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(54) **Organic electroluminescent device and display using same**

Organische elektrolummineszente Vorrichtung und Anzeigegerät mit dieser

Dispositif electroluminescent organique et ecran le contenant

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**EP-A- 1 388 904 EP-A2- 1 408 563**

- **TOSHIO MATSUMOTO ET AL: "27.5L: Late-News Paper: Multiphoton Organic EL device having Charge Generation Layer" 2003 SID INTERNATIONAL SYMPOSIUM - MAY 20, 2003, BALTIMORE, MARYLAND, vol. XXXIV, 20 May 2003 (2003-05-20), page 979, XP007008283**
- **JUNJI KIDO ET AL: "27.1: Invited Paper: High Efficiency Organic EL Devices having Charge Generation Layers" 2003 SID INTERNATIONAL SYMPOSIUM - MAY 20, 2003, BALTIMORE, MARYLAND, vol. XXXIV, 20 May 2003 (2003-05-20), page 964, XP007008279**



EP 2 229 039 B1

## Description

Technical Field

**[0001]** The invention relates to an organic electroluminescent device (organic EL device) and display using the same.

Background Art

**[0002]** An organic EL device has rapidly made progress as a luminescent device with a high efficiency in recent years. The organic EL device advantageously emits light with a high brightness since it is a current-type element. However it also has the following disadvantage because of being a current-type element; current increases at a high brightness, and power consumption thus decreases due to the electric resistance of wiring.
In order to solve the disadvantage, various improvements for enhancing current efficiency have been carried out.
For example, the technique is disclosed that a plurality of organic EL devices are stacked and light emitted from each of the devices is combined, thereby enhancing current efficiency. Specifically USP 5932895 discloses a method of stacking RGB elements, but the method does not-enhance luminous efficiency. J-P-A-H11. 312585, JP-A-H11-312584 and JP-A-2003-45676 disclose a structure of stacking a plurality of elements with an excellent efficiency; however they do not have a satisfactory life time.
Matsumoto T. et al. (2003 SID International Symposium May 20, 2003, Baltimore, Maryland, vol. XXXIV, 20 May 2003, pages 979-981) describe organic EL devices in which two emitting layers are provided and a layer containing ITO is arranged as an intermediate electrode layer. A similar structure is disclosed by Kido et al. (2003 SID International Symposium May 20, 2003, Baltimore, Maryland, vol. XXXIV, 20 May 2003, pages 964-965). The intermediate electrode layer between two emitting layers which is described in EP 1 388 904 A2 may also consist of ITO.
In EP 1 408 563 A2 organic electroluminescent devices are described in which at least two emitting layers may be present which are separated by an intermediate electrode layer which may contain a semiconductive transition metal oxide material wherein the transition metal can be niobium, molybdenum, rhenium, osmium, iridium or platinum.
As stated above, there remain many problems concerning the high efficiency of an organic EL device at the present.
**[0003]** The invention has been made in view of the above-mentioned problems and an object thereof is to provide an organic EL device with a high efficiency and long life time.
**[0004]** In order to attain the object, the inventors conducted various studies through which they have found that it is effective to arrange an intermediate electrode layer made of a semiconductive material with a certain resistivity between emitting layers of an organic EL
device and have made the invention based on their findings.

Disclosure of the Invention

**[0005]** The invention provides the following organic EL device and the like.

1. An organic electroluminescent device comprising:

   at least two or more emitting layers between an anode and a cathode,
   an intermediate electrode layer being interposed between emitting layers,
   the intermediate electrode layer being a single layer comprising a semiconductive material, or a multilayer structure of a plurality of layers, at least one of the layers comprising a semiconductive material,
   which semiconductive material has a resistivity of 0.001 to 10,000 Ω·cm, and
   comprises an acceptor that is a conductive oxide containing a transition metal, and a donor that is an alkali metal and/or an alkaline earth metal.

2. The organic electroluminescent device according to 1, wherein the conductive oxide containing a transition metal is at least one oxide selected from the group of $NbO_x$, $MoO_x$, $ReO_x$, $WO_x$, $OsO_x$, $IrO_x$ and $PtO_x$ wherein x is 0.2 to 5.
3. The organic electroluminescent device according to 1, wherein the acceptor is at least one oxide selected from the group of $Li_xTi_2O_4$, $Li_xV_2O_4$, $Er_xNbOs$, $La_xTiOs$, $Sr_x\ VO_3$, $Ca_xCrO_3$, $Sr_xCrO_3$, $A_xMoO3$ and $AV_2O_5$, wherein A is K, Cs, Rb, Sr, Na, Li or Ca, and x is 0.2 to 5.
4. The organic electroluminescent device according to 1, wherein the semiconductive material has a resistivity of not less than 0.001 Ω·cm but less than 100 Ω·cm.
5. A display comprising a screen comprising the organic electroluminescent device according to any one of 1 to 4.

Brief Description of the Drawings

**[0006]**

Fig. 1 is a view for explaining the function of an intermediate electrode layer.

Best Modes for Carrying Out the Invention

**[0007]** Organic EL devices of the invention are described below.

**[0008]** First, the organic EL device of the invention will be described.

[Intermediate electrode layer]

**[0009]** The organic EL device comprises at least two or more emitting layers between an anode and a cathode, and an intermediate electrode layer interposed between emitting layers, the intermediate electrode layer comprising a semiconductive material having a resistivity of 0.001 to 10,000 Ω·cm.

**[0010]** The intermediate electrode layer can generate both electrons and holes since it comprises a semiconductive material with the above resistivity. Thus it can sufficiently supply carriers to either one of the two emitting layers on both the surfaces thereof.

As shown in Fig. 1, an intermediate electrode layer 6 injects holes from a surface A contact with an emitting layer 4 on a cathode 2 side, while it injects electrons from a surface B contact with an emitting layer 8 on a anode 10 side.

The intermediate electrode layer has good contact with the emitting layers and the other organic layers and the organic EL device of the invention can thus have a longer life time than conventional organic EL devices.

**[0011]** When a material of the intermediate electrode layer has too small a resistivity, current tends to leak. When it has too large a resistivity, voltage increases at the drivig time. The semiconductive material has a resistivity of 0.001 to 10,000 Ω·cm, preferably 0.01 to 100 Ω·cm. The intermediate electrode layer preferably has a thickness of 0.1 to 100 nm to function as a thin film. Too thick the thickness thereof may cause an increase in driving voltage.

**[0012]** The material making up the intermediate electrode layer is not limited so long as it is a semiconductive material with the above resistivity. Electrical conductive oxides are a first embodiment of the invention.

The conductive oxides contain a transition metal.

An example thereof is at least one oxide selected from the group of $NbO_x$, $MoO_x$, $ReO_x$, $WO_x$, $OsO_x$, $IrO_x$ and $PtO_x$ wherein x is 0.2 to 5.

The semiconductive material comprises an acceptor that is a conductive oxide containing a transition metal, and a donor that is an alkali metal and/or an alkaline earth metal.

As the acceptor, preferred are at least one oxide selected from the group of $Li_xTi_2O4$, $Li_xV_2O_4$, $Er_xNbO_3$, $La_xTiO_3$, $Sr_xVO_3$, $Ca_xCrO_3$, $Sr_xCrO_3$, $A_xMoO_3$, $AV_2O_5$, wherein A is K, Cs, Rb, Sr, Na, Li or Ca, and x is 0.2 to 5.

As the alkali metal and alkaline earth metal, the above-mentioned metals are preferred.

**[0013]** In the invention, the intermediate electrode layer may be a single layer or a multilayer structure of a plurality of layers (two or three and more layers). In the case where the intermediate electrode layer is a multilayer structure, at least one layer thereof may be a layer comprising a semiconductive material. The intermediate electrode layer may be a multilayer structure of a plurality of layers that comprise semiconductive materials.

[Emitting layer]

**[0014]** An emitting layer of an organic EL device possesses the following functions:

(a) an injection function; which enables to inject holes from an anode or hole-injecting layer and to inject electrons from a cathode or electron-injecting layer, when an electric field is impressed,

(b) a transport function; which transports injected electric charge (electrons and holes) with an electric field's power, and

(c) an emitting function; which provides a recombination site for electrons and holes to emit light.

There may be a difference in ease of injection between holes and electrons, and also a difference in transport capacity that is represented by mobilities of holes and electrons. However, moving one of the electric charges is preferred.

**[0015]** As methods of forming this emitting layer, known methods such as vacuum deposition, spin coating and LB technique can be applied.

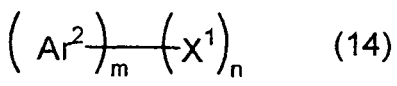
An emitting layer is particularly preferably a molecule-deposited film.

The term "molecule-deposited film" here means a thin film that is formed by depositing a material compound in a vapor

phase and a film formed by solidifying a material compound in a solution state or liquid state. Usually this molecule-deposited film can be distinguished from a thin film formed by the LB technique (a molecule-accumulated film) by differences in agglutination structure and higher dimension stricture, and functional differences caused thereby.

As disclosed in JP-A-57-51781, an emitting layer can also be formed by dissolving a binder such as resins and material compound in a solvent to make a solution and forming a thin film therefrom by spin coating and so on.

**[0016]** The host materials used in the emitting layer may be a material known as a luminescent material having a long life time. It is desirable to use, as the host material of the luminescent material, a material represented by a general formula (14), but the host material is not limited to the following material:



(14)

wherein $Ar^2$ is an aromatic ring with 6 to 50 nucleus carbon atoms, $X^1$ includes substituted or unsubstituted aromatic groups with 6 to 50 nucleus carbon atoms, substituted or unsubstituted aromatic heterocyclic groups with 5 to 50 nucleus carbon atoms, substituted or unsubstituted alkyl groups with 1 to 50 carbon atoms, substituted or unsubstituted alkoxy groups with 1 to 50 carbon atoms, substituted or unsubstituted aralkyl groups with 1 to 50 carbon atoms, substituted or unsubstituted aryloxy groups with 5 to 50 nucleus atoms, substituted or unsubstituted arylthio groups with 5 to 50 nucleus atoms, substituted or unsubstituted carboxyl groups with 1 to 50 carbon atoms, substituted or unsubstituted styryl groups, halogen groups, a cyano group; a nitro group, and a hydroxyl group, m is an integer of 1 to 5, and n is an integer of 0 to 6.

**[0017]** Specific examples of $Ar^2$ include phenyl, naphthyl, anthracene, biphenylene, azulene, acenaphthylene, fluorene, phenanthrene, fluoranthene, acephenanthrylene, triphenylene, pyrene, chrysene, naphthacene, picene, perylene, penthaphene, pentacene, tetraphenylene, hexaphene, hexacene, rubicene, coronene, and trinaphthylene rings.

Preferred examples thereof include phenyl, naphthyl, anthracene, acenaphthylene, fluorene, phenanthrene, fluoranthene, triphenylene, pyrene, chrysene, perylene, and trinaphthylene rings.

More preferred examples thereof include phenyl, naphthyl, anthracene, fluorene, phenanthrene, fluoranthene, pyrene, chrysene, and perylene rings.

**[0018]** In the substituent $X^1$, examples of the substituted or unsubstituted aromatic groups with 6 to 50 nucleus carbon atoms include phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl, 9-phenanthryl, 1-naphthacenyl, 2-naphthacenyl, 9-naphthacenyl, 1-pyrenyl, 2-pyrenyl, 4-pyrenyl, 2-biphenylyl, 3-biphenylyl, 4-biphenylyl, p-terphenyl-4-yl, p-terphenyl-3-yl, p-terphenyl-2-yl, m-terphenyl-4-yl, m-terphenyl-3-yl, m-terphenyl-2-yl, o-tolyl, m-tolyl, p-tolyl, p-t-butylphenyl, p-(2-phenylpropyl)phenyl, 3-methyl-2-naphthyl, 4-methyl-1-naphthyl, 4-methy-1-1-anthryl, 4'-methylbiphenylyl, 4"-t-butyl-p-terphenyl-4-yl, 2-fluorenyl, 9,9-dimethyl-2-fluorenyl and 3-fluorantenyl groups.

Preferred examples thereof include phenyl, 1-naphthyl, 2-naphthyl, 9-phenanthryl, 1-naphthacenyl, 2-naphthacenyl, 9-naphthacenyl, 1-pyrenyl, 2-pyrenyl, 4-pyrenyl, 2-biphenylyl, 3-biphenylyl, 4-biphenylyl, o-tolyl, m-tolyl, p-tolyl, p-t-butylphenyl, 2-fluorenyl, 9,9-dimethyl-2-fluorenyl and 3-fluorantenyl groups.

**[0019]** Examples of the substituted or unsubstituted aromatic heterocyclic groups with 5 to 50 nucleus carbon atoms include 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, pyrazinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 1-indolyl, 2-indolyl, 3-indolyl, 4-indolyl, 5-indolyl, 6-indolyl, 7-indolyl, 1-isoindolyl, 2-isoindolyl, 3-isoindolyl, 4-isoindolyl, 5-isoindolyl, 6-isoindolyl, 7-isoindolyl, 2-furyl, 3-furyl, 2-benzofuranyl, 3-benzofuranyl, 4-benzofuranyl, 5-benzofuranyl, 6-benzofuranyl, 7-benzofuranyl, 1-isobenzofuranyl, 3-isobenzofuranyl, 4-isobenzofuranyl, 5-isobenzofuranyl, 6-isobenzofuranyl, 7-isobenzofuranyl, quinolyl, 3-quinolyl, 4-quinolyl, 5-quinolyl, 6-quinolyl, 7-quinolyl, 8-quinolyl, 1-isoquinolyl, 3-isoquinolyl, 4-isoquinolyl, 5-isoquinolyl, 6-isoquinolyl, 7-isoquinolyl, 8-isoquinolyl, 2-quinoxalinyl, 5-quinoxalinyl, 6-quinoxalinyl, 1-carbazolyl, 2-carbazolyl, 3-carbazolyl, 4-carbazolyl, 9-carbazolyl, 1-phenanthrydinyl, 2-phenanthrydinyl, 3-phenanthrydinyl, 4-phenanthrydinyl, 6-phenanthrydinyl, 7-phenanthrydinyl, 8-phenanthrydinyl, 9-phenanthrydinyl, 10-phenanthrydinyl, 1-acrydinyl, 2-acrydinyl, 3-acrydinyl, 4-acrydinyl, 9-acrydinyl, 1,7-phenanthroline-2-yl, 1,7-phenanthroline-3-yl, 1,7-phenanthroline-4-yl, 1,7-phenanthroline-5-yl, 1,7-phenanthroline-6-yl, 1,7-phenanthroline-8-yl, 1,7-phenanthroline-9-yl, 1,7-phenanthroline-10-yl, 1,8-phenanthroline-2-yl, 1,8-phenanthroline-3-yl, 1,8-phenanthroline-4-yl, 1,8-phenanthroline-5-yl, 1,8-phenanthroline-6-yl, 1,8-phenanthroline-7-yl, 1,8-phenanthroline-9-yl, 1,8-phenanthroline-10-yl, 1,9-phenanthroline-2-yl, 1,9-phenanthroline-3-yl, 1,9-phenanthroline-4-yl, 1,9-phenanthroline-5-yl, 1,9-phenanthroline-6-yl, 1,9-phenanthroline-7-yl, 1,9-phenanthroline-8-yl, 1,9-phenanthroline-10-yl, 1,10-phenanthroline-2-yl, 1,10-phenanthroline-3-yl, 1,10-phenanthroline-4-yl, 1,10-phenanthroline-5-yl, 2,9-phenanthroline-1-yl, 2,9-phenanthroline-3-yl, 2,9-phenanthroline-4-yl, 2,9-phenanthroline-5-yl, 2,9-phenanthroline-6-yl, 2,9-phenanthroline-7-yl, 2,9-phenanthroline-8-yl, 2,9-phenanthroline-10-yl, 2,8-phenanthroline-1-yl, 2,8-phenanthroline-3-yl, 2,8-phenanthroline-4-yl, 2,8-phenanthroline-5-yl, 2,8-phenanthro-

line-6-yl, 2,8-phenanthroline-7-yl, 2,8-phenanthroline-9-yl, 2,8-phenanthroline-10-yl, 2,7-phenanthroline-1-yl, 2,7-phenanthroline-3-yl, 2,7-phenanthroline-4-yl, 2,7-phenanthroline-5-yl, 2,7-phenanthroline-6-yl, 2,7-phenanthroline-8-yl, 2,7-phenanthroline-9-yl, 2,7-phenanthroline-10-yl, 1-phenazinyl, 2-phenazinyl, 1-phenothiazinyl, 2-phenothiazinyl, 3-phenothiazinyl, 4-phenothiazinyl, 10-phenothiazinyl, 1-phenoxazinyl, 2-phenoxazinyl, 3-phenoxazinyl, 4-phenoxazinyl, 10-phenoxazinyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-oxadiazolyl, 5-oxadiazolyl, 3-furazanyl, 2-thienyl, 3-thienyl, 2-methylpyrrole-l-yl, 2-methylpyrrole-3-yl, 2-methylpyrrole-4-yl, 2-methylpyrrole-5-yl, 3-methylpyrrole-1-yl, 3-methylpyrrole-2-yl, 3-methylpyrrole-4-yl, 3-methylpyrrole-5-yl, 2-t-butylpyrrole-4-yl, 3-(2-phenylpropyl)pyrrole-1-yl, 2-methyl-1-indolyl, 4-methyl-1-indolyl, 2-methyl-3-indolyl, 4-methyl-3-indolyl, 2-t-butyl-1-indolyl, 4-t-butyl-1-indolyl, 2-t-butyl-3-indolyl, and 4-t-butyl-3-indolyl groups.

**[0020]** Examples of the substituted or unsubstituted alkyl groups with 1 to 50 carbon atoms include methyl, ethyl, propyl, isopropyl, n-butyl, s-butyl, isobutyl, t-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 2-hydroxyisobutyl, 1,2-dihydroxyethyl, 1,3-dihydroxyisopropyl, 2,3-dihydroxy-t-butyl, 1,2,3-trihydroxypropyl, chloromethyl, 1-chloroethyl, 2-chloroethyl, 2-chloroisobutyl, 1,2-dichloroethyl, 1,3-dichloroisopropyl, 2,3-dichloro-t-butyl, 1,2,3-trichloropropyl, bromomethyl, 1-bromoethyl, 2-bromoethyl, 2-bromoisobutyl, 1,2-dibromoethyl, 1,3-dibromoisopropyl, 2,3-dibromo-t-butyl, 1,2,3-tribromopropyl, iodomethyl, 1-iodoethyl, 2-iodoethyl, 2-iodoisobutyl, 1,2-diiodoethyl, 1,3-diiodoisopropyl, 2,3-diiodo-t-butyl, 1,2,3-triiodopropyl, aminomethyl, 1-aminoethyl, 2-aminoethyl, 2-aminoisobutyl, 1,2-diaminoethyl, 1,3-diaminoisopropyl, 2,3-diamino-t-butyl, 1,2,3-triaminopropyl, cyanomethyl, 1-cyanoethyl, 2-cyanoethyl, 2-cyanoisobutyl, 1,2-dicyanoethyl, 1,3-dicyanoisopropyl, 2,3-dicyano-t-butyl, 1,2,3-tricyanopropyl, nitromethyl, 1-nitroethyl, 2-nitroethyl, 2-nitroisobutyl, 1,2-dinitroethyl, 1,3-dinitroisopropyl, 2,3-dinitro-t-butyl, 1,2,3-trinitropropyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, 4-methylcyclohexyl, 1-adamanthyl, 2-adamanthyl, 1-norbornyl, and 2-norbornyl groups.

**[0021]** The substituted or unsubstituted alkoxy groups with 1 to 50 carbon atoms are groups represented by -OY. Examples of Y include the same substituent as the above-mentioned alkyl group.

**[0022]** Examples of the substituted or unsubstituted aralkyl groups with 1 to 50 carbon atoms include benzyl, 1-phenylethyl, 2-phenylethyl, 1-phenylisopropyl, 2-phenylisopropyl, phenyl-t-butyl, α-naphthylmethyl, 1-α-naphthylethyl, 2-α-naphthylethyl, 1-α-naphthylisopropyl, 2-α-naphthylisopropyl, β-naphthylmethyl, 1-β-naphthylethyl, 2-β-naphthylethyl, 1-β-naphthylisopropyl, 2-β-naphthylisopropyl, 1-pyrrolylmethyl,- 2- (1-pyrrolyl)ethyl, p-methylbenzyl, m-methylbenzyl, o-methylbenzyl, p-chlorobenzyl, m-chlorobenzyl, o-chlorobenzyl, p-bromobenzyl, m-bromobenzyl, o-bromobenzyl, p-iodobenzyl, m-iodobenzyl, o-iodobenzyl, p-hydroxybenzyl, m-hydroxybenzyl, o-hydroxybenzyl, p-aminobenzyl, m-aminobenzyl, o-aminobenzyl, p-nitrobenzyl, m-nitrobenzyl, o-nitrobenzyl, p-cyanobenzyl, m-cyanobenzyl, o-cyanobenzyl, 1-hydroxy-2-phenylisopropyl, and 1-chloro-2-phenylisopropyl groups.

**[0023]** The substituted or unsubstituted aryloxy groups with 5 to 50 nucleus atoms are represented by -OY'. Examples of Y' include the same substituent as the above-mentioned aromatic and aromatic heterocyclic groups.

The substituted or unsubstituted arylthio groups with 5 to 50 nucleus atoms are represented by -SY", and examples of Y" include the same substituent as the above-mentioned aromatic and aromatic heterocyclic groups.

**[0024]** The substituted or unsubstituted carboxyl groups with 1 to 50 carbon atoms are represented by -COOY"', and examples of Y'" include the same substituent as the above-mentioned Y.

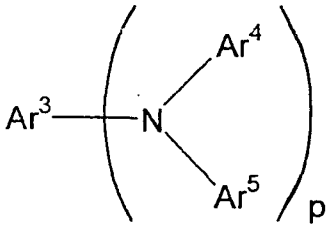
**[0025]** Examples of the substituted or unsubstituted styryl groups include 2-phenyl-1-vinyl, 2,2-diphenyl-1-vinyl, and 1,2,2-triphenyl-1-vinyl groups.

Examples of the halogen groups include fluorine, chlorine, bromine and iodine.

**[0026]** m is preferably an integer of 1 to 2, and n is preferably an integer of 0 to 4.

$Ar^2$s may be the same as or different from each other when m is 2 or more, and $X^1$s may be the same as or different from each other when n is 2 or more.

**[0027]** Moreover a dopant may be added in the emitting layer. The dopant used may be a dopant known as a luminescent material having a long life time. It is preferred to use, as the dopant material of the luminescent material, a material represented by a general formula (15), but, the host material is not limited to the following material:



(15)

wherein $Ar^3$ to $Ar^5$ are each a substituted or unsubstituted aromatic group with 6 to 50 nucleus carbon atoms, or a

substituted or unsubstituted styryl group; and p is an integer of 1 to 4.

**[0028]** In the substituents $Ar^3$ to $Ar^5$. examples of the substituted or unsubstituted aromatic group with 6 to 50 nucleus carbon atoms and the substituted or unsubstituted styryl group each include the same substituent as the above-mentioned $X^1$ represented by the general formula (14).

$Ar^9$s, as well as $Ar^5$s, may be the same as or different from each other when p is 2 or more.

[Anode]

**[0029]** The anode of the organic thin film EL device plays a role for injecting holes into its hole transporting layer or emitting layer. The anode effectively has a work function of 4.5 eV or more. Specific examples of the material of the anode used in the invention include indium tin oxide alloy (ITO), zinc tin oxide alloy (IZO), tin oxide (NESA), gold, silver, platinum, and copper.

The anode can be formed by forming these electrode materials into a thin film by vapor deposition, sputtering or the like. In the invention, in the case where luminescence from the emitting layer is taken out through the anode, the transmittance of the anode to the luminescence is preferably more than 10%. The sheet resistance of the anode is preferably several hundreds Ω/□ or less. The film thickness of the anode, which is varied in accordance with the material thereof, is usually from 10 nm to 1 μm, preferably from 10 to 200 nm.

[Cathode]

**[0030]** For the cathode, the following may be used: an electrode substance made of a metal, an alloy or an electro-conductive compound which has a small work function (4 eV or less), or a mixture thereof. Specific examples of the electrode substance include sodium, sodium-potassium alloy, magnesium, lithium, magnesium/silver alloy, aluminum/aluminum oxide, cesium, calcium, aluminum/lithium alloy, indium, rare earth metals, alkaline chalcogenides and alkaline earth chalcogenides.

This cathode can be formed by making the electrode substance(s) into a thin film by vapor deposition, sputtering or some other method.

In the invention, in the case where luminescence from the emitting layer is taken out through the cathode, it is preferred to make the transmittance of the cathode to the luminescence larger than 10%.

The sheet resistance of the cathode is preferably several hundreds Ω/□ or less, and the film thickness thereof is usually from 10 nm to 1 μm, preferably from 50 to 200 nm.

Next, the other structure of the organic EL devices will be described.

[Hole injecting, transporting layer]

**[0031]** The hole injecting, transporting layer is a layer for helping the injection of holes into the emitting layer so as to transport the holes to a light emitting region. The hole mobility thereof is large and the ionization energy thereof is usually as small as 5.5 eV or less. Such a hole injecting, transporting layer is preferably made of a material which can transport holes to the emitting layer at a lower electric field intensity. The hole mobility thereof is preferably at least $10^{-4}$ $cm^2/V \cdot$ second when an electric field of, e.g., $10^4$ to $10^6$ V/cm is applied.

**[0032]** The material for forming the hole injecting, transporting layer is not particularly limited so long as the material has the above-mentioned preferred natures.

The material can be arbitrarily selected from materials which have been widely used as a hole transporting material in photoconductive materials and known materials used in a hole injecting layer of organic EL devices.

Specific examples thereof include triazole derivatives (see USP No. 3,112,197 and others), oxadiazole derivatives (see USP No. 3,189,447 and others), imidazole derivatives (see JP-B-37-16096 and others), polyarylalkane derivatives (see USP Nos. 3, 615, 402, 3,820,989 and 3,542,544, JP-B-45-555 and 51-10983, JP-A-51-93224, 55-17105, 56-4148, 55-108667, 55-156953 and 56-36656, and others), pyrazoline derivatives and pyrazolone derivatives (see USP Nos. 3,180,729 and 4,278,746, JP-A-55-88064, 55-88065, 49-105537, 55-51086, 56-80051, 56-88141, 57-45545, 54-112637 and 55-74546, and others), phenylene diamine derivatives (see USP No. 3,615,404, JP-B-51-10105, 46-3712 and 47-25336, JP-A-54-53435, 54-110536 and 54-119925, and others), arylamine derivatives (see USP Nos. 3,567,450, 3,180,703, 3,240,597, 3,658,520, 4,232,103, 4,175,961 and 4,012,376, JP-B-49-35702 and 39-27577, JP-A-55-144250, 56-119132 and 56-22437, DE1,110,518, and others), amino-substituted chalcone derivatives (see USP No. 3,526,501, and others), oxazole derivatives (ones disclosed in USP No. 3,257,203, and others), styrylanthracene derivatives (see JP-A-56-46234, and others), fluorenone derivatives (JP-A-54-110837, and others), hydrazone derivatives (see USP Nos. 3,717,462, JP-A-54-59143, 55-52063, 55-52064, 55-46760, 55-85495, 57-11350, 57-148749 and 2-311591, and others), stylbene derivatives (see JP-A-61-210363, 61-228451, 61-14642, 61-72255, 62-47646, 62-36674, 62-10652, 62-30255, 60-93455, 60-94462, 60-174749 and 60-175052, and others), silazane derivatives (USP No. 4,950,950),

polysilanes (JP-A-2-204996), aniline copolymers (JP-A-2-282263), and electroconductive macromolecular oligomers (in particular thiophene oligomers) disclosed in JP-A-1-211399.

**[0033]** As a material of the hole injecting layer, the following can be used: porphyrin compounds (disclosed in JP-A-63-2956965 and others), aromatic tertiary amine compounds and styrylamine compounds (see USP No. 4,127,412, JP-A-53-27033, 54-58445, 54-149634, 54-64299, 55-79450, 55-144250, 56-119132, 61-295558, 61-98353 and 63-295695, and others), in particular, the aromatic tertiary amine compounds.

The following can also be used: 4,4'-bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPD), which has in the molecule thereof two condensed aromatic rings, disclosed in USP No. 5,061,569, and 4,4',4"-tris(N-(3-methylphenyl)-N-phenylamino)triphenylamine (MTDATA), wherein three triphenylamine units are linked to each other in a star-burst form, disclosed in JP-A-4-308688.

Inorganic compounds, such as p-type Si and p-type SiC, as well as the above-mentioned aromatic dimethylidene type compounds listed as the material of the emitting layer can also be used as the material of the hole injecting layer.

**[0034]** The hole injecting, transporting layer can be formed by making the above-mentioned compound(s) into a thin film by a known method, such as vacuum deposition, spin coating, casting or LB technique. The film thickness of the hole injecting, transporting layer is not particularly limited, and is usually from 5 nm to 5 μm. This hole injecting, transporting layer may be a single layer made of one or more out of the above-mentioned materials if this layer contains the compound of the invention in its hole transporting zone. A hole injecting, transporting layer made of a compound different from that in the above-mentioned hole injecting, transporting layer may be stacked thereon.

[Organic semiconductive layer]

**[0035]** The organic semi conductive layer is a layer for helping the injection of holes or electrons into the emitting layer, and is preferably a layer having an electroconductivity of $10^{-10}$ S/cm or more. The material of such an organic semiconductive layer may be an electroconductive oligomer, such as thiophene-containing oligomer or arylamine-containing oligomer disclosed in JP-A-8-193191, an electroconductive dendrimer such as arylamine-containing dendrimer.

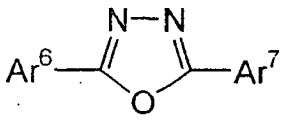
[Electron injecting layer and Electron transporting layer]

**[0036]** The electron injecting layer and the electron transporting layer are each a layer for helping the injection of electrons into the emitting layer, and each have a large electron mobility. The adhesion improving layer is a layer made of a material particularly good in adhesion to the cathode among such electron injecting layers.

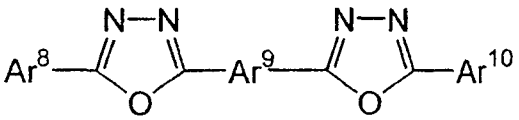
The material used in these layers is, for example, preferably a metal complex of 8-hydroxyquinoline or a derivative thereof. Specific examples of the above-mentioned metal complex of 8-hydroxyquinoline or derivative include metal chelate oxynoid compounds each containing a chelate of oxine (generally, 8-quinolinol or 8-hydroxyquinoline).

**[0037]** The following materials for the electron injecting layer and electron transporting layer can be used in the invention:

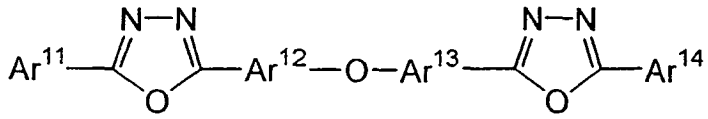
(i) Oxadiazole derivatives represented by the following general formulas (16) to (18):




(16)




(17)

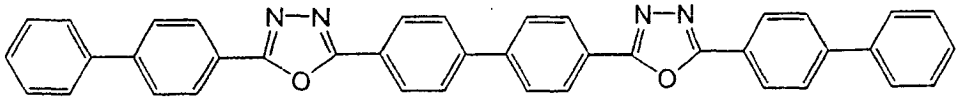


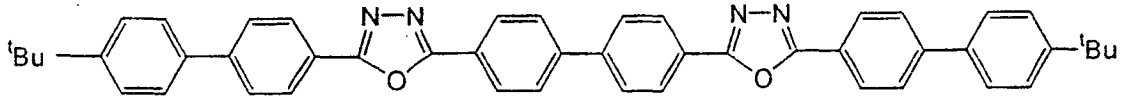
(18)

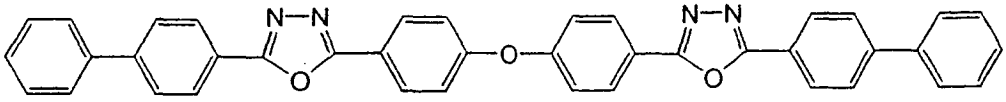
wherein $Ar^6$, $Ar^7$, $Ar^8$, $Ar^{10}$, $Ar^{11}$ and $Ar^{14}$ each represent a substituted or unsubstituted aryl group and may be the same as or different from each other, and $Ar^9$, $Ar^{12}$ and $Ar^{13}$ represent substituted or unsubstituted arylene groups and may be the same as or different from each other.

Examples of the aryl group include phenyl, biphenyl, anthranyl, perylenyl, and pyrenyl groups. Examples of the arylene group include phenylene, naphthylene, biphenylene, anthranylene, perylenylene, and pyrenylene groups. Examples of the substituent include alkyl groups with 1 to 10 carbon atoms, alkoxy groups with 1 to 10 carbon atoms, and a cyano group. The electron transferring compounds are preferably ones having capability of forming a thin film.

**[0038]** Specific examples of the electron transferring compounds include the following:

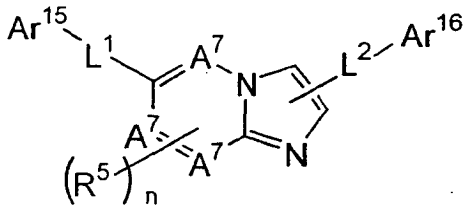






**[0039]**

(ii) Nitrogen-containing heterocyclic derivatives represented by the following general formula (19):



(19)

wherein $A^7$ is a nitrogen atom or carbon atom; $R^5$ is an aryl group which has 6 to 60 carbon atoms and may have a substituent, a heteroaryl group which has 3 to 60 carbon atoms and may have a substituent, an alkyl group which has 1 to 20 carbon atoms, a haloalkyl group which has 1 to 20 carbon atoms, or an alkoxy group which has 1 to 20

carbon atoms; n is an integer of 0 to 4 and when n is an integer of 2 or more, $R^5$s may be the same as or different from each other or $R^5$s adjacent to each other may be bonded to each other to form a substituted or unsubstituted carbocyclic aliphatic ring or a substituted or unsubstituted carbocyclic aromatic ring; $Ar^{15}$ is an aryl group which has 6 to 60 carbon atoms and may have a substituent, or a heteroaryl group which has 3 to 60 carbon atoms and may have a substituent; $Ar^{l6}$ is a hydrogen atom, an alkyl group which has 1 to 20 carbon atoms, a haloalkyl group which has 1 to 20 carbon atoms, an alkoxy group which has 1 to 20 carbon atoms, an aryl group which has 6 to 60 carbon atoms and may have a substituent, or a heteroaryl group which has 3 to 60 carbon atoms and may have a substituent (provided that either one of $Ar^{15}$ and $Ar^{16}$ is a condensed cyclic group which has 10 to 60 carbon atoms and may have a substituent or a condensed heterocyclic group which has 3 to 60 carbon atoms and may have a substituent); $L^1$ and $L^2$ are each a single bond, a condensed cyclic group which has 6 to 60 carbon atoms and may have a substituent, a condensed heterocyclic group which has 3 to 60 carbon atoms and may have a substituent, or a fluorenylene group which may have a substituent.

**[0040]**

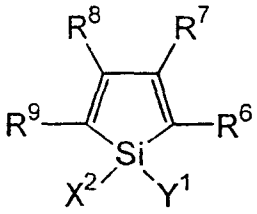
(iii) Nitrogen-containing heterocyclic derivatives represented by the following general formula (20):

$$HAr^{17}\text{-}L^3\text{-}Ar^{18}\text{-}Ar^{19} \qquad (20)$$

wherein $HAr^{17}$ is a nitrogen-containing heterocyclic ring which has 3 to 40 carbon atoms and may have a substituent, $L^3$ is a single bond, an arylene group which has 6 to 60 carbon atoms and may have a substituent, a heteroarylene group which has 3 to 60 carbon atoms and may have a substituent, or a fluorenylene group which may have a substituent, $Ar^{18}$ is a bivalent aromatic hydrocarbon group which has 6 to 60 carbon atoms and may have a substituent, $Ar^{19}$ is an aryl group which has 6 to 60 carbon atoms and may have a substituent or a heteroaryl group which has 3 to 60 carbon atoms and may have a substituent.

**[0041]**

(iv) Silacyclopentadiene derivatives represented by the following general formula (21):

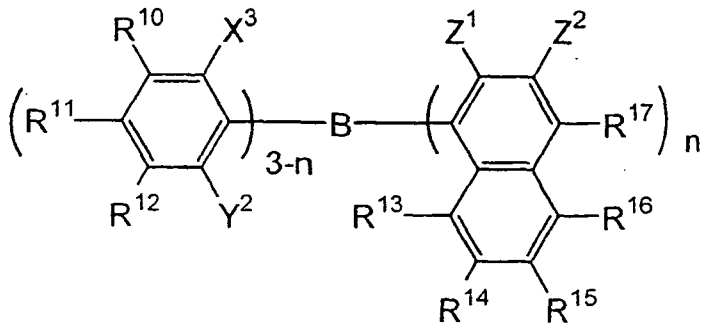



(21)

wherein $X^2$ and $Y^1$ are each a saturated or unsaturated hydrocarbon group with 1 to 6 carbon atoms, an alkoxy group, an alkenyloxy group, an alkynyloxy group, a hydroxyl group, a substituted or unsubstituted aryl group a substituted or unsubstituted heterocyclic group, or $X^2$ or $Y^1$ are bonded to each other to form a saturated or unsaturated ring; $R^6$ to $R^9$ are each a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group with 1 to 6 carbon atoms, an alkoxy group, an aryloxy group, a perfluoroalkyl group, a perfluoroalkoxy group, an amino group, an alkylcarbonyl group, an arylcarbonyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an azo group, an alkylcarbonyloxy group, an arylcarbonyloxy group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, a sulfinyl group, a sulfonyl group, a sulfanyl group, a silyl group, a carbamoil group, an aryl group, a heterocyclic group, an alkenyl group, art alkynyl group, a nitro group, a formyl group, a nitroso group, a formyloxy group, an isocyano group, a cyanate group, an isocyanate group, a thiocyanate group, an isothiocyanate group or a cyano group, or a substituted or unsubstituted fused ring structure formed by two adjacent substituents of $R^6$ to $R^9$: however, in the case where $R^6$ and $R^9$ are a phenyl group, $X^2$ and $Y^1$ are neither an alkyl group nor a phenyl group; in the case where $R^6$ and $R^5$ are a thienyl group, $X^2$, $Y^1$, $R^7$ and $R^8$ do not form the structure where $X^2$ and $Y^1$ are a monovalent hydrocarbon group, and at the same time $R^7$ and $R^8$ are an alkyl group, an aryl group, an alkenyl, or an aliphatic group with a cycle formed by $R^7$ and $R^8$ bonded; in the case where $R^6$ and $R^9$ are a silyl group, $R^7$, $R^8$, $X^2$ and $Y^1$ are each neither a monovalent hydrocarbon group with 1 to 6 carbon atoms nor a hydrogen atom; and in the case where $R^6$ and $R^7$ are bonded to form a condensed structure with a benzene ring, $X^2$ and $Y^1$ are neither an alkyl group nor a phenyl group.

**[0042]**

(v) Borane derivatives represented by the following general formula (22):

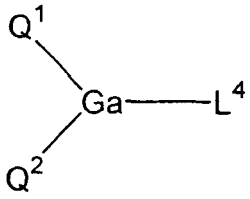


(22)

wherein $R^{10}$ to $R^{17}$ and $Z^2$ are each a hydrogen atom, a saturated or unsaturated hydrocarbon group, an aromatic group, a heterocyclic group, a substituted amino group, a substituted boryl group, an alkoxy group or an aryloxy group; $X^3$, $Y^2$ and $Z^1$ are each a saturated or unsaturated hydrocarbon group, an aromatic group, a heterocyclic group, a substituted amino group, an alkoxy group or an aryloxy group; the substituent of $Z^1$ and $Z^2$ may be bonded to each other to form a condensed ring; n is an integer of 1 to 3, and $Z^1$s may be different from each other when n is 2 or more; however excluded are the compound where n is 1, $X^3$, $Y^2$ and $R^{11}$ are a methyl group and $R^{17}$ is a hydrogen atom or substituted boryl group, and the compound where n is 3 and $Z^1$ is a methyl group.

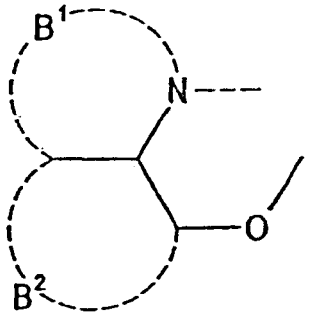
**[0043]**

(vi) Gallium compounds represented by the following general formula (23):



(23)

wherein $Q^1$ and $Q^2$ are a ligand represented by the following general formula (24) and include, but not limited to, quinoline residues such as 8-hydroxy-quinoline and 2-methyl-8- hydroxy-quinoline; $L^4$ is a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group or -OR wherein R is a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group or -O-Ga-$Q^3$ ($Q^4$) wherein $Q^3$ and $Q^4$ are the same legand as $Q^1$ and $Q^2$:




(24)

wherein rings $B^1$ and $B^2$ are each bonded to each other to form a substituted or unsubstituted arylic ring or a substituted or unsubstituted heterocyclic ring.

**[0044]** Specific examples of the rings $B^1$ and $B^2$ include halogen atoms such as chlorine, bromine, iodine and fluorine; substituted or unsubstituted alkyl groups such as methyl, ethyl, propyl, butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, stearyl and trichloromethyl; substituted or unsubstituted aryl groups such as phenyl, naphthyl, 3-methylphenyl, 3-methoxyphenyl, 3-fluorophenyl, 3-trichloromethylphenyl, 3-trifluoromethylphenyl and 3-nitrophenyl; substituted or unsubstituted alkoxy groups such as methoxy, n-butoxy, tert-butoxy, trichloromethoxy, trifluoroethoxy, pentafluoropropoxy, 2,2,3,3-tetrafluoropropoxy, 1,1,1,3,3,3-hexafluoro-2-propoxy and 6-(perfluoroethyl)hexyloxy; substituted or unsubstituted aryloxy groups such as phenoxy, p-nitrophenoxy, p-tert-butylphenoxy, 3-fluorophewoxy; pentafluorophenyl and 3-trifluoromethylphenoxy; substituted or unsubstituted alkylthio groups such as methythio, ethylthio, tert-butylthio, hexylthio, octylthio and trifruoromethyltio; substituted or unsubstituted arylthio groups such as phenylthio, p-nitrophenylthio, p-tert-butylphenylthio, 3-fluorophenylthio, pentafluorophenylthio and 3-trifluoromethylphenylthio; a cyano group; a nitro group, an amino group; mono or di-substituted amino groups such as methylamino, diethylamino, ethylamino, diethylamino, dipropylamino, dibutylamino and diphenylamino; acylamino groups such as bis(acetoxymethyl)amino, bislacetoxyethyl) amino, bis(acetoxypropyl) amino and bis(acetoxybutyl)amino; a hydroxy group; a siloxy group; an acyl group; carbamoyl groups such as methylcarbamoyl, dimethylcarbamoyl, ethylcarbamoyl, diethylcarbamoyl, propylcarbamoyl, butylcarbamoyl and phenylcarbamoyl; a carboxylic group; a sulfonic acid group; an imido group; cycloalkyl groups such as cyclopentyl and cyclohexyl; aryl groups such as phenyl, naphthyl, biphenyl, anthranyl, phenanthryl, fluorenyl and pyrenyl; and heterocyclic groups such as pyridinyl, pyrazinyl, pyrimidinyl, pryidazinyl, triazinyl, indolinyl, quinolinyl, acridinyl, pyrrolidinyl, dioxanyl, piperidinyl, morpholidinyl, piperazinyl, triathinyl, carbazolyl, furanyl, thiophenyl, oxazolyl, oxadiazolyl, benzooxazolyl, thiazolyl, thiadiazolyl, benzothiazolyl, triazolyl, imidazolyl, benzoimidazolyl and puranyl.
Moreover the above-mentioned substitutes may be bonded to each other to form a six-membered aryl or heterocyclic rings.

**[0045]** The metal complexes have the strong nature of an n-type semiconductor and large ability of injecting electrons. Further the energy generated at the time of forming a complex is small and a metal is then strongly bonded to ligands in the complex formed with a large fluorescent quantum efficiency.

**[0046]** In the invention, an electron injecting layer made of an insulator or a semiconductor may be further formed between its cathode and organic layer. At this time, leakage of electric current is effectively prevented so that the electron injecting property can be improved. It is preferred to use, as such an insulator, at least one metal compound selected from the group consisting of alkali metal calcogenides, alkaline earth metal calcogenides, halides of alkali metals, and halides of alkaline earth metals. It is preferred that the electron injecting layer is made of one or more out of these alkali metal calcogenides and the like since the electron injecting property thereof can be further improved. Specifically, preferred examples of the alkali metal calcogenides include $Li_2O$, LiO, $Na_2S$, $Na_2Se$ and NaO. Preferred examples of the alkaline earth metal calcogenides include CaO, BaO, SrO, BeO, BaS, and CaSe. Preferred examples of the halides of alkali metals include LiF, NaF, KF, LiCl, KCl, and NaCl. Preferred examples of the halides of alkaline earth metals include fluorides such as $CaF_2$, $BaF_2$, $SrF_2$, $MgF_2$, and $BeF_2$; and halides other than fluorides.
Examples of the semiconductor constituting the electron transporting layer may be one or any combination of two or more out of oxides, nitrides or oxynitrides containing at least one of Ba, Ca, Sr, Yb, Al, Ga, In, Li, Na, Cd, Mg, Si, Ta, Sb and Zn. The inorganic compound constituting the electron transporting layer preferably forms a microcrystalline or amorphous insulator thin film. If the electron transporting layer is made of the insulator thin film, the thin film becomes a more homogenous thin film. Therefore, pixel defects such as dark spots can be decreased. Examples of such an inorganic compound include the above-mentioned alkali metal calcogenides, alkaline earth metal calcogenides, halides of alkali metals, and halides of alkaline earth metals.

**[0047]** In the invention, a reducing dopant may be consisted in an interfacial region between its electron transferring region or cathode and its organic layer. The reducing dopant is defined as a substance which can reduce an electron transferring compound. Accordingly, various substances which have given reducing properties can be used. For example, at least one substance can be preferably used which is selected from the group consisting of alkali metals, alkaline earth metals, rare earth metals, alkali metal oxides, alkali metal halides, alkaline earth metal oxides, alkaline earth metal halides, rare earth metal oxides, rare earth metal halides, alkali metal organic complexes, alkaline earth metal organic complexes, and rare earth metal organic complexes.

More specific examples of the preferred reducing dopants include at least one alkali metal selected from the group consisting of Na (work function: 2.36 eV), K (work function: 2.28 eV), Rb (work function: 2.16 eV) and Cs (work function: 1.95 eV), and at least one alkaline earth metal selected from the group consisting of Ca (work function: 2.9 eV), Sr (work function: 2.0 to 2.5 eV), and Ba (work function: 2.52 eV). Metals having a work function of 2.9 eV or less are in particular preferred. Among these, a more preferable reducing dopant is at least one alkali metal selected from the group consisting of K, Rb and Cs. Even more preferable is Rb or Cs. Most preferable is Cs.

These alkali metals are particularly high in reducing ability. Thus, the addition of a relatively small amount thereof to an electron injecting zone makes it possible to improve the luminance of the organic EL device and make the life time thereof long. As the reducing dopant having a work function of 2.9 eV or less, any combination of two or more out of these alkali metals is also preferred. Particularly preferred is any combination containing Cs, for example, a combination of Cs and Na, Cs and K, Cs and Rb, or Cs, Na and K. The combination containing Cs makes it possible to exhibit the reducing ability efficiently. The luminance of the organic EL device can be improved and the life time thereof can be made long by the addition thereof to its electron injecting zone.

[Insulator layer]

**[0048]** In the organic EL device, pixel defects based on leakage or a short circuit are easily generated since an electric field is applied to the super thin film. In order to prevent this, it is preferred to insert an insulator thin layer between the pair of electrodes.

Examples of the material used in the insulator layer include aluminum oxide, lithium fluoride, lithium oxide, cesium fluoride, cesium oxide, magnesium oxide, magnesium fluoride, calcium oxide, calcium fluoride, aluminum nitride, titanium oxide, silicon oxide, germanium oxide, silicon nitride, boron nitride, molybdenum oxide, ruthenium oxide, and vanadium oxide.

In the invention, a mixture or laminate thereof may be used.

[Transparent substrate]

**[0049]** The organic EL device of the invention is formed on a transparent substrate. The transparent substrate is a substrate for supporting the organic EL device, and is preferably a flat and smooth substrate having a transmittance of 50% or more to light rays within visible ranges of 400 to 700 nm.

Specific examples thereof include a glass plate and a polymer plate. Examples of the glass plate include soda-lime glass, barium/strontium-containing glass, lead glass, aluminosilicate glass, borosilicate glass, barium borosilicate glass, and quartz. Examples of the polymer plate include polycarbonate, acrylic polymer, polyethylene terephthalate, polyethersulfide, and polysulfone.

[Structure of the organic EL element]

**[0050]** Typical examples of the structure of the organic EL device (A) of the invention include the following:

(a) Anode/emitting layer/intermediate electrode layer/emitting layer/cathode,
(b) Anode/hole injecting layer/emitting layer/intermediate electrode layer/emitting layer/cathode,
(c) Anode/hole injecting layer/emitting layer/intermediate electrode layer/hole injecting layer/emitting layer/cathode,
(d) Anode/emitting layer/electron injecting layer/intermediate electrode layer/emitting layer/electron injecting layer/cathode,
(e) Anode/hole injecting layer/emitting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/emitting layer/electron injecting layer/cathode,
(f) Anode/hole injecting layer/hole transporting layer/emitting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/hole transporting layer/emitting layer/electron injecting layer/cathode,
(g) Anode/hole injecting layer/emitting layer/electron transporting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/emitting layer/electron transporting layer/electron injecting layer/cathode,
(h) Anode/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting

layer/intermediate electrode layer/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/cathode,
(i) Anode/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/adhesion improving layer/cathode,
(j) Anode/insulative layer/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/cathode, and
(k) Anode/inorganic semiconductive layer/insulative layer/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/hole transporting layer/emitting layer/electron transporting layer/electron injecting layer/cathode.

[Examples of producing an organic EL device]

**[0051]** The organic EL device can be produced by forming an anode and an emitting layer, optionally forming a hole injecting layer, an intermediate electrode layer and an electron injecting layer, and further forming a cathode by use of the materials and methods exemplified above. The organic EL device can be produced in the order reverse to the above, i.e., the order from a cathode to an anode.

**[0052]** An example of the production of the organic EL device will be described below which has a structure wherein the following are successively formed over a transparent substrate: anode/hole injecting layer/emitting layer/electron injecting layer/intermediate electrode layer/hole injecting layer/emitting layer/electron injecting layer/cathode.

First, a thin film made of an anode material is formed into a thickness of 1 μm or less, preferably 10 to 200 nm on an appropriate transparent substrate by vapor deposition, sputtering or some other method, thereby forming an anode.

Next, a hole injecting layer is formed on this anode. As described above, the hole injecting layer can be formed by vacuum deposition, spin coating, casting, LB technique, or some other method. Vacuum deposition is preferred since a homogenous film is easily obtained and pinholes are not easily generated. In the case where the hole injecting layer is formed by vacuum deposition, conditions for the deposition are varied in accordance with the used compound (the material for the hole injecting layer), the crystal structure or recombining structure of the hole injecting layer, and others. In general, the conditions are appropriately selected from the following: deposition source temperatures of 50 to 450°C, vacuum degrees of $10^{-7}$ to $10^{-3}$ torr, vapor deposition rates of 0.01 to 50 nm/second, substrate temperatures of - 50 to 300°C, and film thicknesses of 5 nm to 5 μm.

Next, an emitting layer is formed on the hole injecting layer. The emitting layer can be formed by using a desired organic luminescent material and making the material into a thin film by vacuum deposition, sputtering, spin coating, casting or some other method. Of these methods, vacuum deposition is preferred since a homogenous film is easily obtained and pinholes are not easily generated. In the case where the emitting layer is formed by vacuum deposition, conditions for the deposition, which are varied dependently on the used compound, can be generally selected from conditions similar to those for the hole injecting layer.

Next, an electron injecting layer is formed on this emitting layer. Like the hole injecting layer and the emitting layer, the layer is preferably formed by vacuum deposition in order to obtain a homogenous film. Conditions for the deposition can be selected from conditions similar to those for the hole injecting layer and the emitting layer.

Next, an intermediate electrode layer is formed on the electron injecting layer. Furthermore a hole injecting layer is formed on the intermediate electrode layer.

These layers are preferably formed by vacuum deposition in order to obtain a homogenous film like the hole injecting layer and the emitting layer. Conditions for the deposition can be selected from conditions similar to those for the hole injecting layer and the emitting layer.

Next, an emitting layer and electron injecting layer are formed in a way similar to the above-mentioned way.

Lastly, a cathode is stacked thereon to obtain an organic EL device.

The cathode is made of a metal, and vapor deposition or sputtering may be used. However, vacuum deposition is preferred in order to protect underlying organic layers from being damaged when the cathode film is formed.

About the organic EL device production that has been described so far, it is preferred that the formation from the anode to the cathode is continuously carried out, using only one vacuuming operation.

**[0053]** The method for forming each of the layers in the organic EL device of the invention is not particularly limited. A forming method known, such as vacuum deposition or spin coating can be used.

The organic thin film layers in the organic EL device of the invention can be formed by vacuum deposition, molecular beam deposition (MBE method), or a known method of applying a solution wherein one or more organic compounds are dissolved in a solvent, such as dipping, spin coating, casting, bar coating or roll coating.

The film thickness of each of the organic layers in the organic EL device of the invention is not particularly limited. In general, defects such as pinholes are easily generated when the film thickness is too small. Conversely, a high applied

voltage becomes necessary to make the efficiency bad when the film thickness is too large. Usually, therefore, the film thickness is preferably in the range of several nanometers to one micrometer.

**[0054]** In the case where a DC voltage is applied to the organic EL device, luminescence can be observed when the polarity of the anode and that of the cathode are made positive and negative, respectively, and the voltage of 5 to 40 V is applied. Even if a voltage is applied thereto in the state that the polarities are reverse to the above, no electric current flows so that luminescence is not generated at all. In the case where an AC voltage is applied thereto, uniform luminescence can be observed only when the polarity of the anode and that of the cathode are made positive and negative, respectively. The waveform of the AC to be applied may be arbitrarily selected.

**[0055]** The organic EL device of the invention is preferably used for screens of various display equipment such as consumer TVs, large displays, and displays for cellular phones, illuminations and the like.

[Examples]

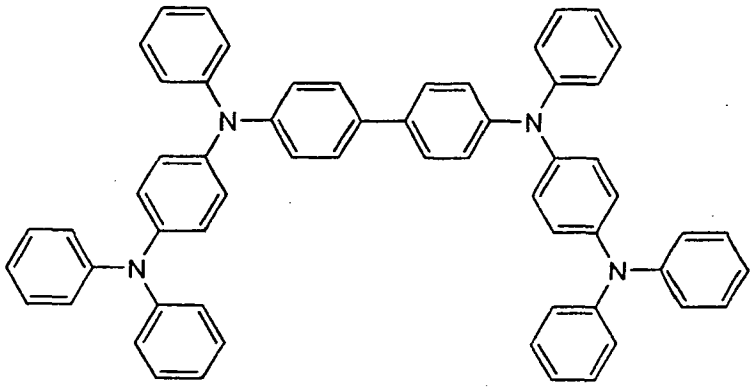
**[0056]** An example of the invention will be described more specifically hereinafter. However, the invention is not limited to this example.

Example 1

**[0057]** A glass substrate, 25 mm x 75 mm x 1.1 mm thick, having an ITO (thickness of 130 nm) transparent electrode (manufactured by Geomatics Co.) was subjected to ultrasonic cleaning in isopropyl alcohol for 5 minutes, ultrasonic cleaning in distilled water having an electric resistance of 20 MΩm for 5 minutes, and then ultrasonic cleaning in isopropyl alcohol for 5 minutes. The resultant ITO substrate was taken out, dried, and immediately subjected to UV ozone cleaning for 30 minutes with a UV ozone equipment manufactured by Samco International Laboratory.

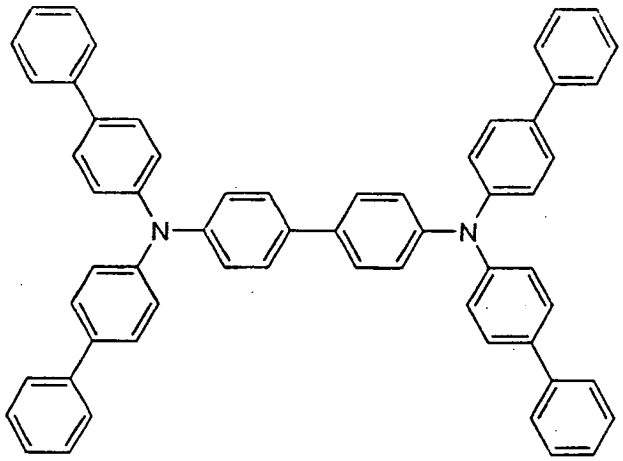
**[0058]** The cleaned glass substrate having transparent electrode lines was set up on a substrate holder in a vacuum deposition device. Then, vacuuming was carried out to $1 \times 10^{-5}$ Pa.

First, an N,N'-bis(N,N'-diphenyl-4-aminophenyl)-N,N-diphenyl-4,4'-diamino-1,1'-biphenyl film (hereinafter referred to as TPD 232 film) was formed into a film in thickness of 60 nm on the surface on which the transparent electrode lines were formed at a deposition rate of 0.1 nm/sec, so as to cover the transparent electrode. The TPD 232 film functioned as a hole injecting layer.



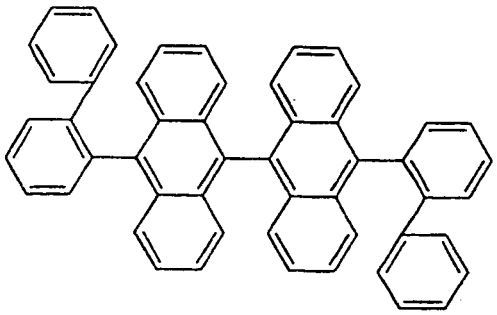

TPD232

**[0059]** After the formation of the TPD 232 film, an N,N,N',N'-tetra(9-biphenyl)-diaminobiphenylene layer (hereinafter referred to as TBDB) having a film thickness of 20 nm was formed on the TPD 232 film at a deposition rate of 0.1 nm/sec. This film functioned as a hole transporting layer.

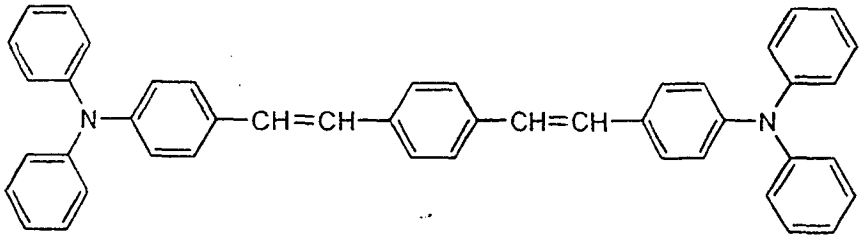


TBDB

**[0060]** Furthermore, a host (hereinafter referred to as H1) was deposited at a deposition rate of 0.2 nm/sec, thereby forming a layer having a thickness of 40 nm on the TBDP film. At this time, as a luminescent molecule, a dopant (hereinafter referred to as D1) was deposited at a deposition rate of 0.01 nm/sec. This layer functioned as the emitting layer.

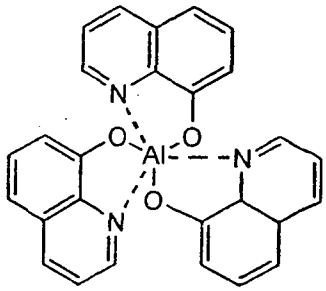


H1



D1

**[0061]** As an electron injecting layer, Alq and Li were deposited at deposition rates of 0.1 nm/sec and 0.01 nm/sec respectively to form a 20 nm thick film. As an intermediate electrode layer, Cs and $MoO_x$ (x is 2 to 3) were co-deposited at deposition rates of 0.01 nm/sec and 0.1 nm/sec respectively to form a 1 nm thick film thereon.



Alq

**[0062]** Next, TPD232, TBDB, H1 and D1, Alq and Li, Cs and $MoO_x$, TPD232, TBDB, H1 and D1, and Alq and Li were similarly formed sequentially.
Furthermore, Al metal was deposited at a deposition rate of 0.8 nm/sec to form a metal cathode, thereby obtaining an organic EL device. The organic EL device contained a total of three emitting layers.

**[0063]** Next, the initial performance of this organic EL device was measured. The results were a driving voltage of 15.0 V, 30 cd/A, and CIEx,y = (0.14, 0.25) at a current density of 1 $mA/cm^2$.
The life time was measured and evaluated at room temperature by driving with a constant direct current. At this time a current was adjusted to the current value at the time of an initial luminance of 3000 nit and the current was continuously applied. A half-life is a period of time until the initial luminance was reduced by half. Moreover a voltage increase during the half-life is the difference in voltage between at the beginning of driving and at the time of reduction by half.

Comparative example 1

**[0064]** An organic EL device was produced in the same manner as in Example 1 except that, as an intermediate electrode layer, ITO was sputtered at a deposition rate of 0.4 nm/sec, thereby forming a 10 nm thick film. The performance thereof was evaluated. The results are shown in Table 1.

Comparative example 2

**[0065]** An organic EL device was produced in the same manner as in Example 1 except that TPD232, TBDB, H1 and D1, and Alq and Li films were formed sequentially, and then an Al film was formed: the number of stacking was one. The performance thereof was evaluated. The results are shown in Table 1.

Comparative example 3

**[0066]** An organic EL device was produced in the same manner as in Example 1 except that, instead of Cs and $MoO_x$, $V_2O_5$ was deposited at a deposition rate of 0.01 nm/sec as an intermediate electrode layer, thereby forming a 1 nm thick film. The performance thereof was evaluated. The results are shown in Table 1.
As a result of life time measurement, a voltage increase during the half-life was larger in this comparative example than in Example 1.

**[0067]**

Table 1

| | Driven at 1 mA/cm$^2$ | | | Life time measurement at initial luminance of 3,000 nit | | Leakage current at -5 V of reverse bias | Intermediate electrode layer | Resistivity of intermediate electrode layer |
|---|---|---|---|---|---|---|---|---|
| | Voltage (V) | L/J (cd/A) | CIEx,y | Half-life (h) | Voltage increase during half-life (V) | (A/cm$^2$) | | ($\Omega$·cm) |
| Example 1 | 15.0 | 30 | 0.14,0.25 | 10000 | 2.5 | $1 \times 10^{-9}$ | $CsMoO_x$ | 0.1 |
| Comparative Example 1 | 15.0 | 29 | 0.14,0.26 | 3000 | 5.0 | $2 \times 10^{-7}$ | ITO | $3 \times 10^{-4}$ |
| Comparative Example 2 | 5.0 | 10 | 0.16,0.26 | 2000 | 1.0 | $5 \times 10^{-9}$ | none | - |
| Comparative Example 3 | 16.0 | 28 | 0.16, 0.26 | 7000 | 8.0 | $5 \times 10^{-9}$ | $VO_x$ | $10^5$ |

Industrial Applicability

**[0068]** The invention provides an organic EL device with a high efficiency and long life time, and a display using the same.

## Claims

**1.** An organic electroluminescent device comprising:

at least two or more emitting layers between an anode and a cathode,
an intermediate electrode layer being interposed between emitting layers,
the intermediate electrode layer being a single layer comprising a semiconductive material, or a multilayer structure of a plurality of layers, at least one of the layers comprising a semiconductive material,
which semiconductive material has a resistivity of 0.001 to 10,000 0-cam, and
comprises an acceptor that is a conductive oxide containing a transition metal, and a donor that is an alkali metal and/or an alkaline earth metal.

**2.** The organic electroluminescent device according to claim 1, wherein the conductive oxide containing a transition metal is at least one oxide selected from the group of $NbO_x$, $MoO_x$, $ReO_x$, $WO_x$, $OsO_x$, $IrO_x$ and $PtO_x$ wherein x is 0.2 to 5.

**3.** The organic electroluminescent device according to claim 1, wherein the acceptor is at least one oxide selected from the group of $Li_xTi_2O_4$, $Li_xV_2O_4$, $Er_xNbO_3$, $La_xTiO_3$, $Sr_xVO_3$, $Ca_xCrO_3$, $Sr_xCrO_3$, $A_xMoO_3$ and $AV_2O_5$, wherein A is K, Cs, Rb, Sr, Na, Li or Ca, and x is 0.2 to 5.

**4.** The organic electroluminescent device according to claim 1, wherein the semiconductive material has a resistivity of not less than 0.001 $\Omega$·cm but less than 100 $\Omega$·cm.

**5.** A display comprising a screen comprising the organic electroluminescent device according to any one of claims 1 to 4.

## Patentansprüche

**1.** Organische Elektrolumineszenz-Vorrichtung, umfassend:

mindestens zwei oder mehr emittierende Schichten zwischen einer Anode und einer Kathode,
eine Zwischenelektrodenschicht, die zwischen den emittierenden Schichten angeordnet ist,
wobei die Zwischenelektrodenschicht eine einzelne Schicht ist, die ein halbleitendes Material umfasst, oder eine Mehrschichtstruktur aus einer Mehrzahl von Schichten, wobei mindestens eine der Schichten ein halbleitendes Material umfasst,
wobei das halbleitende Material einen Widerstand von 0,001 bis 10000 Ω·cm aufweist,
und
einen Akzeptor, der ein ein Übergangsmetall enthaltendes leitfähiges Oxid ist, und einen Donor umfasst, der ein Alkalimetall und/oder ein Erdalkalimetall ist.

2. Organische Elektrolumineszenz-Vorrichtung nach Anspruch 1, wobei das ein Übergangsmetall enthaltende leitfähige Oxid mindestens ein Oxid ist, das ausgewählt wird aus der Gruppe aus $NbO_x$, $MoO_x$, $ReO_x$, $WO_x$, $OsO_x$, $IrO_x$ und $PtO_x$, wobei x 0,2 bis 5 ist.

3. Organische Elektrolumineszenz-Vorrichtung nach Anspruch 1 , wobei der Akzeptor mindestens ein Oxid ist, das ausgewählt wird aus der Gruppe aus $Li_xTi_2O_4$, $Li_xV_2O_4$, $Er_xNbO_3$, $La_xTiO_3$, $Sr_xVO_3$, $Ca_xCrO_3$, $Sr_xCrO_3$, $A_XMoO_3$ und $AV_2O_5$, wobei A K, Cs, Rb, Sr, Na, Li oder Ca ist, und x 0,2 bis 5 ist.

4. Organische Elektrolumineszenz-Vorrichtung nach Anspruch 1, wobei das halbleitende Material einen Widerstand von nicht weniger als 0,001 Ω·cm, aber weniger als 100 Ω·cm aufweist.

5. Display, umfassend einen Bildschirm, der die organische Elektrolumineszenz-Vorrichtung nach einem der Ansprüche 1 bis 4 umfasst.

**Revendications**

1. Dispositif électroluminescent organique comprenant :

au moins deux ou plusieurs couches émettrices entre une anode et une cathode,
une couche d'électrode intermédiaire étant entreposée entre des couches émettrices,
la couche d'électrode intermédiaire étant une seule couche comprenant un matériau semi-conducteur, ou une structure multicouche d'une pluralité de couches, au moins l'une des couches comprenant un matériau semi-conducteur,
lequel matériau semi-conducteur a une résistivité de 0,001 à 10.000 Ω·cm, et
comprend un accepteur qui est un oxyde conducteur contenant un métal de transition, et un donneur qui est un métal alcalin et/ou un métal alcalino-terreux.

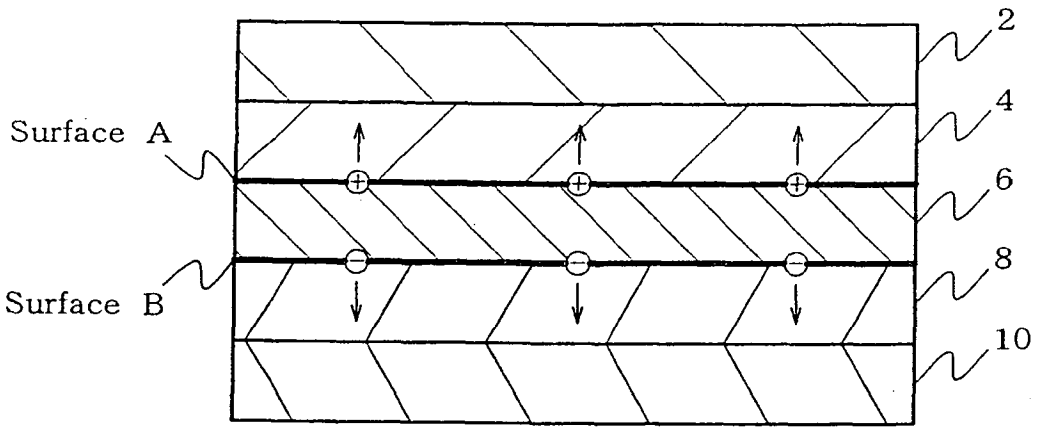
2. Dispositif électroluminescent organique selon la revendication 1, dans lequel l'oxyde conducteur comprenant un métal de transition est au moins un oxyde sélectionné parmi le groupe de $NbO_x$, $MoO_x$, $ReO_x$, $WO_X$, $OsO_x$, $IrO_x$ et $PtO_x$, dans lequel x est 0,2 à 5.

3. Dispositif électroluminescent organique selon la revendication 1, dans lequel l'accepteur est au moins un oxyde sélectionné parmi le groupe de $Li_xTi_2O_4$, $Li_XV_2O_4$, $Er_xNbO_3$, $La_xTiO_3$, $Sr_xVO_3$, $Ca_xCrO_3$, $Sr_xCrO_3$, $A_xMoO_3$ et $AV_2O_5$, dans lequel A est K, Cs, Rb, Sr, Na, Li ou Ca, et x est 0,2 à 5.

4. Dispositif électroluminescent organique selon la revendication 1, dans lequel le matériau semi-conducteur a une résistivité de pas moins de 0,001 Ω·cm, mais moins de 100 Ω·cm.

5. Affichage comprenant un écran comprenant le dispositif électroluminescent organique selon l'une des revendications 1 à 4.

Fig. 1



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|---|---|---|---|
| 专利名称(译) | 有机电致发光器件和使用它的显示器 | | |
| 公开(公告)号 | EP2229039B1 | 公开(公告)日 | 2012-02-29 |
| 申请号 | EP2010166499 | 申请日 | 2004-06-16 |
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| 优先权 | 2003190630 2003-07-02 JP | | |
| 其他公开文献 | EP2229039A1 | | |
| 外部链接 | Espacenet | | |


摘要(译)

一种有机电致发光器件，包括：在阳极（10）和阴极（2）之间的至少两个或更多个发光层（4），（8），以及插入在发光层（4）之间的中间电极层（6），（8），中间电极层（6）是单层或多层的多层结构，至少一层（6）包括电阻率为0.001至10,000Ω·cm的半导体材料。该装置和使用该装置的显示器具有高效率和长寿命。