lines 12-17 page 11, line 16 - page 12, line 7 page 13, line 16 - page 14, line 14 ----- -/--	1-16
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> 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 10 November 2004		Date of mailing of the international search report 19/11/2004
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 Joffreau, P-0

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/015270

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 02/071506 A (EMAGIN CORP) 12 September 2002 (2002-09-12) page 1, lines 15-20 page 2, lines 9-21 page 3, lines 3-8,17-23 page 4, lines 2-7,11-20 page 5, lines 1-20 page 8, lines 3-10,20-22 page 11, lines 9-25 page 12, lines 1-20 page 14, lines 9-18 page 14, line 21 - page 15, line 13 -----	1-16
Y	US 5 693 956 A (LEE HSING-CHUNG ET AL) 2 December 1997 (1997-12-02) column 2, lines 3-67 column 3, lines 1-23 -----	1-16
Y	US 5 757 126 A (HARVEY III THOMAS B ET AL) 26 May 1998 (1998-05-26) page 1, lines 24-38 column 2, lines 6-25,48-60 column 4, lines 26-55 column 5, lines 28-38 column 5, line 57 - column 6, line 14 -----	1-16
Y	WO 00/08899 A (UNIAX CORP) 17 February 2000 (2000-02-17) page 1, lines 8-12 page 4, lines 21-26 page 5, lines 16-22 page 5, line 25 - page 6, line 14 page 9, lines 1-13 page 12, line 7 - page 13, line 12 -----	1-16
A	WO 99/02277 A (FED CORP) 21 January 1999 (1999-01-21) page 1, lines 9,10,18-23 page 3, lines 2-4 page 4, line 24 - page 5, line 7 page 7, line 11 - page 8, line 25 -----	1-16
A	WO 01/89006 A (BATTELLE MEMORIAL INSTITUTE) 22 November 2001 (2001-11-22) page 1, lines 2,3,20,21 page 4, lines 1-16,25-29 page 6, lines 11-14 page 7, lines 3-9,13-15 page 9, lines 14-16,22-28 page 11, lines 19-3 -----	1-16

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2004/015270

## Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 1,2,14 (all partially)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Continuation of Box II.2

Claims Nos.: 1,2,14 (all partially)

Present claims 1, 2 and 14 relate to an extremely large number of possible products. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the products claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the products encompassed an organic semiconductor such as an OLED or a liquid crystal polymer.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US2004/015270

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 0182390	A	01-11-2001	US 2001052752 A1	20-12-2001
			AU 5519401 A	07-11-2001
			WO 0182390 A1	01-11-2001
			US 2002003403 A1	10-01-2002
			WO 02071506 A1	12-09-2002
WO 02071506	A	12-09-2002	US 2001052752 A1	20-12-2001
			AU 5519401 A	07-11-2001
			WO 0182390 A1	01-11-2001
			WO 02071506 A1	12-09-2002
US 5693956	A	02-12-1997	NONE	
US 5757126	A	26-05-1998	US 5686360 A	11-11-1997
			DE 69615510 D1	31-10-2001
			DE 69615510 T2	29-05-2002
			EP 0777280 A2	04-06-1997
			JP 9161967 A	20-06-1997
			TW 447146 B	21-07-2001
WO 0008899	A	17-02-2000	AU 5334999 A	28-02-2000
			CA 2337085 A1	17-02-2000
			CN 1311976 T	05-09-2001
			EP 1121838 A1	08-08-2001
			JP 2002522884 T	23-07-2002
			WO 0008899 A1	17-02-2000
			US 6635989 B1	21-10-2003
			US 2003184222 A1	02-10-2003
			US 2004140766 A1	22-07-2004
			WO 9902277	A
CA 2295676 A1	21-01-1999			
CA 2296026 A1	21-01-1999			
EP 0995183 A2	26-04-2000			
EP 1021255 A1	26-07-2000			
WO 9903087 A2	21-01-1999			
WO 9902277 A1	21-01-1999			
WO 0189006	A	22-11-2001		
			AU 3996901 A	26-11-2001
			CN 1429412 T	09-07-2003
			EP 1282922 A1	12-02-2003
			JP 2003533892 T	11-11-2003
			WO 0189006 A1	22-11-2001