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I served as Chief Examiner of the certified court interpreter test for the State of California and as a translator and interpreter for various federal agencies through the U.S. Department of State of for more than a decade. I served as an instructor at the University of California at Berkeley and the Middlebury Institute of International Studies at Monterey (MIIS) Graduate Program in Translation.

I have more than 30 years of experience in reviewing and editing thousands of technical, legal, and business submitted to, among others, Japanese judicial authorities, U.S. federal courts, the U.S. International Trade Commission (ITC), and the USPTO Patent Trial and Appeal Board (PTAB).

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I certify under penalty of perjury that the foregoing is true and correct.

Executed this 29th day of May 2024 in Contra Costa County of the State of California.

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(19) **Japan Patent Office (JP)**

(12) **Patent Application Gazette (A)**

(11) Published Application No.

2007-277631

(P2007-277631A)

(43) Published: **Oct. 25, 2007**

(51) Int. Cl.[7]			FI			Theme code (for reference)
C23C	***16/02***	***(2006.01)***	C23C	16/02		3K107
C23C	***16/42***	***(2006.01)***	C23C	16/42		4F100
C23C	***16/505***	***(2006.01)***	C23C	16/505		4K030
B32B	***9/00***	***(2006.01)***	B32B	9/00	A	
H05B	***33/04***	***(2006.01)***	H05B	33/04		

Request for examination: Not yet requested; Number of claims: 18 OL (Total of 64 pages) Continued to last page

(21) Filed Appl. No.: 2006-105025 (P2006-105025)

(22) Filed: Apr. 6, 2006

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(74) F Terms (for reference): 3K107 AA01 CC23 DD16 DD18 EE45 EE48 EE50 FF00 FF02 FF14 FF15 GG03

Continued to last page

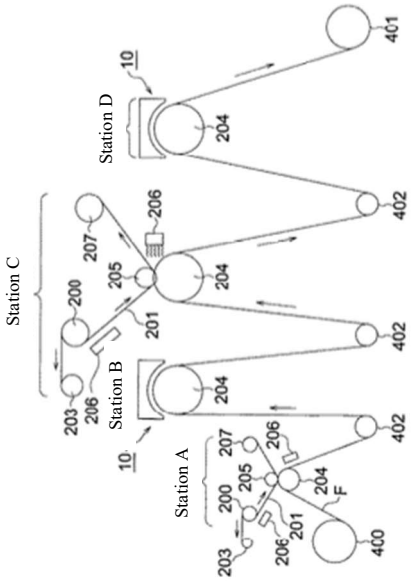
(54) [Title of the Invention] METHOD FOR MANUFACTURING GAS BARRIER THIN FILM LAMINATE, GAS BARRIER THIN FILM LAMINATE, GAS BARRIER RESIN SUBSTRATE MATERIAL AND ORGANIC ELECTROLUMINESCENT DEVICE

(57) [ABSTRACT] (With Revisions)

[PROBLEM] To provide a method for manufacturing a gas barrier thin film laminate that reduces foreign matter trouble in a laminated thin film and has excellent thin film uniformity and gas barrier properties, a gas barrier thin film laminate obtained with the manufacturing method, a gas barrier resin substrate material having the gas barrier thin film laminate on a resin substrate material, and an organic electroluminescent device using the gas barrier resin substrate material.

[SOLUTION MEANS] A method for manufacturing a gas barrier thin film laminate in which at least two ceramic layers are laminated, wherein the method has a foreign matter removal means for removing foreign matter adhered to the surface of at least one ceramic layer.

[SELECTED DRAWING] FIG. 8



[SCOPE OF CLAIMS]

[Claim 1]

A method for manufacturing a gas barrier thin film laminate in which at least two ceramic layers are laminated, wherein the method has a foreign matter removal means for removing foreign matter adhering to a surface of at least one of the ceramic layers before lamination.

[Claim 2]

The method for manufacturing a gas barrier thin film laminate described in claim 1, wherein an average grain size of the foreign matter is between 10 nm and 10 μm inclusive.

[Claim 3]

The method for manufacturing a gas barrier thin film laminate described in claim 1 or 2, wherein a ceramic layer before lamination from which the foreign matter is removed has a carbon content of at least 1% (atomic concentration %).

[Claim 4]

The method for manufacturing a gas barrier thin film laminate described in any of claims 1 or 3, wherein at least one of the ceramic layers is a barrier film with a carbon content of 0.1% (atomic concentration %) or less.

[Claim 5]

The method for manufacturing a gas barrier thin film laminate described in any of claims 1 to 4, wherein the ceramic layers have at least one barrier film whose carbon content is 0.1% (atomic concentration %) or less and at least one buffer film whose carbon content is at least 1% (atomic concentration %).

[Claim 6]

The method for manufacturing a gas barrier thin film laminate described in claim 4 or 5, wherein the ceramic layers have a moisture vapor transmission rate of 1×10^{-3} g/m^2/day.

[Claim 7]

The method for manufacturing a gas barrier thin film laminate described in any of claims 4 to 6, wherein the barrier film has a compressive stress between 0.001 and 20 MPa inclusive.

[Claim 8]

The method for manufacturing a gas barrier thin film laminate described in any of claims 4 to 7, wherein the main component of the barrier film is silicon oxide.

[Claim 9]

The method for manufacturing a gas barrier thin film laminate described in any of claims 4 to 8, wherein the barrier film is formed with a plasma CVD method.

[Claim 10]

The method for manufacturing a gas barrier thin film laminate described in claim 9, wherein the plasma CVD method is carried out at or near atmospheric pressure.

[Claim 11]

The method for manufacturing a gas barrier thin film laminate described in any of claims 5 to 10, wherein the main component of the buffer film is silicon oxide.

[Claim 12]

The method for manufacturing a gas barrier thin film laminate described in any of claims 5 to 11, wherein the buffer film is formed with a plasma CVD method.

[Claim 13]

The method for manufacturing a gas barrier thin film laminate described in claim 12, wherein the plasma CVD method is carried out at or near atmospheric pressure.

[Claim 14]

A gas barrier thin film laminate manufactured with the method for manufacturing a gas barrier thin film laminate described in any of claims 1 to 13.

[Claim 15]

A gas barrier resin substrate material, wherein at least one surface of the resin substrate material has the gas barrier thin film laminate described in claim 14.

[Claim 16]
An organic electroluminescent device having a substrate material, on which are arranged at least an electrode, an organic compound layer, and a sealing film arranged so as to cover the electrode and the organic compound layer, wherein the sealing film is the gas barrier thin film laminate described in claim 14.
[Claim 17]
An organic electroluminescent device having a substrate material, on which are arranged at least an electrode, an organic compound layer, and a sealing film such as to cover the electrode and the organic compound layer and pasted to the substrate to seal the electrode and the organic compound layer, wherein the sealing film is the gas barrier resin substrate material described in claim 15.
[Claim 18]
The organic electroluminescent device described in claim 16 or 17, wherein the substrate material having the electrode and the organic compound layer is the gas barrier resin substrate material described in claim 15.
[DETAILED DESCRIPTION OF THE INVENTION]
[TECHNICAL FIELD]
[0001]
The present invention relates to a method for manufacturing a gas barrier thin film laminate with reduced foreign matter trouble in the laminated thin films and excellent thin film uniformity and gas barrier properties, a gas barrier thin film laminate obtained with that manufacturing method, a gas barrier resin substrate material in which the gas barrier thin film laminate is on a resin substrate material, and an organic electroluminescent device using the gas barrier resin substrate material.
[BACKGROUND TECHNOLOGY]
[0002]
Gas barrier films, which are thin films of metal oxides such as aluminum oxide, magnesium oxide, and silicon oxide formed on the surface of plastic substrates or films, have been widely used for packaging goods that require various gases such as moisture vapor and oxygen to be blocked and for preventing the deterioration of food, industrial goods, pharmaceutical products, and the like. In addition to packaging applications, gas barrier films are used in applications such as liquid crystal display elements, solar cells, and electroluminescent (EL) substrates. In particular, in order to meet the advanced demand for long-term reliability, high degree of freedom of shape, and curved surface display capability, in addition to the requirements for weight reduction and size increase in recent years, transparent plastic and other such film substrate materials have begun to be adopted in place of glass substrates, which are heavy, easily broken, and difficult to make in a large surface area, for transparent substrate materials, which are increasingly being applied to liquid crystal display elements, EL elements, and the like.
[0003]
In addition to meeting the above requirements, plastic film is more productive and cost-effective than glass because of its roll-to-roll capability.
[0004]
However, film substrate materials such as transparent plastic have the problem of gas barrier properties being inferior to glass. If a substrate material with inferior gas barrier properties is used, moisture vapor and air can permeate, degrading the liquid crystal in the liquid crystal cell, for example, and resulting in display defects that degrade the display quality.
[0005]
It is known, for example, to form a metal oxide thin film on a film substrate and make a film substrate material with gas barrier properties in order to solve such problems. Gas barrier films used for packaging materials and liquid crystal display elements include, for example, gas barrier films with silicon oxide deposited on a plastic film (refer, for example, to Patent Document 1) and aluminum oxide deposited on a film substrate (refer, for example, to Patent Document 2), both of which have a moisture vapor barrier property of about 1 $g/m^2/day$.
[0006]
In recent years, due to the development of organic EL displays, which require further gas barrier performance, and larger liquid crystal displays, high-definition displays, and the like, the demand for gas barrier performance on film substrates has risen to about 0.1 $g/m^2/day$ for the moisture vapor barrier.

[0007]

In response, the sputtering and CVD methods, in which a thin film is formed using plasma generated by glow discharge under low-pressure conditions, are being investigated as means to achieve higher barrier performance. In addition, a technology has been proposed to fabricate a barrier film with a structure consisting of alternating layers of organic and inorganic films with a vacuum deposition method (refer, for example, to Patent Document 3).

[0008]

However, these thin film deposition methods require processing under reduced-pressure conditions, and in order to obtain low pressure, the vessel needs an expensive vacuum chamber, and there is also a further need to install a vacuum exhaust apparatus. In addition, because processing is carried out in a vacuum, a large vacuum chamber must be used when processing large-area substrates, and a high-power vacuum exhaust apparatus is also required. As a result, the equipment is extremely expensive, and at the same time, when the surface treatment of plastic substrates with high water absorption is carried out, it takes a long time to obtain the prescribed vacuum level because the absorbed water vaporizes, resulting in the problem of high processing costs. Furthermore, each time a treatment is performed, the vacuum of the vacuum chamber has to be broken for removal, and the next process, such as forming an organic film, has to be performed under atmospheric pressure, resulting in a significant loss of productivity, especially as more organic and inorganic films are layered to achieve moisture vapor barrier properties.

[0009]

In response to the above problems, in the formation of a barrier film with an alternating layered structure of organic/inorganic films, a method of forming an inorganic film using discharge plasma treatment near atmospheric pressure is disclosed, and coating and vacuum deposition methods are also mentioned as organic film formation methods (refer, for example, to Patent Document 4). However, even though the inorganic film is formed with the atmospheric pressure plasma technique in this method, it is not appropriate to form the organic film by coating, which requires a drying step, and vacuum deposition, which requires a vacuum chamber, in terms of achieving high productivity. The disclosed inorganic film formation method uses expensive argon as the discharge gas, which causes high raw material costs, and uses the known single-frequency pulse electric field processing conditions described in Patent Appl. Publication No. JP 2001-49443 as the discharge plasma processing conditions, which not only results in a film that is not of good quality and has low plasma density, but a slow film formation speed and extremely low productivity.

[0010]

Another method of forming an organic film (plasma polymerization film) using discharge plasma under pressure near atmospheric pressure has been disclosed (refer, for example, to Patent Documents 5 and 6). In such a thin film formation method using a discharge plasma technique, it is known that if foreign matter is attached to the surface of the substrate material being used, pinholes will be produced and the barrier property will be inhibited when thin film formation is performed subsequently. As a means to solve such a problem, a method for removing foreign matter on the substrate material on which the gas barrier film is formed is known, and, for example, a method for manufacturing a plastic film in which foreign matter adhering to the film is removed upstream of the portion where a functional film is provided when forming the functional film on at least one side of a film in a plastic film production line, specifically, a method for removing foreign matter using an adhesive rotating roll whose adhesive strength is 500-5000 Pa is disclosed (refer, for example, to Patent Document 7).

[0011]

However, in the case of gas barrier thin film laminates in which a metal oxide thin film is formed on a film substrate material and high barrier performance is required, during, for example, the thin film formation process using discharge plasma, minute particles of the thin film forming material or the like are formed during plasma discharge, and these particles (foreign matter) attached to the already-formed first barrier film, and when a second barrier film is next formed, pinhole failure is caused by the foreign matter attached to the surface, resulting in a significant deterioration of the gas barrier performance.

[0012]

As a result of the present inventors' examination of the above problems, it was found that particles are easily generated by plasma etching, especially when a second barrier film is deposited on a ceramic film containing carbon.

[Patent Document 1] Japanese Patent Publication No. JP S53-12953
[Patent Document 2] Japanese Patent Appl. Publication No. JP S58-217344
[Patent Document 3] WO No. 00/026973 Pamphlet
[Patent Document 4] Japanese Patent Appl. Publication No. JP 2003-191370
[Patent Document 5] Japanese Examined Patent Application Publication No. JP H2-48626
[Patent Document 6] Japanese Patent Appl. Publication No. JP H10-340797
[Patent Document 7] Japanese Patent Appl. Publication No. JP 2000-13020

[DISCLOSURE OF THE INVENTION]

[PROBLEM TO BE SOLVED BY THE INVENTION]

[0013]

The present invention was invented in view of the above-mentioned problems, and it is an object of the present invention to provide a method for manufacturing a gas barrier thin film laminate that reduces foreign matter trouble in a laminated thin film and has excellent thin film uniformity and gas barrier properties, a gas barrier thin film laminate obtained using that manufacturing method, a gas barrier resin substrate material having the gas barrier thin film laminate on a resin substrate material, and an organic electroluminescent device using the gas barrier resin substrate material.

[MEANS TO SOLVE THE PROBLEM]

[0014]

The above-mentioned object of the present invention is achieved with the following configuration.

[0015]

1. A method for manufacturing a gas barrier thin film laminate in which at least two ceramic layers are laminated, wherein the method has a foreign matter removal means for removing foreign matter attached to a surface of at least one of the ceramic layers before lamination.

[0016]

2. The method for manufacturing a gas barrier thin film laminate described in 1, wherein an average grain size of the foreign matter is between 10 nm and 10 μm inclusive.

[0017]

3. The method for manufacturing a gas barrier thin film laminate described in 1 or 2, wherein a ceramic layer before lamination from which the foreign matter is removed has a carbon content of at least 1% (atomic concentration %).

[0018]

4. The method for manufacturing a gas barrier thin film laminate described in any of 1 or 3, wherein at least one of the ceramic layers is a barrier film with a carbon content of 0.1% (atomic concentration %) or less.

[0019]

5. The method for manufacturing a gas barrier thin film laminate described in any of 1 to 4, wherein the ceramic layers have at least one barrier film whose carbon content is 0.1% (atomic concentration %) or less and at least one buffer film whose carbon content is at least 1% (atomic concentration %).

[0020]

6. The method for manufacturing a gas barrier thin film laminate described in any of 1 to 5, wherein the ceramic layers have a moisture vapor transmission rate of 1×10^{-3} g/m^2/day.

[0021]

7. The method for manufacturing a gas barrier thin film laminate described in any of 4 to 6, wherein the barrier film has a compressive stress between 0.001 and 20 MPa inclusive.

[0022]

8. The method for manufacturing a gas barrier thin film laminate described in any of 4 to 7, wherein the main component of the barrier film is silicon oxide.

[0023]

9. The method for manufacturing a gas barrier thin film laminate described in any of 4 to 8, wherein the barrier film is formed with a plasma CVD method.

[0024]

10. The method for manufacturing a gas barrier thin film laminate described in 9, wherein the plasma CVD method is carried out at or near atmospheric pressure.

[0025]

11. The method for manufacturing a gas barrier thin film laminate described in any of 5 to 10, wherein the main component of the buffer film is silicon oxide.

[0026]

12. The method for manufacturing a gas barrier thin film laminate described in any of 5 to 11, wherein the buffer film is formed with a plasma CVD method.

[0027]

13. The method for manufacturing a gas barrier thin film laminate described in 12, wherein the plasma CVD method is carried out at or near atmospheric pressure.

[0028]

14. A gas barrier thin film laminate manufactured with the method for manufacturing a gas barrier thin film laminate described in any of 1 to 13.

[0029]

15. A gas barrier resin substrate material, wherein at least one surface of a resin substrate material has the gas barrier thin film laminate described in 14.

[0030]

16. An organic electroluminescent device having a substrate material, on which are arranged at least an electrode, an organic compound layer, and a sealing film arranged so as to cover the electrode and the organic compound layer, wherein the sealing film is the gas barrier thin film laminate described in 14.

[0031]

17. An organic electroluminescent device having a substrate material, on which are arranged at least an electrode, an organic compound layer, and a sealing film that covers the electrode and the organic compound layer and is pasted to the substrate material to seal the electrode and the organic compound layer, wherein the sealing film is the gas barrier resin substrate material described in 15.

[0032]

18. The organic electroluminescent device described in 16 or 17, wherein the substrate material having the electrode and the organic compound layer is the gas barrier resin substrate material described in 15.

[EFFECT OF THE INVENTION]

[0033]

According to the present invention, it is possible to provide a method for manufacturing a gas barrier thin film laminate that reduces foreign matter trouble in a laminated thin film and has excellent thin film uniformity and gas barrier properties, a gas barrier thin film laminate obtained with that manufacturing method, a gas barrier resin substrate material having the gas barrier thin film laminate on a resin substrate material, and an organic electroluminescent device using the gas barrier resin substrate material.

[BEST CONFIGURATION FOR REDUCING THE INVENTION TO PRACTICE]

[0034]

The best configuration for reducing the present invention to practice is described below in detail.

[0035]

As a result of diligent investigation of these problems, the present inventors found that, in a method for manufacturing a gas barrier thin film laminate in which at least two ceramic layers are laminated, a method for manufacturing a gas barrier thin film laminate having a foreign matter removal means for removing foreign matter attached to the surface of at least one ceramic layer before lamination reduces foreign matter trouble in laminated thin films and is excellent in thin film uniformity and gas barrier properties, and arrived at the present invention.

[0036]

As is conventionally known, simply applying a foreign matter removal treatment only to the substrate material before forming a gas barrier thin film laminate is not sufficient for the gas barrier properties when applied to fields where advanced of gas barrier properties are required, such as organic electroluminescent devices. In further detail, while a gas barrier film substrate material formed with a metal oxide thin film on a conventionally known film substrate has only a moisture vapor barrier property of about 2 $g/m^2/day$ or an oxygen transmission rate of about 2 $ml/m^2/day$ at most, as mentioned above, the development of organic electroluminescent displays, larger liquid crystal displays, high-definition displays, and the like, which require even higher gas barrier performance, has increased the demand for gas barrier performance in the film substrate up to 10^{-3} $g/m^2/day$ in the moisture vapor barrier.

[0037]

Therefore, the present inventors investigated a method for manufacturing a gas barrier thin film laminate provided with high gas barrier performance, and as a result, while a certain level of effect was certainly found against foreign matter trouble caused by foreign matter in conventional methods of removing only foreign matter and the like adhered to the substrate when a first ceramic layer thin film is formed on a substrate material and then a second ceramic layer is laminated in a method for manufacturing a gas barrier thin film laminate in which at least two ceramic layers are successively laminated, when, for example, gas containing a thin film forming gas is supplied and a high-frequency electric field is applied to the discharge space to excite the gas using a plasma CVD method, there is often a contribution to the formation of the first ceramic layer, but in some instances, there are micro-particles in the discharge space that attach to the surface of the first ceramic layer. It was found that the generation of such micro-particles (foreign matter) occurs particularly in the first ceramic layer (what is referred to as the ceramic layer before lamination in the present invention) when the carbon content is at least 1% (carbon concentration%).

[0038]

Building on such results, the present invention is characterized by, for example, providing a foreign matter removal means that removes foreign matter adhered to the first ceramic layer surface after being formed on the substrate material but before the second ceramic layer is formed.

[0039]

The present invention is described below in detail.

[0040]

In the method for manufacturing a gas barrier thin film laminate of the present invention, a foreign matter removal means for removing foreign matter adhering to the surface of at least one ceramic layer before lamination is provided in a method for manufacturing a gas barrier thin film laminate in which at least two ceramic layers are laminated.

[0041]

As a foreign matter removal means applicable in the present invention, a means that can effectively remove foreign matter with an average grain size of 10 nm to 10 μm inclusive adhering to the surface of at least one ceramic layer before lamination is preferable, though this range is not particularly limiting.

[0042]

Examples of the foreign matter removal means according to the present invention include a contact-type foreign matter removal device and a non-contact-type foreign matter removal device.

[0043]

The contact-type foreign matter removal apparatus is a method for removing foreign matter in which an adhesive tape, an adhesive roller, a brush roller, or the like is brought into direct contact with a ceramic layer surface formed on the substrate material before lamination. The contact-type foreign material removal device using an adhesive roller includes, for example, a contact-type foreign material removal method using adhesive tape (e.g., Cleaning Tape EC-315 manufactured by Sumiron Co., Ltd.), a contact-type foreign material removal device using a rubber roller and an adhesive roller (e.g., the CM6 series manufactured by Teknek Ltd. in the UK), a contact-type web cleaner consisting of a cleaning roller, an adhesive roller, and an electrostatic removal bar (e.g., manufactured by Kelva in Sweden), and a turbo cleaner consisting of a high-speed rotating brush and a vacuum cleaner (e.g., Turbo Cleaner TURBO-F model by Shinko Co., Ltd.). However, the Turbo Cleaner is not a favorable apparatus for use in the present invention because the target size of foreign matter is 10 μm or larger, the Turbo Cleaner cannot completely remove foreign matter from the entire area because of the use of brushes, and scratches and the like result on the parts that come in contact with the brushes.

[0044]

It is preferable to use a static eliminating means in combination with the contact-type foreign matter removal means from the perspective of enhancing the efficiency of foreign matter removal. In addition to the ordinary blower type (ion air irradiation) and contact type (static removal bar), a high-density static removal system (Patent Appl. Publication No. JP H7-263173) can be used as the static removal means, which system consists of a static removal device with a plurality of positive and negative ion generating static removing electrodes and ion suction electrodes facing each other to sandwich the substrate material, followed by a positive and negative direct current type static removal device.

[0045]

FIG. 1 is a schematic configuration drawing showing an example of a contact-type foreign material removal device.

[0046]

FIG. 1a) is a schematic configuration drawing showing an example of a contact-type foreign material removal means using adhesive tape. A foreign matter removal unit peels off and winds up a protective sheet 202 with a protective sheet take-up roller 203 from an adhesive tape supply roller, which has an adhesive tape 201 and the protective sheet 202 stacked in roll form, while the adhesive tape 201 is supplied to a contact section of a gas barrier film F forming a ceramic layer before lamination. The gas barrier film F has a ceramic layer formed in the previous process using, for example, a plasma CVD method, and foreign matter P attaches to the surface of the gas barrier film F during the formation process. The surface of the gas barrier film F and the adhesive tape 201 are made to meet while being pressed together by a guide roller 204 and a nip roller 205, and the foreign matter P adhering to the gas barrier film surface is transferred to the adhesive tape 201 for removal. Then the adhesive tape 201 holding the foreign matter is wound up on a take-up roller 207.

[0047]

In addition, a static removal device 206 is installed near the separation area of the adhesive tape 201 and the protective sheet 202 with the object of removing static electricity generated when the adhesive tape 201 is peeled off of the protective sheet 202 and when the gas barrier film F is separated from the adhesive tape 201. In this way, the second ceramic layer is laminated in a later process on the gas barrier film F that had adhering foreign matter removed in an earlier process.

[0048]

FIG. 1b) is a schematic configuration drawing showing an example of a contact-type web cleaner configured from a cleaning roller, an adhesive roller, and an electrostatic removal bar, in which a gas barrier film F conveyed from the previous process and a cleaning roller 210 are made to meet via a guide roller 204, and foreign matter P attached to the gas barrier film F is transferred to the cleaning roller 210, and then the foreign matter P on the cleaning roller 210 is transferred again to an adhesive roller 211 located above the cleaning roller 210. This adhesive roller 211 is replaced with a new adhesive roller 211 when the limit of foreign matter the adhesive area section can hold is approached. A static removal device 206 is arranged downstream of the gas barrier film F from which foreign matter P has been removed to remove static electricity generated when the gas barrier film F is separated from the cleaning roller 210.

[0049]

As the non-contact foreign matter removal device, the main method is to release and remove adhered foreign matter in a non-contact state by blowing ultrasonic vibration air or blown air on the foreign matter adhered to the surface of the gas barrier layer formed on the gas barrier film F.

[0050]

As a non-contact, ultrasonic-type foreign matter removal device, an ultrasonic dry cleaner consisting of an ultrasonic vibration air generator and a vacuum head that sucks released foreign matter (e.g., models UVU-F, VUV-F, NSHV-F, VUV-HG, and VUV-FI & FII manufactured by Shinko Co., Ltd.) can be used. This removal method uses an ultrasonic transmitter to generate ultrasonic vibrating air, which is sprayed onto the surface of the gauze [*sic*: gas] barrier layer to which foreign matter has adhered, the turbulence caused by the collision of the ultrasonic air destroys the boundary layer between the gauze [*sic*: gas] barrier layer surface and the foreign matter, and the air cutter effect removes the foreign matter. The removed foreign matter is suctioned by the vacuum head arranged at the top and discharged out of the system. In this process, it is preferable to use a static removal device to remove static before blowing ultrasonic vibrating air to ensure the release of foreign matter.

[0051]

FIG. 2 is a schematic configuration drawing showing an example of a non-contact-type foreign matter removal device that uses ultrasonic waves.

[0052]

In FIG. 2, as in FIG. 1, a gas barrier film F that has foreign matter P adhered to the surface and is conveyed from the previous process via a guide roller 204 is subjected to the removal of static electricity using an static removal device 206 before removal of the foreign matter, and then an ultrasonic-type foreign matter removal apparatus arranged at a position opposite to the top of the guide roller 204 removes the foreign matter. The foreign material removal device is constituted of pressure heads 300 that generate ultrasonic vibration air and a vacuum head 303 that suctions and removes the released foreign material P. Inside each of the pair of pressure heads 300 is an ultrasonic wave generator 301, which generates ultrasonic vibration air that is blown toward the foreign material P through air blowing holes 302, which are arranged diagonally, to release the foreign material P from the gas barrier film F, and the released foreign material P is then sucked through a suction hole 305 of the vacuum head section 303, which is located at the center of the vacuum head 303, and removed.

[0053]

Another non-contact-type foreign matter removal apparatus that uses blown air is a non-contact web cleaner (e.g., the Web Cleaner manufactured by Kelva). This non-contact-type web cleaner consists of a cleaner head installed above the gas barrier film and a suction head arranged below the gas barrier film. Air is blown from a slit in the center of the cleaner head, and air is sucked from air suction holes on both sides of the suction head. At this time, the flow of air imparts slight vibrations to the gas barrier film, and these vibrations remove foreign matter, which is then eliminated through the air suction holes.

[0054]

In the method for manufacturing a gas barrier thin film laminate of the present invention, it is essential to have a foreign matter removal means to remove foreign matter adhering to the surface of at least one ceramic layer before lamination, but a similar foreign matter removal treatment is also favorably applied to the substrate material before forming the gas barrier thin film laminate from the perspective of increasing the foreign matter removal efficiency and further enhancing the homogeneity of the thin film.

[0055]

Next, the gas barrier thin film laminate of the present invention is described.

[0056]

The ceramic layer composing the gas barrier thin film laminate of the present invention is favorably constituted as described below from the perspective of enhancing the effect of the foreign matter removal means according to the present invention.

[0057]

1) The ceramic layer to which the foreign matter removal means according to the present invention is applied favorably has a carbon content of at least 1% (atomic concentration %) from the perspective of better demonstrating the effect of the present invention.

[0058]

2) At least one of the ceramic layers is preferably a barrier film with a carbon content of 0.1% (atomic concentration %) or less.

[0059]

3) The ceramic layer preferably has a structure of one or more layers of a barrier film with a carbon content of 0.1% (atomic concentration %) or less and a buffer film with a carbon content of at least 1% (atomic concentration %).

[0060]

The gas barrier thin film laminate and the ceramic layer constituting same are described below in detail.

[0061]

The gas barrier thin film laminate of the present invention has high gas barrier performance, but it is preferable that the moisture vapor transmission rate be 0.001 $g/m^2/day$ or less and the oxygen transmission rate be 0.001 $ml/m^2/day/atm$ or less, these properties impart excellent gas barrier performance to organic EL devices when the gas barrier thin film laminate is used as a substrate or the like in a display such as an organic EL device, and by using the plasma CVD method according to the present invention, this gas barrier thin film laminate and this resin substrate have high transparency and are excellent gas barrier resin substrate materials with little coloration.

[0062]

The moisture vapor transmission rate ($g/m^2/day$) is measured by the method described in JIS K 7129B. The PERMATRAN-W3/33MG module, a water vapor transmission coefficient measuring device manufactured by MOCON, can be used for measurement.

[0063]

The oxygen transmission coefficient ($ml/m^2/day/atm$) can also be measured according to JIS K 7126B using the OX-TRAN 2/21 ML module manufactured by MOCON, which is an oxygen transmission rate analyzer.

[0064]

The gas barrier thin film laminate of the present invention is a laminated film having at least two ceramic films formed on a resin substrate material.

[0065]

In detail, these at least two ceramic films comprise a buffer film and a barrier film. The gas barrier thin film laminate of the present invention consists of a laminate comprising these buffer and barrier films (each of which may have two or more layers).

[0066]

To ensure the gas barrier performance, the barrier film, which is at least one layer of the ceramic films composing the gas barrier thin film laminate of the present invention, favorably has a moisture vapor transmission rate of 1×10^{-3} $g/m^2/day$ or less.

[0067]

The gas barrier thin film laminate of the present invention consists of a barrier film and a buffer film, and as described below, the barrier film, which has a high density and low gas and moisture vapor permeability, is a ceramic film that has a dense structure, is rigid, and breaks easily, and therefore by laminating a flexible ceramic film with the same composition and relatively low density and flexibility compared to the gas barrier film as a buffer film to relieve stress, both flexibility and gas barrier performance are attained.

[0068]

In the present invention, the gas barrier thin film laminate comprising a buffer film and a barrier film is composed of a buffer film and a barrier film, both of which contain ceramic materials, and the ceramic materials composing each film may be metal oxides, metal nitrides, metal carbides, metal sulfides, metal halides, and mixtures thereof (metal oxynitrides, metal oxide halides, metal nitride carbides, and the like). Of these, metal oxides, metal oxynitrides, and metal nitrides are preferable, and specific examples include silicon oxide, aluminum oxide, silicon oxide nitride, aluminum oxide nitride, magnesium oxide, zinc oxide, indium oxide, and tin oxide.

[0069]

In particular, at least one of silicon oxide, silicon oxide nitride, and silicon nitride is preferable.

[0070]

In the present invention, therefore, the buffer film and the gas barrier film have identical compositions, and it is preferable that each film has identical compositions. Having identical compositions as intended in the present invention means that at least 50% and preferably at least 70% of the substances composing the films are composed of the same compounds.

[0071]

The thickness of the gas barrier thin film laminate comprising the buffer film and the ceramic film is preferably in the range of 1-5000 nm, and even more preferably in the range of 5-500 nm, although the optimum conditions vary depending on the type and composition of the materials used and the materials are selected as appropriate. This is because if the gas barrier thin film laminate is thinner than the above range, it is difficult to obtain a uniform film and barrier properties against gases. In particular, the thickness of the barrier film should be in the range of 1-5000 nm, and even more preferably in the range of 5-500 nm. If the barrier film is thicker than this range, it is difficult to maintain flexibility in the gas barrier resin substrate material (film), and the gas barrier resin substrate material may crack or otherwise be damaged due to external factors such as bending and pulling after film formation.

[0072]

The buffer film acts as a stress reliever, but if the buffer film is also used as an adhesion film to improve the adhesion between the substrate material and the barrier film, the buffer film is preferably be 1-500 nm more preferably 20-200 nm.

[0073]

If provided on the top layer, the buffer film serves as a protective film, in which case a buffer film thickness of 1-1000 nm is preferable and 100–800 nm is even more preferable.

[0074]

In the present invention, at least the barrier film of the gas barrier thin film laminate comprising a buffer film and a barrier film containing ceramic material preferably has a compressive stress of 0.001 to 20 MPa inclusive.

[0075]

Compressive stress is a stress generated inside the formed film, and in the case of compressive stress, a film formed on the substrate material shrinks in relation thereto, which is expressed as positive internal stress, and conversely, when tensile stress causes a negative curl, that stress is expressed as negative internal stress (tensile stress).

[0076]

<Method for measuring internal stress>

The measurement of internal stress in a ceramic material film is carried out with the following method. A ceramic film of the same composition and thickness as the measurement film is produced on a quartz substrate 10 mm wide, 50 mm long, and 0.1 mm thick to a thickness of 1 μm with the same method, and the curl produced in the sample is measured with the thin film property evaluation apparatus MH4000 manufactured by NEC San-ei Instruments, Ltd., with the concave side of the sample facing up. In general, a positive curl, in which the film side shrinks in relation to the substrate material due to compressive stress, is considered positive internal stress (compressive stress), and conversely, a negative curl caused by tensile stress is considered negative internal stress (tensile stress).

[0077]

In the case of such a film with low internal stress, the internal strain is small, which means that the film is smooth and, on average, resistant to deformation by bending and the like, and therefore, among the films composing the product thin film [*sic:* the thin film] laminate of the present invention, at least the barrier film in particular preferably has low compressive stress of 0.001 to 20 MPa inclusive.

[0078]

Since the ceramic layer according to the present invention is formed to have a moisture vapor transmission rate of 1×10^{-3} g/m^2/day or less and is a high-density film with a dense structure, the ceramic layer is susceptible to breakage and cracking, and preferably has a low internal stress with a low compressive stress of 0.001 to 20 MPa inclusive. If the internal stress is too high, the ceramic layer is particularly susceptible to breakage and cracking, sufficient care must be taken in manufacturing and further processing the film material using this ceramic layer, and the process yield and the like are low. Conversely, if the internal stress is too low, the stress may be partially tensile, and the film will similarly crack or fissure easily, resulting in a non-durable membrane.

[0079]

In the present invention, a ceramic film comprising a ceramic material such as silicon oxide or silicon oxynitride can be easily formed on the resin substrate material using methods such as a sol-gel method, vacuum deposition, sputtering, plasma CVD, and even plasma CVD at or near atmospheric pressure.

[0080]

In the present invention, it is preferable to form the ceramic material films with compressive stress as low as between 0.001 and 20 MPa inclusive using any of these methods.

[0081]

However, the plasma CVD method is preferable over sol-gel methods (wet methods) such as spray and spin coating because with the sol-gel methods, it is difficult to obtain molecular-level smoothness and the use of solvents and the like limits the substrate materials that can be used. Of these methods, the plasma CVD method at or near atmospheric pressure (hereinafter referred to as the atmospheric pressure plasma CVD method) is preferable for being suitable for producing low-strain ceramic material films with low internal stress because a depressurization chamber and the like are not required and film manufacturing is high speed for highly productive film formation. The expression near atmospheric pressure indicates a pressure of 20-110 kPa, but 93-104 kPa is preferable to obtain the favorable effect described in the present invention. The details of the formation conditions of the ceramic material film with the atmospheric pressure plasma CVD method are described below.

[0082]

As the ceramic material in the laminate comprising a buffer film and a barrier film containing the ceramic material described above, it is preferable to use silicon oxide or silicon oxide nitride as the main material, and it is particularly preferable to use silicon oxide as the main material.

[0083]

Using silicon oxide as the main material means that the film has at least 50% and preferably at least 70% of silicon oxide in the ceramic composition.

[0084]

In particular, the barrier film is preferably a dense film with a high density, while the buffer film is a flexible film with a slightly lower density. The density of these films can be found with an X-ray reflectometry method or the like.

[0085]

For an overview of the X-ray reflectivity method, refer to *X-sen Kaisetsu Handbook* [X-Ray Diffraction Handbook], page 151 (Rigaku Corporation (Ed.). 2000. International Academic Publishing) and *Chemical Industry*, January 1999, no. 22.

[0086]

However, the density in ceramic films is closely correlated with the carbon content, for example, the barrier film is preferably a ceramic composition with at least Si and O atoms, and the buffer film is likewise preferably a ceramic composition with at least Si, O, and C atoms.

[0087]

In the present invention, it is preferable to separate the buffer film and the barrier film in a thin film laminate comprising these films according to the present invention constituted of ceramic compositions, and the difference in the content of raw material compounds, the difference in hardness between the films or the like may be used as a method for confirming the difference in density between the thin films, but is preferable to measure the difference in carbon content in each ceramic film to separate the buffer film and barrier film.

[0088]

That is, in the gas barrier thin film laminate with a buffer film and a barrier film of the present invention, a low density film correlates to a high carbon content film, and a high density film correlates to a low carbon content film, so the difference in carbon content between the ceramic material films makes it possible to confirm the boundary portion of each film (layer), which has a different density.

[0089]

To make the ceramic material film dense in the present invention, when, for example, silicon oxide, silicon oxide nitride, or silicon nitride, which are preferable as the barrier film in the present invention, is used, a film with low carbon atom content between 0 and 0.1 at% inclusive is preferable. When, for example, silicon oxide, silicon oxide nitride, or silicon nitride is used to make the buffer film the same composition as the gas barrier film and a relatively flexible layer, the carbon content should be higher than that of the barrier film. Preferably, the carbon content of the film is in the range of 1.0-40 at%. Here, at% represents the atomic concentration %, which is described below.

[0090]

In the present invention, the carbon content amounts are in atomic concentration % and can be found with known analytical means, but are calculated in the present invention with the XPS method and are defined below.

[0091]

atomic concentration % = number of carbon atoms / total number of atoms × 100

The XPS surface analysis device used in the present invention is the ESCALAB-200R manufactured by VG Scientifics [*sic*: VG Scientific]. Specifically, Mg is used as the X-ray anode, and measurement is carried out with an output of 600 W (acceleration voltage: 15 kV, emission current: 40 mA). The energy resolution is set so as to be 1.5-1.7 eV when defined by the half-value width of the clean [*sic*: normal] Ag 3d5/2 peak.

[0092]

First, the binding energy range is measured in the range of 0 to 1100 eV with a data acquisition interval of 1.0 eV to find which elements are detected.

[0093]

Next, narrow scanning is carried out on the photoelectron peak that imparts the maximum intensity for all detected elements except for the etching ion species with a data acquisition interval of 0.2 eV, and the spectrum of each element is measured.

[0094]

The resulting spectra are transferred to the Common Data Processing System (ver. 2.3 or later being preferable) manufactured by VAMAS-SCA-Japan to prevent differences in the results of content calculation due to differences in measuring equipment and computers, then processing is carried out with said software, and the content of the elements (carbon, oxygen, silicon, titanium, and the like) in each analysis target is found in atomic concentration (at%).

[0095]

Before quantification processing, the count scale is calibrated for each element and 5-point smoothing processing is carried out. The quantification processing uses the peak area intensity (cps*eV) with the background removed. The Shirley method is used for background processing. The Shirley method can be found in D. A. Shirley, Phys. Rev., B5, 4709(1972).

[0096]

As described above, when the gas barrier thin film laminate formed with the atmospheric pressure plasma CVD method is configured, the ceramic film of the present invention with low internal stress is particularly desirable because the ceramic film provides a laminated film that is resistant to stress, such as bending resistance, and also provides a ceramic laminated film that is resistant to degradation of the gas barrier performance, and has low light absorption from the film, little coloration and the like caused by differences in the refractive index between layers due to multilayer lamination, and high transmittance. The barrier film containing ceramic material with low internal stress formed by the atmospheric pressure plasma method according to the present invention, and preferably the buffer film, provides a film with high transparency, uniform light absorption, and a light absorption rate of 0.1% or less in the visible light range of 380-800 nm.

[0097]

The buffer film and the barrier film according to the present invention preferably have identical compositions, but even if the compositions are identical, for example, in the case of the atmospheric pressure plasma CVD method, differences will arise in the degree of filling of ceramic particles, the trace amounts of impurity particles that are mixed in, and the like depending on the manufacturing conditions and the film forming gas used (type, ratio, and the like of the raw material gas, additive gas, and the like), and therefore physical properties such as the density, for example, will be different.

[0098]

The buffer film according to the present invention contains the same composition as the barrier film and has a film density that is lower than the gas barrier film, but a density value of 90% or less than that of the gas barrier film is preferable. These buffer film layers do not block moisture vapor as well as barrier films but are flexible and, as buffer films, serve as stress relief layers, adhesion layers, or protective layers, even though they are films with the same composition.

[0099]

Next, the constituent elements of the gas barrier thin film laminate and the gas barrier resin substrate material of the present invention are described.

[0100]

<<The buffer film and the gas barrier film>>

The raw material used for manufacturing the buffer film and the barrier film (hereinbelow collectively referred to as the ceramic material film or the ceramic film) according to the present invention is described.

[0101]

The ceramic material film according to the present invention can be produced using the plasma CVD method or the atmospheric pressure plasma CVD method by selecting the conditions, such as an organometallic compound that is the raw material, a decomposition gas, a decomposition temperature, and the power input, and the composition can be varied to include metal carbides, metal nitrides, metal oxides, metal sulfides, metal halides, and mixtures thereof (e.g., metal oxynitrides, metal oxide halides, metal nitride carbides).

[0102]

For example, if a silicon compound is used as the raw material compound and oxygen is used as the decomposition gas, silicon oxide is produced. If a zinc compound is used as the raw material compound and carbon disulfide is used as the decomposition gas, zinc sulfide is formed. This is because the plasma space contains a high density of extremely active charged particles and active radicals, which promote multi-stage chemical reactions in the plasma space at a very high speed, and elements in the plasma space are converted into thermodynamically stable compounds in an extremely short period of time.

[0103]

Such inorganic raw materials can be either gaseous, liquid, or solid under normal temperature and pressure, as long as said inorganic raw materials have typical or transition metal elements. Gases can be introduced directly into the discharge space, while liquids and solids should be vaporized by heating, bubbling, depressurization, ultrasonic irradiation, or the like before use. Use may be made after dilution with a solvent, which may be an organic solvent such as methanol, ethanol, n-hexane, or a mixture thereof. These diluting solvents are decomposed into molecular and atomic forms during the plasma discharge process and therefore the effects of the diluting solvents can be mostly ignored.

[0104]

Such organometallic compounds include, as the silicon compound, silane, tetramethoxysilane, tetraethoxysilane, tetra n-propoxysilane, tetraisopropoxysilane, tetra n-butoxysilane, tetra t-butoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diethyldimethoxysilane, diphenyldimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, phenyltriethoxysilane, (3,3,3-trifluoropropyl)trimethoxysilane, hexamethyldisiloxane, bis(dimethylamino)dimethylsilane, bis(dimethylamino)methylvinylsilane, bis(ethylamino)dimethylsilane, N,O-bis(trimethylsilyl)acetamide, bis(trimethylsilyl)carbodiimide, diethylaminotrimethylsilane, dimethylaminodimethylsilane, hexamethyldisilazane, hexamethylcyclotrisilazane, heptamethyldisilazane, nonamethyltrisilazane, octamethylcyclotetrasilazane, tetrakis dimethylaminosilane, tetraisocyanato silane, tetramethyldisilazane, tris(dimethylamino)silane, triethoxyfluorosilane, allyldimethylsilane, allyltrimethylsilane, benzyltrimethylsilane, bis(trimethylsilyl)acetylene, 1,4-bis trimethylsilyl-1,3-butadiyne, di-t-butylsilane, 1,3-disilabutane, bis(trimethylsilyl)methane, cyclopentadienyltrimethylsilane, phenyldimethylsilane, phenyltrimethylsilane, propargylic trimethylsilane, tetramethylsilane, trimethylsilylacetylene, 1-(trimethylsilyl)-1-propyn, tris(trimethylsilyl)methane, tris(trimethylsilyl)silane, vinyl trimethylsilane, hexamethyldisilane, octamethylcyclotetrasiloxane, tetramethylcyclotetrasiloxane, hexamethylcyclotetrasiloxane, and M Silicate 51.

[0105]

Titanium compounds include, for example, titanium methoxide, titanium ethoxide, titanium isopropoxide, titanium tetraisopropoxide, titanium n-butoxide, titanium diisopropoxide (bis-2,4-pentanedionate), titanium diisopropoxide (bis-2,4-ethylacetoacetate), titanium di-n-butoxide (bis-2,4-pentanedionate), titanium acetylacetonate, and butyl titanate dimer.

[0106]

Zirconium compounds include zirconium n-propoxide, zirconium n-butoxide, zirconium t-butoxide, zirconium tri-n-butoxide acetylacetonate, zirconium di-n-butoxide bisacetylacetonate, zirconium acetylacetonate, zirconium acetate, and zirconium hexafluoropentanedione.

[0107]

Aluminum compounds include aluminum ethoxide, aluminum triisopropoxide, aluminum isopropoxide, aluminum n-butoxide, aluminum s-butoxide, aluminum t-butoxide, aluminum acetylacetonate, and triethyl di-aluminum tri-s-butoxide.

[0108]

Boron compounds include diborane, tetraborane, boron fluoride, boron chloride, boron bromide, borane-diethyl ether complexes, borane-THF complexes, borane-dimethyl sulfide complexes, boron trifluoride diethyl ether complexes, triethylborane, trimethoxyborane, triethoxyborane, tri(isopropoxy)borane, borazole, trimethylborazole, triethylborazole, and triisopropylborazole.

[0109]

Tin compounds include tetraethyl tin, tetramethyl tin, di-n-butyl tin diacetate, tetrabutyl tin, tetraoctyltin, tetraethoxy tin, methyltriethoxy tin, diethyldiethoxy tin, triisopropyl ethoxy tin, diethyl tin, dimethyl tin, diisopropyl tin, dibutyl tin, diethoxy tin, dimethoxy tin, diisopropoxy tin, dibutoxy tin, tin dibutylate, tin diacetoacetonate, ethyl tin acetoacetonate, ethoxy tin acetoacetonate, and dimethyl tin diacetoacetonate, and tin halides include tin dichloride and tin tetrachloride.

[0110]

Other organometallic compounds include, for example, antimony ethoxide, arsenic triethoxide, barium 2,2,6,6-tetramethylheptanedionate, beryllium acetylacetonate, bismuth hexafluoropentanedionate, dimethylcadmium, calcium 2,2,6,6-tetramethylheptanedionate, chromium trifluoropentanedionate, cobalt acetylacetonate, copper hexafluoropentanedione, magnesium hexafluoropentanedionate-dimethyl ether complexes, gallium ethoxide, tetraethoxygermane, tetramethoxygermane, hafnium t-butoxide, hafnium ethoxide, indium acetylacetonate, indium 2,6-dimethylaminoheptanedionate, ferrocene, lanthanum isopropoxide, lead acetate, lead tetraethyl, neodymium acetylacetonate, platinum hexafluoropentanedione, trimethylcyclopentadienyl platinum, rhodium dicarbonyl acetylacetonate, strontium 2,2,6,6-tetramethylheptanedionate, tantalum methoxide, tantalum trifluoroethoxide, tellurium ethoxide, tungsten ethoxide, vanadium triisopropoxide oxide, magnesium hexafluoroacetylacetonate, zinc acetylacetonate, and diethylzinc.

[0111]

The decomposition gas used to decompose these metal-containing raw material gases to obtain inorganic compounds include hydrogen gas, methane gas, acetylene gas, carbon monoxide gas, carbon dioxide gas, nitrogen gas, ammonia gas, nitrous oxide gas, nitrogen oxide gas, nitrogen dioxide gas, oxygen gas, moisture vapor, fluorine gas, hydrogen fluoride, trifluoroalcohol, trifluoro toluene, hydrogen sulfide, sulfur dioxide, carbon disulfide, and chlorine gas.

[0112]

Various types of metal carbides, metal nitrides, metal oxides, metal halides, and metal sulfides can be obtained by appropriately selecting a decomposition gas containing metal elements and a raw material gas.

[0113]

These reactive gases are mixed with a discharge gas that tends to become plasma, and the gases are fed into a plasma discharge generator. Nitrogen gas and/or group 18 atoms of the periodic table, specifically helium, neon, argon, krypton, xenon, radon, and the like, are used as such discharge gases. Of these, nitrogen, helium, and argon are especially preferable.

[0114]

The discharge gas and the reactive gas are mixed and supplied to the plasma discharge generator (plasma generator) as a thin film forming (mixed) gas to form the film. The ratio of discharge gas to reactive gas varies depending on the properties of the film to be obtained, but the reactive gas should be supplied so that the ratio of the discharge gas is at least 50% to the total gas mixture.

[0115]

In the ceramic film composing the gas barrier thin film laminate according to the present invention, it is preferable that the inorganic compound contained in the ceramic film be at least one selected from silicon oxide, silicon oxide nitride, silicon nitride, alumina oxide, or a mixture thereof, and silicon oxide is particularly preferable from the perspective of moisture permeability, light permeability, and suitability for atmospheric pressure plasma CVD, which is described below.

[0116]

For example, the above organosilicon compound can be further combined with oxygen gas or nitrogen gas in a predetermined ratio to obtain a ceramic film of silicon oxide, silicon oxide nitride, silicon nitride, or the like, according to the present invention containing an O atom and/or an N atom as well as an Si atom.

[0117]

In further detail, the gas barrier thin film laminate or the gas barrier resin substrate material of the present invention is obtained by a laminate structure composed of two types of thin films with different properties, two types of film with identical compositions produced with the atmospheric pressure plasma method described above, that is,

a barrier film: a dense film with a low water vapor transmission coefficient comprising a ceramic composition with low or no carbon content and having at least Si and O atoms, and a buffer film: a flexible film with a larger water vapor transmission coefficient and a lower density than the barrier film consisting of a film with a high content of carbon atoms with Si, O, and C atoms.

[0118]

In addition, these ceramic material films, especially the barrier film, have low internal strain with an internal stress (compressive stress) between 0.001 and 20 MPa inclusive, providing crack-resistant films that are resistant to bending and other stresses when laminated. The barrier film and the buffer film each has a light absorption rate of 0.1% or less in the range of 380 nm to 800 nm and a light reflection rate of 10% or less and compose an excellent laminated film with little coloration when laminated.

[0119]

The gas barrier thin film laminate of the present invention may have a configuration of one or more barrier films and buffer films, one example configuration being a resin substrate material, a buffer film, a barrier film, and a protective film (which also serves as a buffer film), and may also have a configuration of two or more sets of these laminates, i.e., for example, two sets of a gas barrier laminate comprising a buffer film (which also serves as an adhesion film), a barrier film, a buffer film, a barrier film, and a buffer film (which also serves as a protective film) on a resin substrate material. Of course, a configuration having three or more barrier films and buffer films is also acceptable.

[0120]

The second or third gas barrier thin film laminate does not need to be exactly the same as the first thin film laminate, and the buffer film and the barrier film composing each laminate need not be exactly the same as long as the required properties as buffer and barrier films, such as water vapor transmission coefficient, density, and composition are met. However, using the same thin film laminate is preferable in terms of production efficiency. The adhesion film to improve adhesion to the resin substrate material is preferably also formed as a buffer film, and the protective film is also preferably a buffer film.

[0121]

FIG. 3 shows a cross-sectional view of a typical example of the configuration of the gas barrier resin substrate material of the present invention. For example, a polyethylene terephthalate (PET) film is used as the resin substrate material, and the polymer film described below is formed to improve adhesion between the gas barrier thin film laminate and the resin substrate material (film) and to ensure smoothness.

(1) Resin substrate material 1 (125 μm) / polymer film 2 (6 μm) / buffer film 3 (100 nm) / gas barrier film 4 (50 nm) / protective film 5 (500 nm)

(2) Resin substrate material 1 / polymer film 2 / buffer film film [*sic*] 3 / gas barrier film 4 / second buffer film 3′ (100 nm) / second gas barrier film 4 ′ (50 nm) / protective film 5

The numerical values in parentheses above indicate the thickness of the respective film. In each case, the protective film may be the same film as the buffer film, and the buffer film adjacent to the polymer layer essentially serves to improve adhesion to the substrate material, including the polymer layer.

[0122]

In the present invention, it is preferable to have a polymer film between the buffer film or the barrier film and the resin substrate material (resin film substrate material described below). This is with the object of improving adhesion and bonding between the buffer film or the gas barrier film and the resin substrate of the gas barrier thin film laminate, and to ensure smoothness.

[0123]

The polymer film is in the range of 0.1 to 10 μm in thickness, preferably in the range of 1-10 μm.

[0124]

A resin-coated layer of acrylic resin, polyester resin, urethane resin, or the like is preferable as the polymer film, and can be easily formed by coating the corresponding resin solution on the resin substrate material by roll coating, gravure coating, dip coating, or another known method.

[0125]

In the present invention, it is also preferable that these polymer layers be formed from a thermosetting resin or an active ray-curable resin, and it is particularly preferable to form the resin-curing layer using an ultraviolet ray-curing resin. It is also preferable to perform corona discharge or glow discharge treatment on the surface of the resin substrate material (film) before forming these layers.

[0126]

The resin-curing layer is preferably formed by polymerizing a component containing one or more monomers having ethylenically unsaturated bonds, and as a resin layer formed by polymerizing a component containing a monomer having ethylenically unsaturated bonds, a layer formed by curing an active ray-curable resin or a thermosetting resin is preferably used, but the active ray-curable resin layer is particularly preferable. Here, an active ray-curable resin layer refers to a layer whose main component is a resin that cures through a cross-linking reaction or the like upon active ray irradiation such as of ultraviolet rays or electron beams.

[0127]

Ultraviolet ray-curable resins and electron beam-curable resins are typical examples of active ray-curable resins, but resins that cure with active ray irradiation other than ultraviolet rays and electron beams are also acceptable.

[0128]

Ultraviolet ray-curable resins include, for example, ultraviolet ray-curable acrylic urethane resins, ultraviolet ray-curable polyester acrylate resins, ultraviolet ray-curable epoxy acrylate resins, ultraviolet ray-curable polyol acrylate resins, and ultraviolet ray-curable epoxy resins, but preferably have acrylic as the main component such as, for example, ultraviolet ray-curable acrylic urethane resins, ultraviolet ray-curable polyester acrylate resins, ultraviolet ray-curable epoxy acrylate resins, and ultraviolet ray-curable polyol acrylate resins.

[0129]

Specific examples include trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, and alkyl modified dipentaerythritol pentaacrylate.

[0130]

Ultraviolet ray-curable acrylic urethane resins are generally easily formed by reacting an isocyanate monomer or a prepolymer with a polyester polyol and then reacting the resulting product with an acrylate monomer having a hydroxyl group such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate (hereinafter acrylate including methacrylate when only acrylate is indicated), and 2-hydroxypropyl acrylate, and the substances described in Patent Appl. Publication No. JP S59-151110 can be used.

[0131]

Ultraviolet ray-curable polyester acrylate resins are generally easily formed by reacting a polyester polyol with a 2-hydroxyethyl acrylate or 2-hydroxyacrylate monomer, and the substances described in Patent Appl. Publication No. JP S59-151112 can be used.

[0132]

Specific examples of ultraviolet ray-curable epoxy acrylate resins include those produced by adding a reactive diluent and a photoinitiator to epoxy acrylate as an oligomer, and causing a reaction, and the substances described in Patent Appl. Publication No. JP H1-105738 can be used.

[0133]

Specifically, the photoinitiator includes benzoin and derivatives, acetophenone, benzophenone, hydroxybenzophenone, Michler's ketone, α-amyloxime ester, thioxanthone, and derivatives thereof. The photoinitiator may be used together with a photosensitizer.

[0134]

The photoinitiators can also be used as photosensitizers. When using an epoxy acrylate-based photoreactant, a sensitizer such as n-butylamine, triethylamine, or tri-n-butylphosphine can also be used.

[0135]

As resin monomers, for example, common monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, benzyl acrylate, cyclohexyl acrylate, vinyl acetate, and styrene can be used as monomers with one unsaturated double bond. As monomers with two or more unsaturated double bonds, ethylene glycol diacrylate, propylene glycol diacrylate, divinylbenzene, 1,4-cyclohexane diacrylate, 1,4-cyclohexyldimethyl a diacrylate [*sic*: 1,4-cyclohexyldimethyl diacrylate], and, as mentioned above, trimethylolpropane triacrylate and pentaerythritol tetraacrylate can be used.

[0136]

Commercially available ultraviolet ray-curable resins that may be appropriately selected and used in the present invention include the Adeka Optomer KR and BY series: KR-400, KR-410, KR-550, KR-566, KR-567, and BY-320B (manufactured by ADEKA Corporation); Koei Hard A-101-KK, A-101-WS, C-302, C-401-N, C-501, M-101, M-102, T-102, D-102, NS-101, FT-102Q8, MAG-1-P20, AG-106, and M-101-C (manufactured by Koei Chemical Co., Ltd.); Seika Beam PHC2210(S), PHC X-9(K-3), PHC2213, DP-10, DP-20, DP-30, P1000, P1100, P1200, P1300, P1400, P1500, P1600, and SCR 900 (manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.); KRM7033, KRM7039, KRM7130, KRM7131, UVECRYL29201, and UVECRYL29202 (manufactured by Daicel-UCB Company, Ltd.); RC-5015, RC-5016, RC-5020, RC-5031, RC-5100, RC-5102, RC-5120, RC-5122, RC-5152, RC-5171, RC-5180, RC-5181 (manufactured by Dainippon Ink and Chemicals, Inc.); Orlex no. 340 Clear (manufactured by Chugoku Marine Paints, Ltd.); Sanrad H-601 (manufactured by Sanyo Chemical Industries, Ltd.); SP-1509 and SP-1507 (manufactured by Showa Highpolymer Co., Ltd.); RCC-15C (Grace Japan Co., Ltd.); and Aronix M-6100, M-8030, and M-8060 (manufactured by Toagosei Co., Ltd.), and the like.

[0137]

These active ray-curable resin layers can be applied using a known method.

[0138]

Any light source that generates ultraviolet light can be used without limitation as a light source for curing the ultraviolet ray-curable resin with a photo-curing reaction. For example, a low-pressure mercury lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, an ultra high-pressure mercury lamp, a carbon arc lamp, a metal halide lamp, a xenon lamp, or the like can be used. Irradiation conditions vary with each lamp, but an irradiation light intensity of 20-10,000 mJ/cm^2 is sufficient and preferably 50-2,000 mJ/cm^2. The near-ultraviolet region to the visible light region enables efficient formation with use of a sensitizer with absorption maxima in that region.

[0139]

The organic solvent for the ultraviolet ray-curable resin layer composition coating solution can be appropriately selected from, for example, hydrocarbons, alcohols, ketones, esters, glycol ethers, and other organic solvents, or a mixture of these solvents can be used. For example, an organic solvent containing at least 5 mass% of propylene glycol monoalkyl ether (alkyl group with 1-4 carbon atoms) or propylene glycol monoalkyl ether acetate (alkyl group with 1-4 carbon atoms) or the like is preferably used, and 5-80 mass% is even more preferable.

[0140]

The appropriate wet film thickness of the ultraviolet ray-curable resin composition coating solution is 0.1-30 μm, preferably 0.5-15 μm. The ultraviolet ray-curable resin composition is preferably irradiated with ultraviolet rays during or after coating and drying, with 0.5 seconds to 5 minutes being preferable as the irradiation time, and 3 seconds to 2 minutes being more preferable from the perspective of curing efficiency of the ultraviolet ray-curable resin and the work efficiency.

[0141]

As the polymer film according to the present invention, a plasma polymerization film formed using the atmospheric pressure plasma CVD method is preferable. That is, in the atmospheric pressure plasma CVD method, at least one or more organic compounds are contained in the thin film forming gas, and the polymer film may be formed by plasma polymerization of the organic compounds.

[0142]

In the atmospheric pressure plasma CVD method, the thin film forming gas comprises the discharge gas and the raw material components, and additional gases may also be used.

[0143]

In the atmospheric pressure plasma CVD method, known organic compounds can be used as the raw material components for plasma polymerization contained in the thin film forming gas, but among those organic compounds, those having at least one or more unsaturated bonds or cyclic structures in the molecule can be preferably used, and in particular, monomers, oligomers, and the like of (meth)acrylic compounds, epoxy compounds, or oxetane compounds can be preferably used, but organic compounds with acrylic as the main component, such as acrylic and methacrylic compounds are particularly preferable.

[0144]

There are no particular limitations on useful (meth)acrylic compounds, but the following compounds are representative examples: monofunctional acrylic esters such as 2-ethylhexyl acrylate, 2-hydroxypropyl acrylate, glycerol acrylate, tetrahydrofurfuryl acrylate, phenoxyethyl acrylate, nonylphenoxyethyl acrylate, tetrahydrofurfuryloxyethyl acrylate, tetrahydrofurfuryloxyhexanolide acrylate, 1,3-dioxane alcohol acrylate with ε-caprolactone adduct, and 1,3-dioctyl acrylate; methacrylates substituting methacrylate for these acrylates, for example, bifunctional acrylic esters such as ethylene glycol diacrylate, triethylene glycol diacrylate, pentaerythritol diacrylate, hydroquinone diacrylate, resorcinol diacrylate, hexanediol diacrylate, neopentyl glycol diacrylate, tripropylene glycol diacrylate, neopentyl glycol hydroxypivalate diacrylate, diacrylate of neopentyl glycol adipate, diacrylate of ε-caprolactone adduct of neopentyl glycol hydroxypivalate, 2-(2-hydroxy-1,1-dimethylethyl)-5-hydroxymethyl-5-ethyl-1,3-dioxane diacrylate, tricyclodecane dimethylol acrylate, ε-caprolactone adduct of tricyclodecane dimethylol acrylate, and diacrylate of diglycidyl ether of 1,6-hexanediol; methacrylic acid esters substituting methacrylate for these acrylates, for example, polyfunctional acrylic ester acids such as trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, trimethylolethane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, dipentaerythritol hexaacrylate with ε-caprolactone, pyrogallol triacrylate, propionic acid-dipentaerythritol triacrylate, propionic acid-dipentaerythritol tetraacrylate, and hydroxypivalylaldehyde-modified dimethylolpropane triacrylate; methacrylic acids substituting methacrylate for these acrylates; and the like. The compounds mentioned above are also examples of the active ray-curable resins.

[0145]

The discharge gas is similar to the case of the gas barrier layer described above, and includes nitrogen, noble gases, air, and the like. The noble gas is selected from the group 18 elements of the periodic table, specifically helium, neon, argon, krypton, xenon, radon, and the like, and in the present invention, nitrogen, argon and helium are preferable as discharge gases, and nitrogen is particularly preferable.

[0146]

In plasma polymerization, the amount of discharge gas is preferably 70-99.99 volume% of the thin film forming gas supplied inside the discharge space.

[0147]

In the plasma polymerization method, in addition to the aforementioned raw material gas and discharge gas, additive gases may be introduced to control the reaction and film quality, and a mixture of hydrogen, oxygen, nitrogen oxides, ammonia, methane and other hydrocarbons, alcohols, organic acids, or water of 0.001% to 30 volume% of the gas may be used.

[0148]

The surface roughness Ra of the polymer film obtained with these methods is preferably smooth with a surface roughness of 5 nm or less. The surface average roughness is the centerline average roughness, and if the centerline average roughness is 5 nm or higher, the homogeneity of the gas barrier layer formed on the polymer film is impaired and defects (pores) form in the gas barrier layer, resulting in a decrease in gas barrier performance.

[0149]

The centerline average roughness (Ra) as used in the present invention is defined by JIS-B-0601 for JIS surface roughness. In other words, the centerline average roughness (Ra) is the value obtained from the following equation expressed in micrometers (μm) when a portion of the roughness curve with a measurement length L (2.5 mm in the present invention) is extracted in the direction of the centerline, the cutoff value is 0.8 mm, the centerline of the extracted portion is on the X axis, the direction of vertical magnification is on the Y axis, and the roughness curve is represented by Y = f(X):

[0150]

[Mathematical Formula 1]

$$Ra = \frac{1}{L}\int_0^L |f(x)|dx$$

[0151]

The centerline average roughness (Ra) was measured after 24 hours of humidity control at 25°C and 65% RH under the condition that the samples did not overlap each other. The non-overlapping condition shown here includes, for example, a method in which the edge portion of the support is wound in a raised state, a method in which the supports are stacked with a piece of paper between, and a method in which a frame of cardboard or the like is produced and the four corners are secured. The WYKO RST-Plus non-contact 3D micro-surface profiling system, for example, can be used as the measurement device.

[0152]

While there are no particular restrictions on how to achieve the centerline average roughness (Ra) of the support surface specified in the present invention, a polymer film obtained from the above-mentioned active ray-curable resin or a smooth polymer film obtained from plasma polymerization is preferable. The smooth planar surface reduces defects in the barrier film and the buffer film, resulting in a laminate with high gas barrier performance.

[0153]

<<Resin film>>

The resin (film) substrate material used in the gas barrier resin substrate material of the present invention is not particularly limited as long as the material is a resin film capable of holding the gas barrier layer described above.

[0154]

Specifically, a polyolefin (PO) resin such as a homopolymer or a copolymer or a copolymer [*sic*] of ethylene, polypropylene, butene, or the like, an amorphous polyolefin resin (APO) such as cyclic polyolefin, a polyester resin such as polyethylene terephthalate (PET) and polyethylene 2,6-naphthalate (PEN), a polyamide (PA) resin such as nylon 6, nylon 12, and copolymerized nylon, a polyvinyl alcohol (PVA) resin, a polyvinyl alcohol resin such as an ethylene-vinyl alcohol copolymer (EVOH), a polyimide (PI) resin, a polyetherimide (PEI) resin, a polysulfone (PS) resin, a polyethersulfone (PES) resin, a polyether ether ketone (PEEK) resin, a polycarbonate (PC) resin, a polyvinyl butyrate (PVB) resin, a polyarylate (PAR) resin, and a fluorinated resin such as an ethylene tetrafluoroethylene copolymer (ETFE), a trifluoroethylene chloride (PFA), an ethylene tetrafluoride-perfluoroalkyl vinyl ether copolymer (FEP), a polyvinylidene fluoride (PVDF), a polyvinyl fluoride (PVF), and a perfluoroethylene-perfluoropropylene-perfluorovinyl ether copolymer (EPA) may be used.

[0155]

In addition to the resins listed above, a photocurable resin such as a resin composition comprising an acrylate compound with a radical-reactive unsaturated compound, a resin composition comprising an acrylate compound and a mercapto compound with a thiol group, and a resin composition in which an oligomer such as epoxy acrylate, urethane acrylate, polyester acrylate, polyether acrylate, or the like is dissolved in a multifunctional acrylate monomer and mixtures thereof may be used. Furthermore, one, two, or more of these resins can be laminated by means of lamination, coating, or the like, and used as a resin film.

[0156]

These materials may be used alone or mixed as appropriate. Of these, commercially available products may be favorably used such as ZEONEX and ZEONOR (manufactured by Zeon Corporation), the amorphous cyclic polyolefin resin film ARTON (manufactured by JSR Corporation), the polycarbonate film PURE-ACE (manufactured by TEIJIN LIMITED), and the cellulose triacetate films Konica Tac KC4UX and KC8UX (manufactured by Konica Minolta Opto, Inc.).

[0157]

The resin film is preferably transparent. This is because when the resin film is transparent and the gas barrier layer formed on the resin film is also transparent, a transparent gas barrier film can be formed that can be used as a transparent substrate for organic EL elements and the like.

[0158]

The resin films listed above can be either unstretched or stretched.

[0159]

The resin film according to the present invention can be manufactured with any of the common methods conventionally known. For example, the material resin can be melted by an extruder, extruded with an annular die or a T-die, and quenched to manufacture a substantially amorphous, unoriented, and unstretched substrate material. A stretched substrate material can also be manufactured by stretching the unstretched substrate material in the direction of the substrate material flow (longitudinal axis) or perpendicular to the substrate material flow direction (transverse axis) using a known method such as uniaxial stretching, tenter-type sequential biaxial stretching, tenter-type simultaneous biaxial stretching, or tubular-type simultaneous biaxial stretching. In this case, the stretching magnification can be selected appropriately according to the resin used as the raw material for the substrate material, but 2-10 times in both the longitudinal and transverse axial directions is preferable.

[0160]

The resin film substrate material according to the present invention may also undergo surface treatment such as corona treatment, flame treatment, plasma treatment, glow discharge treatment, roughening treatment, or chemical treatment before forming the gas barrier film, the polymer film, or the like.

[0161]

Long resin films rolled up in rolls are convenient. The thickness of the resin film cannot be generally stipulated because the thickness depends on the application of the resulting gas barrier film, but when the gas barrier film is used for packaging purposes, there are no particular restrictions, and from the standpoint of suitability as a packaging material, a thickness in the range of 3-400 μm, especially 6-30 μm is preferable.

[0162]

The thickness of the resin film used in the present invention in film is preferably 10-200 μm and more preferably 50-100 μm.

[0163]

The moisture vapor permeability of the gas barrier film of the present invention when used in applications requiring advanced moisture vapor barrier performance such as organic EL displays and high-definition color liquid crystal displays is 0.01 $g/m^2/day$ or less measured according to JIS K 7129B, and more preferably 1×10^{-3} $g/m^2/day$ or less, and in the case of organic EL display applications, the moisture vapor transmission rate should be less than 1×10^{-5} $g/m^2/day$ because even a very small amount of moisture vapor can cause dark spots to grow, resulting in an extremely short display life.

[0164]

Next, the atmospheric pressure plasma method, which is the plasma CVD method according to the present invention, is described.

[0165]

For the formation of the buffer film and the barrier film comprising ceramic materials and the thin film laminate of the buffer film and the barrier film according to the present invention, it is preferable to apply a plasma CVD method using plasma polymerization, and the atmospheric plasma method performed under atmospheric or near-atmospheric pressure is particularly preferable. For the atmospheric pressure plasma method, the thin film formation methods described in Patent Appl. Publication No. JP H10-154598, Patent Appl. Publication No. 2003-49272, WO No. 02/048428 Pamphlet, and the like can be used, but the thin film formation method described in Patent Appl. Publication No. JP 2004-68143 is preferable for forming a dense, high gas barrier, low compressive stress ceramic material film, and by selecting the thin film forming gas and adjusting the formation conditions, it is possible to form a buffer film and a gas barrier film, as well as form a polymer film by plasma polymerization on the resin substrate material. It is also possible to continuously form these polymer films and ceramic material films by unrolling a web-like substrate from a source roll-like roll.

[0166]

The atmospheric plasma method according to the present invention is carried out under atmospheric pressure or near atmospheric pressure, which is about 20-110 kPa, and 93-104 kPa is preferable in order to obtain the favorable effect described in the present invention.

[0167]

The discharge condition in the present invention is the application of two or more electric fields of different frequencies to the discharge space, with the first high-frequency electric field superimposed on the second high-frequency electric field.

[0168]

The frequency ω2 of the second high-frequency electric field is higher than the frequency ω1 of the first high-frequency electric field, and the relationship between the strength V1 of the first high-frequency electric field, the strength V2 of the second high-frequency electric field, and the strength IV of the discharge initiation electric field IV

satisfies $V1 \geq IV > V2$ and

$V1 > IV \geq V2$

and the power density of the second high-frequency electric field is at least 1 W/cm^2.

[0169]

High frequency is defined as having a frequency of at least 0.5 kHz.

[0170]

When both superimposed high-frequency electric fields are sine waves, the electrical fields become a component in which the frequency ω1 of the first high-frequency electric field and the frequency ω2 of the second high-frequency electric field that is higher than the frequency ω1 are superimposed, and the waveform is a sawtooth waveform in which the sine wave of frequency ω2, which is higher than the frequency ω1, is superimposed on the sine wave of frequency ω1.

[0171]

In the present invention, the strength of the discharge initiation electric field refers to the minimum electric field strength that can cause a discharge in the discharge space (electrode configuration and the like) and with the reaction conditions (gas conditions and the like) used in the actual thin film formation method. The discharge initiation electric field strength varies somewhat depending on the gas species supplied to the discharge space, the dielectric species of the electrodes, the distance between the electrodes, and the like, but in the same discharge space, the strength is governed by the discharge initiation electric field strength of the discharge gas.

[0172]

It is presumed that by applying a high-frequency electric field as described above to the discharge space, a discharge capable of forming thin films can be generated, producing the high-density plasma necessary for high-quality thin film formation.

[0173]

What is important here is that such a high-frequency electric field is applied between opposing electrodes, i.e., in the same discharge space. It is not preferable to place two application electrodes side by side to apply different high-frequency electric fields to different discharge spaces that are separated from each other as in the case of Patent Appl. Publication No. JP H11-16696.

[0174]

The superposition of continuous waves, such as sine waves, was described above, but the present invention is not so limited, and it does not matter if both waves are pulse waves, or if one is continuous and the other is pulse wave. It is also possible to have a third electric field with yet a different frequency.

[0175]

As a specific method of applying the high-frequency electric field of the present invention to the same discharge space, for example, an atmospheric pressure plasma discharge treatment device is used in which a first power supply is connected to apply a first high-frequency electric field with a frequency of ω1 and an electric field strength of V1 to the first electrode composing a counter electrode, and a second power supply is connected to apply a second high-frequency electric field with a frequency of ω2 and an electric field strength of V2 to the second electrode.

[0176]

The atmospheric pressure plasma discharge treatment device is provided with a gas supply means that supplies the discharge gas and the thin film forming gas between the opposing electrodes. An electrode temperature control means that controls the temperature of the electrodes is preferably provided.

[0177]

It is also preferable to connect a first filter to the first electrode, the first power supply, or therebetween and a second filter to the second electrode, the second power supply, or therebetween so that the first filter facilitates the passage of the current of the first high-frequency electric field from the first power supply to the first electrode and grounds the current of the second high-frequency electric field, making it difficult for the current of the second high-frequency electric field to pass from the second power supply to the first power supply. The second filter is the opposite with a function that facilitates the passage of the second high-frequency electric field current from the second power source to the second electrode and grounds the first high-frequency electric field current, making it difficult for the first high-frequency electric field current to pass from the first power source to the second power source. Here, difficult to pass through preferably means 20% or less of the current and more preferably 10% or less of the current passes through. Conversely, facilitating passage preferably means passing 80% or more of the current and more preferably passing 90% or more.

[0178]

For example, as the first filter, a capacitor of several 10 pF to tens of thousands pF or a coil of several μH can be used, depending on the frequency of the second power supply. As the second filter, a coil of 10 μH or more can be used depending on the frequency of the first power supply, and the filters can be used by grounding through the coils or the capacitor.

[0179]

Furthermore, the first power supply of the atmospheric pressure plasma discharge treatment device of the present invention preferably has the ability to apply a higher electric field strength than the second power supply.

[0180]

The application electric field strength and the discharge initiation electric field strength referred to in the present invention are as measured with the following methods.

[0181]

Method of measuring the application electric field strength V1 and V2 (unit: kV/mm):

A high-frequency voltage probe (P6015A) is set at each electrode, and the output signal of the high-frequency voltage probe is connected to an oscilloscope (TDS3012B manufactured by Tektronix, Inc.) to measure the electric field strength at a given time.

[0182]

Method of measuring the electric field strength IV (unit: kV/mm) at the onset of discharge:.

The discharge gas is supplied between the electrodes, the electric field strength between these electrodes is increased, and the electric field strength at which discharge begins is defined as the discharge initiation electric field strength IV. The measuring instrument is the same as that for the application electric field strength measurement.

[0183]

The positions where the electric field strength is measured by the high-frequency voltage probe and the oscilloscope for the above measurements are shown in FIG. 4 below.

[0184]

By adopting the discharge conditions stipulated in the present invention, even a discharge gas with a high discharge initiation electric field strength, such as nitrogen gas, for example, can initiate a discharge and maintain a high-density, stable plasma state, enabling high-performance thin film formation.

[0185]

When the discharge gas is nitrogen gas, the discharge initiation electric field strength IV (1/2 V p-p) is about 3.7kV/mm according to the above measurement, and therefore, in the above relationship, the nitrogen gas can be excited to a plasma state by applying the first application electric field strength as V1 ≥ 3.7 kV/mm.

[0186]

The frequency of the first power supply can preferably be 200 kHz or less. The electric field waveform can be a continuous wave or a pulse wave. The lower limit is desirably around 1 kHz.

[0187]

As the frequency of the second power supply, 800 kHz or higher is preferably used. The higher the frequency of the second power supply, the higher the plasma density and the denser and better quality of thin films that can be obtained. An upper limit of about 200 MHz is desirable.

[0188]

The application of high-frequency electric fields from such two power sources is necessary for the first high-frequency electric field to initiate discharge of the discharge gas with a high discharge initiation electric field strength, and the high frequency and the high power density of the second high-frequency electric field increases the plasma density to form dense, high-quality thin films, which are an important aspect of the present invention.

[0189]

By increasing the output density of the first high-frequency electric field, the output density of the second high-frequency electric field can be increased while maintaining the uniformity of the discharge. This enables the production of more uniform high-density plasma, which can both further increase the film formation speed and improve the film quality.

[0190]

As described above, the atmospheric pressure plasma discharge treatment device used in the present invention discharges the gas between the opposing electrodes to create a plasma state of the gas introduced between the opposing electrodes, and exposes the substrate material, which is placed statically between the opposing electrodes or transferred between the electrodes, to the gas in the plasma state, thereby forming a thin film on the substrate material. As another method, a jet-type atmospheric pressure plasma discharge treatment device similarly discharges between the opposing electrodes, excites the gas introduced between the opposing electrodes or puts the gas into a plasma state, and blows a jet of the excited or plasma state gas out of the opposing electrodes, exposing the substrate (which may be static or conveyed) in the vicinity of the opposing electrodes, forming a thin film on the substrate.

[0191]

FIG. 4 is a schematic drawing showing an example of a jet-type atmospheric pressure plasma discharge treatment device useful in the present invention.

[0192]

The jet-type atmospheric pressure plasma discharge treatment device has a plasma discharge treatment apparatus and an electric field application means with two power sources, as well as a gas supply means and an electrode temperature control means, which are not shown in FIG. 4 (but are shown in FIG. 5 described below).

[0193]

A plasma discharge treatment device 10 has opposing electrodes comprising a first electrode 11 and a second electrode 12, a first high-frequency electric field of a frequency ω1, an electric field strength of V1, and a current I1 from a first power source 21 is applied between the opposing electrodes from the first electrode 11, and a second high-frequency electric field of a frequency ω2, an electric field strength V2, and a current I2 from a second power source 22 is applied between the opposing electrodes from the second electrode 12. The first power supply 21 applies a higher high frequency electric field strength than the second power supply 22 (V1 > V2), and the first frequency ω1 of the first power supply 21 applies a lower frequency than the second frequency ω2 of the second power supply 22.

[0194]

A first filter 23 is installed between the first electrode 11 and the first power supply 21 and is designed to facilitate the passage of current from the first power supply 21 to the first electrode 11 and to ground the current from the second power supply 22, making it difficult for current to pass from the second power supply 22 to the first power source 21.

[0195]

A second filter 24 is installed between the second electrode 12 and the second power supply 22 and is designed to facilitate the passage of current from the second power supply 22 to the second electrode and to ground the current from the first power source 21, making it difficult for current to pass from the first power source 21 to the second power source.

[0196]

A thin film forming gas G, mentioned above, is introduced into a space (discharge space) 13 between the opposing electrodes, the first electrode 11 and the second electrode 12, from the gas supply means as shown in FIG. 5 described below, and the high-frequency electric field is applied between the first electrode 11 and the second electrode 12 using the first power supply 21 and second power supply 22 to generate a discharge, causing the thin film forming gas G to be in a plasma state while being blown out in a jet shape below the opposing electrodes (on the bottom side of the paper), the treatment space created by the lower surface of the opposing electrodes and a substrate material F is filled with a gas G° in a plasma state, and a thin film is formed near a treatment position 14 on the substrate material F, which is either unwound from the source roll (unwinder) of the substrate material (not shown in the figure) or conveyed from the previous process. During thin film formation, a medium from the electrode temperature control means, as illustrated in FIG. 5 described below, is piped through to heat or cool the electrodes. Depending on the temperature of the substrate material during plasma discharge treatment, the physical properties, the composition, and the like of the resulting thin film may vary, and it is desirable to control for this variation as appropriate. As a medium for temperature control, an insulating material such as distilled water or oil is preferably used. During plasma discharge treatment, it is desirable to regulate the temperature inside the electrodes evenly so as to avoid temperature irregularities in the width and length direction of the substrate material as much as possible.

[0197]

FIG. 4 also shows the measuring instruments and the measurement positions used to measure the application electric field strength and the discharge initiation electric field strength. 25 and 26 are high-frequency voltage probes, and 27 and 28 are oscilloscopes.

[0198]

By arranging a plurality of jet-type atmospheric pressure plasma discharge treatment devices parallel to the conveyance direction of the substrate material F and simultaneously discharging gases in the same plasma state, a plurality of thin film layers can be formed at the same location, enabling formation of the desired film thickness in a short period of time. Also, by arranging a plurality of devices parallel to the conveyance direction of the substrate material F, supplying each device with a different thin film forming gas, and jetting the gas in different plasma states, it is possible to form different laminated thin film layers.

[0199]

FIG. 5 is a schematic drawing showing an example of an atmospheric pressure plasma discharge treatment device that treats the substrate material between opposing electrodes and is useful for the present invention.

[0200]

The atmospheric pressure plasma discharge treatment device of the present invention has at least a plasma discharge treatment device 30, an electric field application means 40 with two power sources, a gas supply means 50, and an electrode temperature adjustment means 60.

[0201]

A thin film is formed by treating the substrate material F with plasma discharge among opposing electrodes 32 (hereinafter also referred to as the discharge space 32 between the opposing electrodes) between a roll rotating electrode (first electrode) 35 and a rectangular cylindrical fixed electrode group (second electrode) (hereinafter the rectangular cylindrical fixed electrode group referred to as the fixed electrode group) 36.

[0202]

In the discharge space 32 formed between the roll rotating electrode 35 and the fixed electrode group 36, a first high-frequency electric field of a frequency ω1, an electric field strength V1, and a current I1 is applied to the roll rotating electrode 35 from a first power supply 41, and a second high-frequency electric field of a frequency ω2, an electric field strength V2, and a current I2 is applied to the fixed electrode group 36 from a second power supply 42.

[0203]

A first filter 43 is installed between the roll rotating electrode 35 and the first power supply 41 and is designed to facilitate the passage of current from the first power supply 41 to the first electrode and to ground the current from the second power supply 42, making it difficult for current to pass from the second power supply 42 to the first power supply. A second filter 44 is installed between the fixed electrode group 36 and the second power supply 4 and is designed to facilitate the passage of current from the second power supply 42 to the second electrode and to ground the current from the first power supply 41, making it difficult for current to pass from the first power supply 41 to the second power supply.

[0204]

In the present invention, the roll rotating electrode 35 may be used as the second electrode and the rectangular cylindrical fixed electrode group 36 as the first electrode. In any case, the first power supply is connected to the first electrode and the second power supply to the second electrode. The first power supply preferably applies a higher high-frequency electric field strength than the second power supply (V1 > V2). The frequencies have the capacity to be $\omega 1 < \omega 2$.

[0205]

The current is preferably I1 < I2. The current I1 of the first high-frequency electric field is preferably 0.3-20 mA/cm^2 and more preferably 1.0-20 mA/cm^2. The current I2 of the second high-frequency electric field is preferably 10-100 mA/cm^2 and more preferably 20-100 mA/cm^2.

[0206]

A thin film forming gas G generated by a gas generation device 51 of a gas supply means 50 is introduced into a plasma discharge treatment vessel 31 from an air supply port 52 by controlling the flow rate with an gas flow adjustment means not illustrated.

[0207]

The substrate material F is either unwound and conveyed from a source roll, which is not illustrated, or is conveyed from the previous process in the direction of the arrow, is passed through a guide roll 64 to a nip roll 65, where it is intercepted by air and the like that come along with the substrate material, and is wound in contact with the roll rotating electrode 35 while being transferred in the interval with the cylindrical rectangular fixed electrode group 36.

[0208]

During the transfer, an electric field is applied from both the roll rotating electrode 35 and the fixed electrode group 36 to generate discharge plasma between the opposing electrodes (in the discharge space) 32. The substrate material F forms a thin film by means of the gas in the plasma state while being wound around the roll rotating electrode 35 while in contact therewith.

[0209]

A plurality of rectangular cylindrical fixed electrodes are provided along a circumference larger than the circumference of the roll electrode, and the discharge area of the electrodes is expressed as the sum of the areas of the surfaces opposing the roll rotating electrode 35 of all the rectangular cylindrical fixed electrodes opposing the roll rotating electrode 35.

[0210]

The substrate material F passes through the nip roll 66 and the guide roll 67, and is either wound up by a take-up machine not illustrated or transferred to the next process.

[0211]

A treatment exhaust gas G′ after discharge treatment is discharged from an exhaust port 53.

[0212]

To heat or cool the roll rotating electrode 35 and the fixed electrode group 36 during thin film formation, a medium whose temperature is regulated by the electrode temperature control means 60 is fed to both electrodes through a pipe 61 by a feed pump P to regulate the temperature from inside the electrodes. 68 and 69 are dividers that partition the plasma discharge treatment vessel 31 from the outside world.

[0213]

FIG. 6 is a perspective drawing showing an example of the structure of a conductive metal base material of the roll rotating electrode shown in FIG. 5 and a dielectric coated thereon.

[0214]

In FIG. 6, a roll electrode 35a is made of a conductive metallic base material 35A and a dielectric 35B coated thereon. To control the temperature of the electrode surface during plasma discharge treatment and to maintain the surface temperature of the substrate material F at a predetermined value, the structure is designed to allow circulation of a temperature control medium (water, silicon oil, or the like).

[0215]

FIG. 7 is a perspective drawing showing an example of the structure of a conductive metallic base material of a rectangular cylindrical electrode and a dielectric coated thereon.

[0216]

In FIG. 7, a rectangular cylindrical electrode 36a has a conductive metallic base material 36A coated with an inductor 36B as in FIG. 6, and the structure of the electrode is a metallic pipe, which serves as a jacket to control the temperature during discharge.

[0217]

The rectangular cylindrical electrode 36a shown in FIG. 7 can also be a round cylindrical electrode, but the rectangular cylindrical electrode has the effect of expanding the discharge range (discharge area) more than a round cylindrical electrode and is therefore preferably used in the present invention.

[0218]

In FIG. 6 and FIG. 7, the roll electrode 35a and the rectangular cylindrical electrode 36a are each made by thermal-spraying ceramic as dielectrics 35B and 36B on the conductive metallic base materials 35A and 36A, respectively, and then sealed with an inorganic compound sealing material. The ceramic dielectrics should be coated on one side to about 1 mm. Alumina, silicon nitride, and the like are preferably used as ceramic materials for thermal spraying, of which alumina is particularly preferable because it is easy to work. The dielectric layers may be lining-treated dielectrics with inorganic material provided by lining.

[0219]

As the conductive metallic substrate materials 35A and 36A, titanium metal, a titanium alloy, silver, platinum, stainless steel, aluminum, iron, and other metals, as well as composites of iron and ceramic or aluminum and ceramic can be used, but for reasons described below, titanium metal or a titanium alloy is particularly preferable.

[0220]

The distance between the opposing first and second electrodes refers to the shortest distance between the dielectric surface of one of the electrodes and the conductive metallic base material surface of the other electrode. If both electrodes have dielectrics, the distance between the opposing first and second electrodes is the shortest distance between the dielectric surfaces. The distance between the electrodes is determined by considering the thickness of the dielectric on the conductive metallic base material, the size of the application electric field strength, the purpose of using plasma, and the like, but in any case, 0.1-20 mm is preferable from the perspective of uniform discharge, and 0.5-2 mm is particularly preferable.

[0221]

Details on conductive metallic base materials and dielectrics useful in the present invention are provided below.

[0222]

The plasma discharge treatment vessel 31 is preferably made of Pyrex (registered trademark) glass or the like, but metal can also be used as long as there is insulation with respect to the electrodes. For example, the inner surface of an aluminum or stainless steel frame can be lined with a polyimide resin or the like, and the metal frame can be thermal-sprayed with ceramic to provide insulation. In FIG. 4, both sides of both of the parallel electrodes (up to near the substrate material surface) are preferably covered with a material such as described above.

[0223]

For the first power supply (high-frequency power supply) to be installed in the atmospheric pressure plasma discharge treatment device of the present invention, commercially available devices such as

Application power source symbol	Manufacturer	Frequency	Product name
A1	Shinko Electric Co., Ltd.	3 kHz	SPG3-4500
A2	Shinko Electric Co., Ltd.	5 kHz	SPG5-4500
A3	Kasuga Denki, Inc.	15 kHz	AGI-023
A4	Shinko Electric Co., Ltd.	50 kHz	SPG50-4500
A5	Haiden Research Institute	100 kHz*	PHF-6k
A6	Pearl Kogyo Co., Ltd.	200 kHz	CF-2000-200k
A7	Pearl Kogyo Co., Ltd.	400 kHz	CF-2000-400k

can be listed and any of these used.

[0224]

For the second power supply (high-frequency power supply), commercially available devices such as

Application power source symbol	Manufacturer	Frequency	Product name
B1	Pearl Kogyo Co., Ltd.	800 kHz	CF-2000-800k
B2	Pearl Kogyo Co., Ltd.	2 MHz	CF-2000-2M
B3	Pearl Kogyo Co., Ltd.	13.56 MHz	CF-5000-13M
B4	Pearl Kogyo Co., Ltd.	27 MHz	CF-2000-27M
B5	Pearl Kogyo Co., Ltd.	150 MHz	CF-2000-150M

can be listed and any of these preferably used.

[0225]

Of the above power supplies, the one marked with an asterisk (*) is the Heiden Research Institute impulse high-frequency power supply (100 kHz in continuous mode). The others are high-frequency power supplies to which only continuous sine waves can be applied.

[0226]

In the present invention, it is preferable to employ an electrode capable of applying such an electric field and maintaining a uniform and stable discharge state in the atmospheric pressure plasma discharge treatment device.

[0227]

In the present invention, the power applied between the opposing electrodes is supplied to the second electrode (second high-frequency electric field) at a power (power density) of at least 1 W/cm^2 to excite the discharge gas and generate plasma, giving energy to the thin film forming gas to form a thin film. The upper limit of the power supplied to the second electrode is preferably 50 W/cm^2 and more preferably 20 W/cm^2. The lower limit is preferably 1.2 W/cm^2. The discharge area (cm^2) refers to the area within which discharge occurs between the electrodes.

[0228]

By supplying a power (output density) of at least 1 W/cm^2 to the first electrode (first high-frequency electric field) as well, the output density can be improved while maintaining the uniformity of the second high-frequency electric field. This enables the generation of a more uniform high-density plasma, which can further improve both the film formation speed and the film quality. Preferably, the value is 5 W/cm^2 or higher. The upper limit of the power supplied to the first electrode is preferably 50 W/cm^2.

[0229]

The waveform of the high-frequency electric field is not particularly limited here. There is a continuous oscillation modes with a continuous sine wave shape called continuous mode, an intermittent oscillation mode that turns on and off intermittently called pulse mode, and so forth, and while either of these modes can be adopted, the continuous sine wave method is preferable at least for the second electrode side (second high-frequency electric field) because a denser and better quality film is obtained.

[0230]

Electrodes used in this method of thin film formation by atmospheric pressure plasma must be able to withstand harsh conditions both structurally and in terms of performance. Such an electrode is preferably a dielectric coated on a metallic base material.

[0231]

In the dielectric-coated electrode used in the present invention, the properties preferably match between the various metallic base materials and the dielectric, and one such property is a combination where the difference in linear thermal expansion coefficient between the metallic base material and the dielectric is 10 x 10^{-6}/° C or less. Preferably, the difference is 8 x 10^{-6}/° C or less, even more preferably 5 x 10^{-6}/° C or less, and yet even more preferably 2 x 10^{-6}/° C or less. The coefficient of linear thermal expansion is a well-known material-specific physical property value.

[0232]

Combinations of a conductive metallic base material and a dielectric for which the difference in the coefficient of linear thermal expansion is in this range include:

1: a metallic substrate material that is pure titanium or a titanium alloy, and a dielectric that is a thermal-sprayed ceramic coating

2: a metallic base material that is pure titanium or a titanium alloy, and a dielectric that is glass lined

3: a metallic base material that is stainless steel, and a dielectric that is a thermal-sprayed ceramic coating

4: a metallic base material that is stainless steel, and a dielectric that is glass lined

5: a metallic base material that is a composite of ceramic and iron, and a dielectric that is a thermal-sprayed ceramic coating

6: a metallic substrate material that is a composite of ceramic and iron, and a dielectric that is glass lined

7: a metallic substrate material that is a composite of ceramic and aluminum, and a dielectric that is a thermal-sprayed ceramic coating and

8: a metal substrate material that is a composite of ceramic and aluminum, and a dielectric that is glass lined. In terms of the difference in linear thermal expansion coefficients, items 1, 2, and 5 to 8 are preferable, and item 1 is particularly preferable.

[0233]

In the present invention, titanium or a titanium alloy is particularly useful as the metallic base material because of the characteristics described above. By using titanium or a titanium alloy as the metallic base material and making the dielectric as described above, the electrode will not deteriorate during use and can withstand prolonged use under harsh conditions, especially cracking, peeling, falling off, and the like.

[0234]

The metallic base material of the electrodes useful for the present invention is a titanium alloy or a titanium metal containing at least 70 mass% titanium. In the present invention, the titanium content in the titanium alloy or the titanium metal can be used without any problem as long as there is at least 70 mass%, but preferably there is 80 mass% or more titanium. Titanium alloys and titanium metals useful for the present invention that can be utilized are those commonly used as industrial pure titanium, corrosion-resistant titanium, high-strength titanium, and the like. Industrial pure titanium includes TIA, TIB, TIC, TID, and the like, all of which contain very small amounts of iron atoms, carbon atoms, nitrogen atoms, oxygen atoms, hydrogen atoms, and the like and have a titanium content of at least 99 mass%. As a corrosion-resistant titanium alloy, T15PB can be preferably used, contains lead in addition to the above content atoms, and has a titanium content of at least 98 mass%. As titanium alloys, T64, T325, T525, TA3, and the like, which contain aluminum in addition to the above atoms except lead, and also contain vanadium and tin, can be preferably used, and the titanium content is at least 85 mass%. These titanium alloys and titanium metals have a coefficient of thermal expansion about 1/2 as large as that of stainless steel, e.g., AISI 316, can be combined with the dielectric described below, which is applied over the titanium alloy or the titanium metal as a metallic base material, and can withstand high temperature and long use.

[0235]

As for the characteristics required of the dielectric, specifically, an inorganic compound with a relative permittivity of 6-45 is preferable, and such dielectrics include ceramics such as alumina and silicon nitride, and glass-lined materials such as silicate glass and borate glass. Among these, those created by thermal spraying of ceramic or glass lining as described below are preferable. Dielectrics created by thermal-spraying alumina are especially preferable.

[0236]

Further, as one of the specifications to withstand high power as described above, the porosity of the dielectric is preferably 10 volume% or less, preferably 8 volume% or less, and preferably greater than 0 volume% and 5 volume% or less. The porosity of the dielectric can be measured by the BET adsorption method or a mercury porosimeter. In the embodiments described below, the porosity is measured using a piece of dielectric coated on a metallic base material with a mercury porosimeter manufactured by Shimadzu Corporation. High durability is achieved when the dielectric has a low porosity. A dielectric that has such holes while still having low porosity can be a high-density, high-adhesion ceramic thermal-spray coating or the like applied with an atmospheric plasma thermal-spraying method or the like as described below. To further reduce the porosity, it is preferable to perform a sealing treatment.

[0237]

The atmospheric plasma thermal-spraying method described above is a technology in which a fine powder of ceramic or the like, wires, or the like are fed into a plasma heat source and sprayed as fine particles in a molten or semi-molten state onto a metallic base material to be coated, forming a coating. The plasma heat source is a high-temperature plasma gas in which molecular gas is heated to a high temperature, dissociated into atoms, and further energized to emit electrons. The jet velocity of the plasma gas is large, and the thermal-sprayed material impacts the metallic base material at a higher velocity than in conventional arc or flame spraying, resulting in a high-density film with high adhesion strength. For details, reference can be made to the thermal-spraying method for forming a thermal barrier coating on a member exposed to high temperatures described in Patent Appl. Publication No. JP 2000-301655. This method can achieve the porosity of the dielectric (ceramic thermal-spray coating) to be coated as described above.

[0238]

Another preferable specification to withstand high power is a dielectric thickness of 0.5-2 mm. The thickness variation is desirably be 5% or less, preferably 3% or less, and even more preferably 1% or less.

[0239]

To further reduce the porosity of the dielectric, it is preferable to further seal the thermal-sprayed film of ceramic or the like with an inorganic compound as described above. As the aforementioned inorganic compound, metal oxides are preferable, and among these, those containing silicon oxide (SiOx) as a main component are particularly preferable.

[0240]

The inorganic compound of the sealing treatment is preferably formed by curing in a sol-gel reaction. When the inorganic compound for the sealing treatment has a metal oxide as a main component, a metal alkoxide or the like is applied as a sealing liquid on the ceramic thermal-spray coating and cured with a sol-gel reaction. When the inorganic compound has silica as a main component, alkoxysilane is preferably used as the sealing liquid.

[0241]

Energy treatment is preferably used to accelerate the sol-gel reaction. Energy treatments include thermal curing (preferably at 200° C or lower) and ultraviolet ray irradiation. In addition, diluting the sealing solution and sequentially repeating coating and curing several times as a method of sealing treatment further improves mineralization and produces a dense electrode without degradation.

[0242]

When the dielectric coated electrode according to the present invention is sealed with a sealing solution of metal alkoxide or the like that is coated on the thermal-sprayed ceramic film and then cured with a sol-gel reaction, the metal oxide content after curing is preferably 60 mol% or more. When alkoxysilane is used as the metal alkoxide in the sealing solution, the SiOx (x is 2 or less) content after curing is preferably 60 mol% or more. The SiOx content after curing is measured by analyzing the cross section of the dielectric layer with X-ray photoelectron spectroscopy (XPS).

[0243]

In the electrode for the thin film deposition method of the present invention, it is preferable from the perspective of obtaining the effect described in the present invention to adjust the maximum height of surface roughness (Rmax) specified in JIS B 0601 at least on the side of the electrode in contact with the substrate material to be 10 μm or less, but it is even more preferable that the maximum value of surface roughness be 8 μm or less, and adjusting to 7 μm or less is especially preferable. By using methods such as polishing the dielectric surface of the dielectric-coated electrodes, the thickness of the dielectric and the gap between electrodes can be kept constant, the discharge state can be stabilized, distortion and cracks due to thermal contraction differences and residual stress can be eliminated, and durability can be greatly improved with high accuracy. It is preferable that the dielectric surface be polished at least on the side of the dielectric in contact with the substrate material. Furthermore, the centerline average surface roughness (Ra) specified in JIS B 0601 is preferably 0.5 μm or less and even more preferably 0.1 μm or less.

[0244]

Another preferable specification for dielectric-coated electrodes used in the present invention to withstand high power is a heat resistance temperature of at least 100° C. Even more preferable is a heat resistance temperature of at least 120° C, and particularly preferable is a heat resistance temperature of at least 150° C. The upper limit is 500° C. The heat resistance temperature refers to the highest temperature that can be withstood under the voltage used in the atmospheric pressure plasma treatment in a state where insulation breakdown does not occur and normal discharge is possible. Such a heat resistance temperature can be achieved by using the above-mentioned ceramic thermal-spraying, by applying a dielectric made of layered glass lining with different amounts of bubbles, or by appropriately combining means of appropriately selecting materials within the above-mentioned range of differences in linear thermal expansion coefficient between the metallic base material and the dielectric.

[0245]

FIG. 8 is a schematic configuration drawing showing an example of the method for manufacturing a gas barrier thin film laminate of the present invention.

[0246]

From a source winding roller 400 of the substrate material downstream, the resin film F is unrolled while being held by a guide roller 204 and a support roller 402, and at a station A, foreign matter adhering to the resin film F is removed by the foreign matter removal means using adhesive tape. Next, at a station B, a first ceramic layer is formed by a plasma discharge treatment device 10. The ceramic layer formed at this time is preferably a buffer film with a carbon content of 1% (atomic concentration %) or more. Next, foreign matter attached on the ceramic layer in the atmospheric pressure plasma discharge process at the station B is removed by the foreign matter removal means according to the present invention at a station C before the second ceramic layer is laminated. FIG. 8 shows a contact-type foreign matter removal device using adhesive tape (for details, refer to FIG. 1 a)).

[0247]

Next, after the foreign matter on the ceramic layer is removed with the foreign matter removal device, a second ceramic layer is formed at a station D, and the fabricated gas barrier thin film laminate is laminated in a roll form on a take-up roller 401 and rolled up. The ceramic layer formed at this time is preferably a barrier film with a carbon content of 0.1% (atomic concentration %) or less. Next, the gas barrier thin film laminate of the present invention can then be obtained by providing the station C, the station B or the station D at a plurality of locations as required.

[0248]

[Sealing of the organic electroluminescent element]

The organic electroluminescent device of the present invention can be obtained by forming a transparent conductive film on a resin substrate material having the gas barrier thin film laminate formed in this manner, using the transparent conductive film as the anode, further laminating an organic electroluminescent (EL) material film that constitutes an organic electroluminescent element and a metal layer that serves as the cathode, forming the organic EL element, then further forming a sealing material film on the cathode and sealing the organic EL element. For example, the gas barrier thin film laminate of the present invention can be formed on the cathode using the atmospheric pressure plasma CVD method to cover and seal the entire organic EL device.

[0249]

To form the gas barrier thin film laminate comprising a ceramic film on the cathode, the aforementioned methods for forming a gas barrier laminate can be used as is. For example, the sol-gel method, the vacuum deposition method, the sputtering method, and the like can be used, but the plasma CVD method or the plasma CVD method at or near atmospheric pressure is preferable. The gas barrier thin film laminate comprising ceramic films such as the buffer film and the barrier film is formed on the cathode using these methods. In addition to one gas barrier thin film laminate set, two or more sets may also be formed. The outermost layer is preferably formed with a buffer film as a protective film.

[0250]

The organic EL element can be sealed by using, as the sealing film, other sealing materials, e.g., known gas barrier films used for packaging materials and the like, e.g., silicon oxide or aluminum oxide deposited on a plastic film, deposited aluminum oxide, ceramic layers and shock-absorbing polymer layers alternately laminated, and the like, as well as a metal foil or the like laminated with a polymer film, stacking the sealing film on the gas barrier resin substrate film forming the organic EL element, and bonding with an adhesive.

[0251]

As the sealing material, a material with high gas barrier performance, e.g., a glass sealing can or the like may be stacked and bonded to the gas barrier resin substrate material on which the organic EL element is formed for sealing.

[0252]

When using a sealing material for sealing, among the known gas barrier films used for packaging materials mentioned above, resin-laminated (polymer film-laminated) metal foil in particular cannot be used as a gas barrier film on the light-extracting side, but resin-laminated metal foil is a low-cost, low moisture permeability sealing material that is preferable as a sealing film when light extraction is not intended (transparency is not required).

[0253]

In the present invention, a metal foil refers to a metal foil or film formed by rolling or other means, unlike a thin metal film formed by sputtering or deposition or a conductive film formed from a conductive paste or some other flowable electrode material.

[0254]

There is no particular restriction on the type of metal as the metal foil, and examples include a copper (Cu) foil, an aluminum (Al) foil, a gold (Au) foil, a brass foil, a nickel (Ni) foil, a titanium (Ti) foil, a copper alloy foil, a stainless steel foil, a tin (Sn) foil, and a high nickel alloy foil. An Al foil is a particularly preferable metal foil among these various metal foils.

[0255]

The thickness of the metal foil is preferably 6-50 μm. If the thickness is less than 6 μm, pinholes may open up during use depending on the material used for the metal foil, and the required barrier properties (moisture permeability and oxygen transmission rate) may not be achieved. If the thickness exceeds 50 μm, the cost may increase depending on the material used for the metal foil, or the organic EL element may become thicker, reducing the advantages of the film.

[0256]

Various materials listed in *Kino-sei Hoso Zairyo no Shin-Tenkai* "New Developments in Functional Packaging Materials" (Toray Research Center, Inc.) can be used as the resin film in the metal foil laminated with a resin film (polymer film), and examples include polyethylene resins, polypropylene resins, polyethylene terephthalate resins, polyamide resins, ethylene-vinyl alcohol copolymer resins, ethylene-vinyl acetate copolymer resins, acrylonitrile-butadiene copolymer resins, cellophane resins, vinylon resins, and vinylidene chloride resins. Resins such as polypropylene and nylon resins may be stretched or even coated with a vinylidene chloride resin. Polyethylene resins may also be used whether low or high density.

[0257]

Among the above-mentioned polymer materials, nylon (Ny), vinylidene chloride (PVDC)-coated nylon (KNy), unstretched polypropylene (CPP), stretched polypropylene (OPP), PVDC-coated polypropylene (KOP), polyethylene terephthalate (PET), PVDC coated cellophane (KPT), polyethylene-vinyl alcohol copolymer (EVAL), low density polyethylene (LDPE), high density polyethylene (HDPE), and linear low density polyethylene (LLDPE) are preferably used. In addition, these thermoplastic films can naturally be used as multilayer films made by co-extruding with various films according to need, laminating by pasting at different stretching angles, and so on. Furthermore, it is naturally possible to combine the density and molecular weight distribution of the film used to obtain the required packaging material properties.

[0258]

The thickness of the polymer film cannot be generally stipulated, but 3-400 μm is preferable, 10-200 μm is more preferable, and 10-50 μm is even more preferable.

[0259]

For coating (laminating) the polymer film on one side of the metal foil, commonly used laminating machines can be used. Polyurethane, polyester, epoxy, acrylic, and other adhesives can be used as the adhesive. A curing agent may be used in combination if necessary. Dry lamination, hot-melt lamination, and extrusion lamination methods can also be used, but the dry lamination method is preferable.

[0260]

Films in which one side of a metal foil is coated with a polymer film are commercially available for packaging materials. For example, a dry laminate film (the adhesive layer being a two-liquid reactive urethane adhesive with a thickness of 1.5 μm) consisting of an adhesive layer/aluminum film 9 μm/polyethylene terephthalate (PET) 38 μm is available, and can be used to seal the cathode side of the organic EL element.

[0261]

After forming each layer of the organic EL element on a resin film substrate material (gas barrier resin substrate material) having the gas barrier thin film laminate of the present invention, to seal using the above sealing material, the cathode surface can be covered with the above sealing film under an environment purged with inert gas and bonded with an adhesive.

[0262]

As an adhesive, the two-liquid reactive urethane adhesives, epoxy adhesives, and the like can be used, but photocurable adhesives are preferable in the present invention. The photocurable adhesive between the sealing material and the gas barrier resin substrate material is irradiated from the substrate material side with light in the ultraviolet to visible region, which can be obtained from a high-pressure mercury vapor lamp or a halogen lamp, to cure the photocurable adhesive, thereby integrating the substrate material and the sealing material.

[0263]

As the photocurable adhesive, commercially available products can be used such as cationic photocurable adhesives with epoxy resin as the main component, for example, the ultraviolet ray-curing epoxy adhesive XNR5493T (manufactured by Nagase-CIBA, Ltd.), and radical photocurable adhesives with acrylic resin as the main component, for example, trade name Rakkusutorakku LCR0641 manufactured by Toagosei Co., Ltd. In the case of the gas barrier resin substrate material according to the present invention, since both the buffer film and the barrier film comprise a ceramic film, absorption in the ultraviolet-blue region is less than that of a buffer film made of an organic polymer and laminated with a ceramic film, so when light irradiates through the substrate and sealing is performed, the material cures sufficiently even at low irradiation doses for good productivity.

[0264]

In the present application, “ultraviolet region (light)” refers to light with a wavelength in the range of 250-400 nm, and “visible region (light)” refers to light with a wavelength in the range of 400-700 nm.

[0265]

In addition to N_2, rare gases such as He and Ar are preferably used as the inert gas, a mixture of He and Ar is also preferable, and the ratio of inert gas in the gas is preferably 90-100 volume%. Sealing under an environment purged by inert gas improves the shelf life.

[0266]

For example, when using a metal foil laminated with the aforementioned resin film (polymer film) as the sealing film to seal the organic EL element, the laminated resin film surface can be placed facing the cathode surface of the organic EL element to seal.

[0267]

When using a metal foil laminated with a resin film (polymer film), it is preferable to form a ceramic film on the metal foil on the side opposite the polymer film, face the ceramic film surface toward the cathode of the organic EL element, and bond and paste. When the polymer film surface of the sealing film is pasted to the cathode of the organic EL element, partial conductivity may occur as may associated electrical illumination, which may result in dark spots. Silicon oxide, silicon oxide nitride, or the like is preferable as the ceramic film to be formed on the metal foil, and may also be the barrier film or the buffer film according to the present invention. These ceramic films can be formed by deposition, plasma CVD, or the other methods as described above. The film thickness is in the range of 1-2000 nm, preferably 20-1000 nm.

[0268]

The sealing method for pasting the sealing film to the cathode of the organic EL element includes using an adhesive as described above, and laminating a resin film that can be fused with a commonly used impulse sealer, e.g., a thermally bondable film such as an ethylene-vinyl acetate copolymer (EVA), a polypropylene (PP) film, or a polyethylene (PE) film, and then sealing by fusion bonding with an impulse sealer.

[0269]

The dry lamination method is excellent as the adhesion method in terms of workability. This method generally uses a curable adhesive layer about 1.0-2.5 μm [thick]. However, if too much adhesive is applied, tunneling, soaking, fine wrinkles, and the like may occur, so preferably the amount of adhesive is preferably adjusted so as to be 3-5 μm thick when dry.

[0270]

Hot melt lamination is a method in which a hot melt adhesive is melted to coat an adhesive layer on the substrate material, and the thickness of the adhesive layer can generally be set in a wide range from 1 to 50 μm. EVA, EEA, polyethylene, butyl rubber, and the like are commonly used as base resins for hot melt adhesives, and rosin, xylene resin, terpene resin, styrene resin, or the like is added as an adhesive coating agent and wax or the like as a plasticizer.

[0271]

Extrusion lamination is a method of coating molten resin on a substrate material at high temperature using a die, and the thickness of the resin layer can be set in a wide range, generally from 10 to 50 μm.

[0272]

LDPE, EVA, PP, and the like are commonly used as resins used on extrusion laminates.

[0273]

Specific examples of the sealed organic electroluminescent devices of the present invention are provided below.

[0274]

FIG. 9 shows a cross-sectional configuration drawing with an example of an organic EL device in which each layer of an organic EL element comprising an anode, a light emission layer or the like, an organic layer, and a cathode is formed on the gas barrier resin substrate material of the present invention, and then a gas barrier thin film laminate comprising the buffer film and the barrier film according to the present invention is formed on the cathode and sealed. In the drawing, the organic EL element is configured by laminating, in order, an anode 6 comprising ITO, an organic layer (comprising a hole transport layer, a light emission layer, an electron transport layer, and the like) 7, and a cathode 8 on a resin substrate material 1 on which a gas barrier thin film laminate 9 is formed. On top, a buffer film 3/a barrier film 4/a buffer film 3 of the present invention and a ceramic (silicon oxide) film are formed in order to form the gas barrier thin film laminate 9. The gas barrier thin film laminate 9 on the resin substrate material and the gas barrier thin film laminate formed on the cathode may also each comprise two or more barrier films and two or more buffer films. The arrow indicates the direction of light extraction.

[0275]

FIG. 10 is a cross-sectional configuration drawing showing an example of the organic EL device in which each layer of an organic EL element comprising an anode, a light emission layer or the like, an organic layer, and a cathode is formed on the gas barrier resin substrate material of the present invention, and then covered with a separate sealing film for adhesive sealing.

[0276]

FIG. 10(a) shows an organic EL device in which each organic EL element layer comprising an anode, an organic layer such as a light emission layer, and a cathode is formed on the gas barrier resin substrate material of the present invention, and then another gas barrier resin substrate material of the present invention is used as a sealing film.

[0277]

Figure 10(a) shows a structure in which each layer of an organic EL element comprising an anode 6 comprising ITO, an organic layer 7 such as a light emission layer, and a cathode 8 is formed on a resin substrate material 1 having a gas barrier thin film laminate 9 of the present invention, and then a separate resin substrate material 1 having a gas barrier thin film laminate 9 of the present invention is bonded and sealed using an adhesive ad so that the ceramic film side is facing the cathode.

[0278]

FIG. 10(b) shows a cross-sectional schematic diagram of an organic EL element in which each layer of the organic EL element comprising an anode, an organic layer such as a light emission layer, and a cathode is formed on the gas barrier resin substrate material of the present invention, then the gas barrier resin substrate material is bonded for sealing with a resin-laminated aluminum foil having a silicon oxide film and the above-mentioned gas barrier resin substrate material used as the substrate.

[0279]

In FIG. 10(b), an anode (ITO) 6, an organic layer 7 containing a light emission layer, and a cathode (e.g., aluminum) 8 are each formed on a gas barrier resin substrate material on which a polymer film 2 for improving adhesion formed on a resin substrate material 1 and a gas barrier thin film laminate 9 comprising a buffer film and a barrier film according to the present invention are formed on the resin substrate material to form an organic EL element. A separate sealing film S is stacked on the cathode and the perimeter of the substrate material film is bonded to seal the organic EL element containing an organic EL material layer. In the sealing film S, a silicon oxide film S1 according to the present invention is formed on a metal (aluminum) foil S2, and on the opposite side of the metal foil, a resin layer S3 is laminated and bonded so that the ceramic film 3 side is in contact with the cathode. The arrow indicates the direction of light extraction.

[0280]

For sealing gas barrier films together, a film thickness of 300 μm or less is desirable because a film thickness exceeding 300 μm makes handling difficult during sealing and makes it difficult to carry out thermal bonding with an impulse sealer or the like.

[0281]

The sealing of the organic EL element of the present invention can also be carried out using an inorganic material such as a glass with a low moisture vapor transmission rate and gas permeability as well as using a substrate material such as the sealing film described above.

[0282]

FIG. 11 shows an example of an organic EL device in which the organic EL element is sealed using a glass sealing can.

[0283]

FIG. 11 shows a sealed element in which an organic EL layer 102 comprising a hole injection/transport layer, a light emission layer, a hole blocking layer, an electron transport layer, and the like and then a cathode 103 are formed on a gas barrier resin substrate material 101 according to the present invention to fabricate an organic EL element provided with a transparent electrode, and the result is irradiated and bonded using a glass sealing can 104 and an ultraviolet ray-curable adhesive 107. 105 is barium oxide, a moisture capturing agent.

[0284]

For example, after forming these organic EL layers and the cathode, the glass sealing can is used for a sealing structure after internal nitrogen replacement under, for example, a nitrogen atmosphere (e.g., using a glove box replaced with high-purity nitrogen gas of at least 99.999% purity) without contact with the atmosphere. The moisture capturing agent, barium oxide, can be produced by pasting, for example, high-purity barium oxide powder manufactured by Aldrich using a fluororesin semi-permeable film with an adhesive (Microtex S-NTF8031Q manufactured by Nitto Denko Co., Ltd.) Other commercially available water capturing agents can be favorably used such as those from Japan Core Tex, Inc., and Futaba Corporation.

[0285]

In addition, formation of the sealing structure is not limited to a sealing structure using the aforementioned glass sealing can, and water-absorbing substances may be placed in the sealing space, or a layer that absorbs moisture vapor such as a water-absorbing layer may be added in the structure.

[0286]

[Organic EL element]

Next, the structural layers of the organic EL element according to the present invention are described in detail. Preferable specific examples of the layer structures of the organic EL element are shown below, but the present invention is not limited thereto.

[0287]

(1) anode / light emission layer / electron transport layer / cathode

(2) anode / hole transport layer / light emission layer / electron transport layer / cathode

(3) anode / hole transport layer / light emission layer / hole blocking layer / electron transport layer / cathode

(4) anode / hole transport layer / light emission layer / hole blocking layer / electron transport layer / cathode buffer layer / cathode

(5) anode /anode buffer layer / hole transport layer / light emission layer / hole blocking layer / electron transport layer / cathode buffer layer / cathode

(Anode)

For the anode in the organic EL element, metals, alloys, electrically conductive compounds, and mixtures thereof with large work functions (4 eV or higher) are preferably used as the electrode material. Specific examples of such electrode materials include metals such as Au, and conductive transparent materials such as CuI, indium tin oxide (ITO), SnO_2, and ZnO. Materials such as IDIXO (In_2O_3-ZnO), which are amorphous and can be used to make transparent conductive films, can also be used. The anode is a thin film of this electrode material formed by deposition, sputtering, the aforementioned (atmospheric pressure) plasma CVD method, or the like. The pattern of a desired shape may be formed with photolithography, or a pattern may be formed through a mask at the time of formation. When extracting luminescence from the anode, the transmittance is made greater than 10%. The sheet resistance of the anode is preferably no greater than several hundred ohms/sq. The thickness of the film is ordinarily chosen in the range of 10-1000 nm and preferably 10-200 nm.

[0288]

(Cathode)

For the cathode, metals (referred to as electron injection metals), alloys, electrically conductive compounds, and mixtures thereof with small work functions (4 eV or lower) are preferably used as electrode materials. Specific examples of such electrode materials include sodium, sodium-potassium alloys, magnesium, lithium, magnesium/copper mixtures, magnesium/silver mixtures, magnesium/aluminum mixtures, magnesium/indium mixtures, aluminum/aluminum oxide (Al_2O_3) mixtures, indium, lithium/aluminum mixtures, rare earth metals, and the like. Among these, from the perspective of electron injectivity and durability against oxidation, mixtures of an electron injection metal and a second metal that is a stable metal with a larger work function value such as, for example, a magnesium/silver mixture, a magnesium/aluminum mixture, a magnesium/indium mixture, an aluminum/aluminum oxide (Al_2O_3) mixture, a lithium/aluminum mixture, aluminum, and the like are suitable. The cathode can be fabricated by forming a thin film of this electrode material with a method such as deposition or sputtering. The sheet resistance as a cathode is preferably no greater than several hundred ohms/sq, and the film thickness is ordinarily chosen in the range of 10 nm to 5 μm and preferably 50-200 nm. So that the emitted light can pass through, it is convenient if either the anode or the cathode of the organic EL element is transparent or semi-transparent for improved luminance of the emitted light.

[0289]

In addition, a transparent or semi-transparent cathode can be fabricated by fabricating a film of the metal described above to 1-20 nm thick for the cathode and then fabricating thereon the conductive transparent material mentioned in the description of the anode, and by applying this process, an element in which both the anode and the cathode have transparency can be fabricated.

[0290]

The gas barrier resin substrate material with a transparent electrode can be pre-fabricated by forming a transparent conductive film as the anode, a metal thin film as the cathode, and the like on the gas barrier resin substrate material having the gas barrier thin film laminate according to the present invention on the resin substrate material, and the gas barrier resin substrate material with a transparent electrode can be used to form the following organic thin film layer and the other electrode to similarly form an organic EL electrode. Either of the electrode materials can be formed on the resin substrate material, but from the standpoint of fabrication or constitution, it is preferable to fabricate a transparent conductive film that will serve as the anode.

[0291]

Next, the injection layer, the blocking layer, the electron transport layer, and the like used as the constituent layers of the organic EL element of the present invention are described.

[0292]

(Injection layer: electron injection layer, hole injection layer)

Injection layers are provided as needed, and include an electron injection layer and a hole injection layer, which may be present between the anode and the light emission layer or hole transport layer, and between the cathode and the light emission layer or electron transport layer, as described above.

[0293]

The injection layer is provided between an electrode and an organic layer to lower the drive voltage and improve the light emission brightness, is described in detail in Volume 2, Chapter 2, “Denkyoku Zairyo” [Electrode Materials] (pp. 123-166) in “Yuki EL Soshi to Sono Kogyoka Saizensen [Organic EL Elements and the Frontline of Their Industrialization] (November 30, 1998, published by NTS, Inc.),” and includes a hole injection layer (anode buffer layer) and an electron injection layer (cathode buffer layer).

[0294]

The anode buffer layer (hole injection layer) is described in detail in Patent Appl. Pub. Nos. JP H9-45479, JP H9-260062, JP H8-288069, and the like, and specific examples include a phthalocyanine buffer layer as typified by copper phthalocyanine, an oxide buffer layer as typified by vanadium oxide, an amorphous carbon buffer layer, and a polymer buffer layer using a conductive polymer such as polyaniline (emeraldine) or polythiophene.

[0295]

The cathode buffer layer (electron injection layer) is described in detail in Patent Appl. Pub. Nos. JP H6-325871, JP H9-17574, JP H10-74586, and the like, and specific examples include metal buffer layers typified by strontium, aluminum, and the like, alkali metal compound buffer layers typified by lithium fluoride, alkaline earth metal compound buffer layers typified by magnesium fluoride, and oxide buffer layers typified by aluminum oxide. The buffer layer (injection layer) is desirably a very thin film, and the thickness is preferably in the range of 0.1 nm to 5 μm, depending on the material.

[0296]

(Blocking layers: hole blocking layer, electron blocking layer)

The blocking layer is provided as necessary in addition to the basic constituent layers of the organic compound thin film, as described above. Hole blocking layers are described, for example, in Patent Appl. Pub. Nos. JP H11-204258 and JP H11-204359, page 237 of "Yuki EL Soshi to Sono Kogyoka Saizensen [Organic EL Elements and the Frontline of Their Industrialization] (November 30, 1998, published by NTS, Inc.)," and the like.

[0297]

A hole blocking layer in a broad sense has the function of an electron transport layer, comprises a hole blocking material that has the function of transporting electrons but a significantly small ability to transport holes, and can improve the probability of recombination between electrons and holes by blocking holes while transporting electrons. The structure of the electron transport layer described below can be used as the hole blocking layer according to the present invention if necessary.

[0298]

In contrast, an electron blocking layer in a broad sense has the function of a hole transport layer in a broad sense, comprises a material that has the function of transporting holes but a significantly small ability to transport electrons, and can improve the probability of recombination of electrons and holes by transporting holes but blocking electrons. The structure of the hole transport layer described below can be used as an electron blocking layer if necessary.

[0299]

(Light emission layer)

The light emission layer according to the present invention emits light by recombination of electrons and holes injected from the electrode or the electron transport layer and the hole transport layer, and the portion that emits light may be within the light emission layer or at the interface between the light emission layer and an adjacent layer.

[0300]

The light emission layer of the organic EL element of the present invention preferably contains a host compound and a dopant compound listed below. This allows for even higher light emission efficiency.

[0301]

There are two major types of light emission dopants: fluorescent dopants, which emit fluorescence, and phosphorescent dopants, which emit phosphorescence.

[0302]

Typical examples of the former (fluorescent dopants) include coumarin dyes, pyran dyes, cyanine dyes, croconium dyes, squalium dyes, oxobenzanthracene dyes, fluorescein dyes, rhodamine dyes, pyrylium dyes, perylene dyes, stilbene dyes, polythiophene dyes, and rare earth complex phosphors.

[0303]

Typical examples of the latter (phosphorescent dopants) are preferably complex-based compounds containing metals of group 8, 9, or 10 in the periodic table of elements, more preferably iridium compounds and osmium compounds, of which iridium compounds are the most preferable. Specifically, the compounds are those described in the following patent gazettes.

[0304]

WO No. 00/70655 Pamphlet, Patent Appl. Pub. Nos. JP 2002-280178, JP 2001-181616, JP 2002-280179, JP 2001-181617, JP 2002-280180, JP 2001-247859, JP 2002-299060, JP 2001-313178, JP 2002-302671, JP 2001-345183, and JP 2002-324679, WO No. 02/15645 Pamphlet, Patent Appl. Pub. Nos. JP 2002-332291, JP 2002-50484, JP 2002-332292, and JP 2002-83684, Patent Appl. Pub. Gazette No. 2002-540572, Patent Appl. Pub. Nos. JP 2002-117978, JP 2002-338588, 2002-170684, 2002-352960, WO No. 01/93642 Pamphlet, Patent Appl. Pub. Nos. JP 2002-50483, JP 2002-100476, JP 2002-173674, JP 2002-359082, JP 2002-175884, JP 2002-363552, JP 2002-184582, and JP 2003-7469, Patent Appl. Pub. Gazette No. 2002-525808, Patent Appl. Publication No. JP 2003-7471, Patent Appl. Pub. Gazette No. 2002-525833, Patent Appl. Pub. Nos. JP 2003-31366, JP 2002-226495, JP 2002-234894, JP 2002-235076, JP 2002-241751, JP 2001-319779, JP 2001-319780, JP 2002-62824, JP 2002-100474, JP 2002-203679, JP 2002-343572, and JP 2002-203678, and the like.

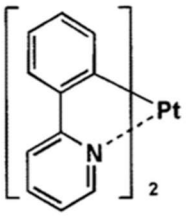
[0305]

A portion of the specific examples is shown below.

[0306]

[Formula 1]

Pt−1



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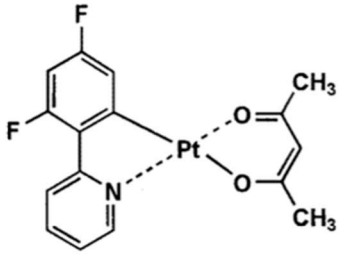

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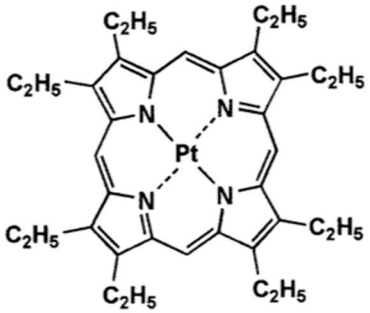

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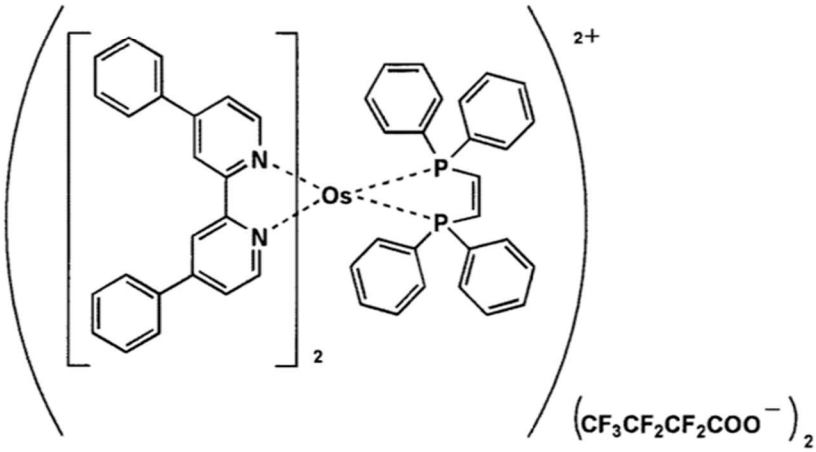
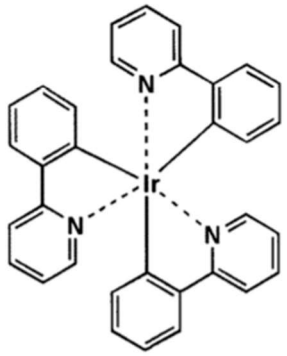


[0307]

[Formula 2]

Ir−1



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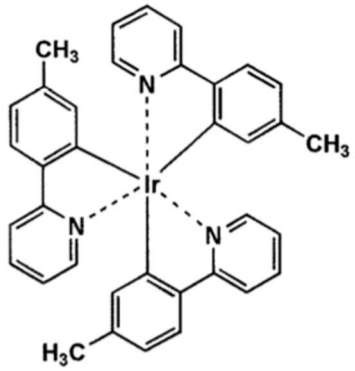

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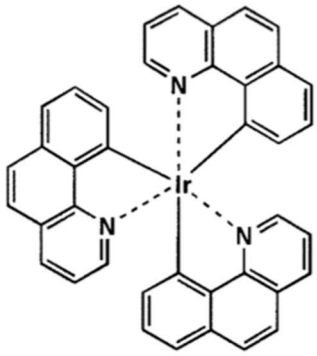

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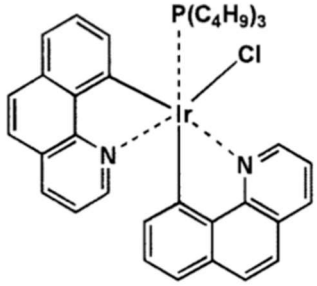

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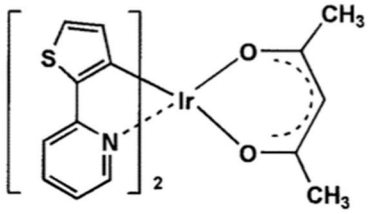

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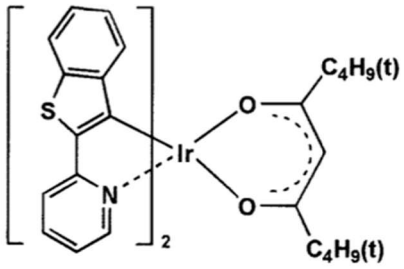
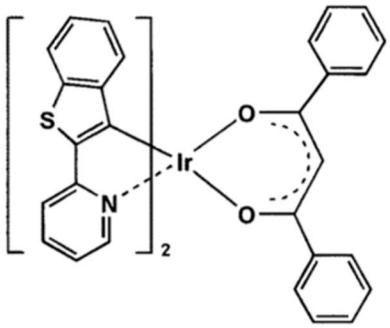


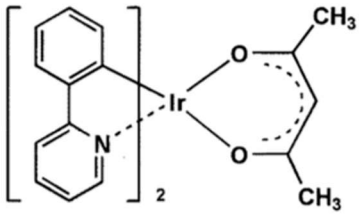
[0308]

[Formula 3]

Ir−7



Ir−8



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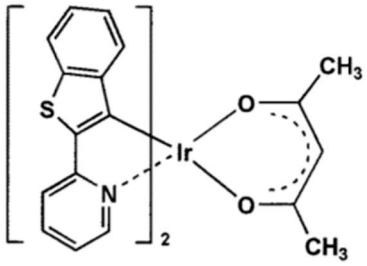

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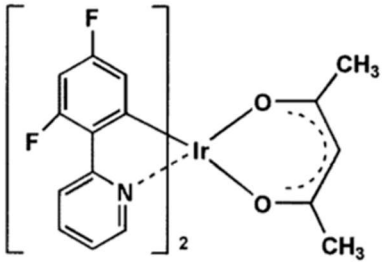

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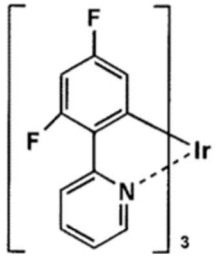

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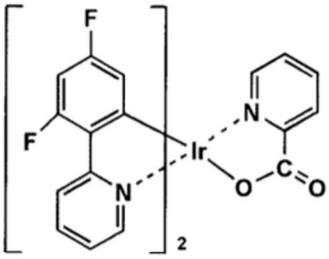
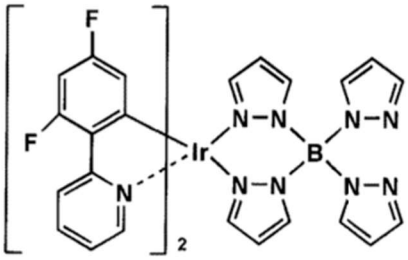
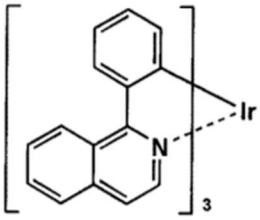


Ir−13



Ir−14



[0309]

The light emitting dopant may be a mixture of a plurality of compounds.

[0310]

<Light emission host>

A light emission host (also called simply a “host”) is the compound with the highest mixing ratio (mass) in a light emission layer consisting of two or more compounds, and other compounds are called "dopant compounds" (also called simply "dopants"). For example, if the light emission layer consists of two compounds, i.e., compound A and compound B, and the mixing ratio is A:B = 10:90, compound A is the dopant compound and compound B is the host compound. Furthermore, if the light emission layer consists of three compounds, i.e., compound A, compound B, and compound C, and the mixing ratio is A:B:C = 5:10:85, compound A and compound B are dopant compounds, and compound C is the host compound.

[0311]

There are no particular structural restrictions on the light emission host used in the present invention, but typical examples include carbazole derivatives, triarylamine derivatives, aromatic borane derivatives, nitrogen-containing heterocyclic compounds, thiophene derivatives, furan derivatives, oligoarylene compounds, and the like that have a basic skeleton, as well as carboline derivatives and diazacarbazole derivatives (diazacarbazole derivatives being those in which at least one carbon atom of the hydrocarbon ring composing the carboline ring of a carboline derivative is replaced by a nitrogen atom).

[0312]

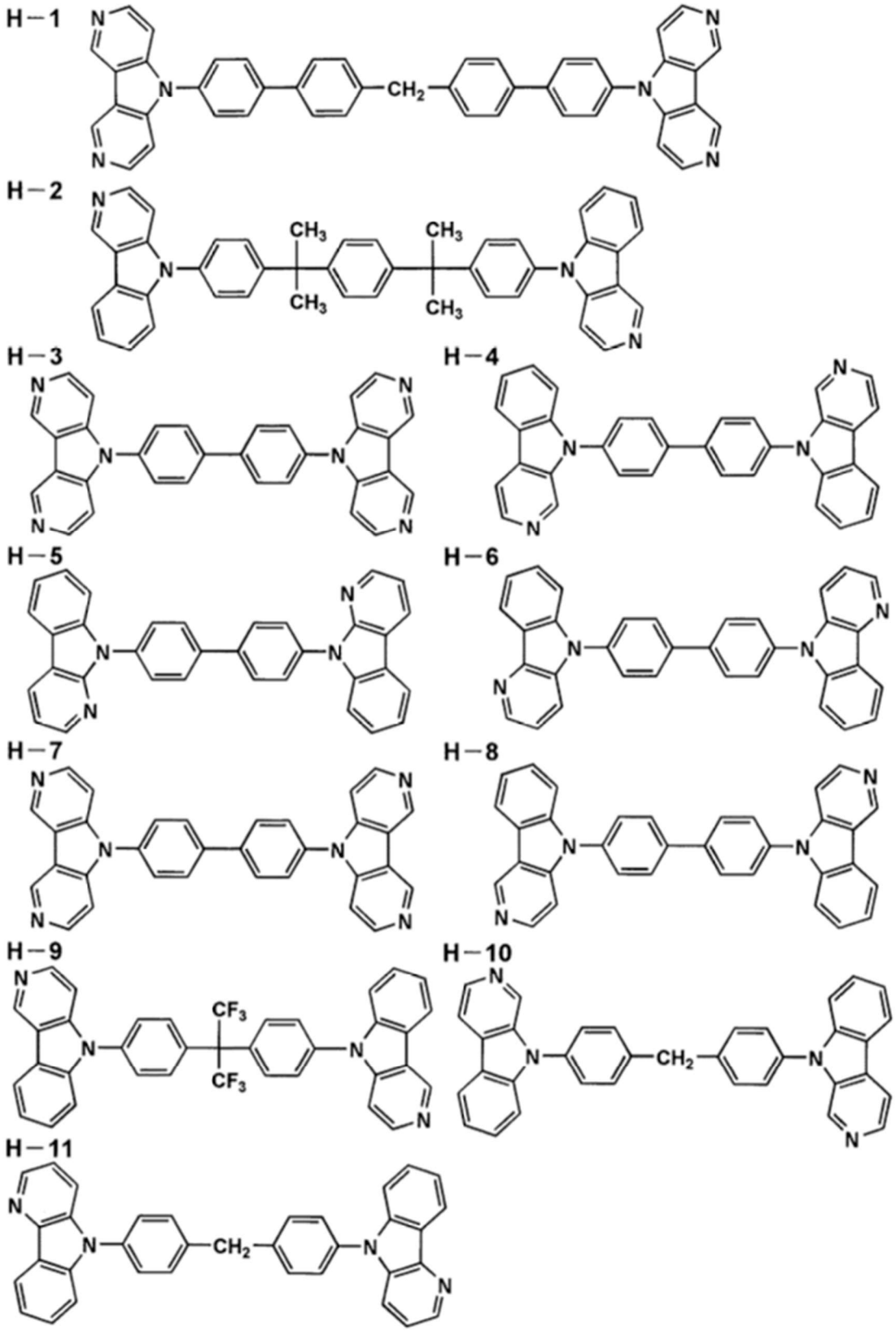
Among these, carboline derivatives and diazacarbazole derivatives are particularly preferable.

[0313]

Specific examples of carboline derivatives, diazacarbazole derivatives, and the like are given below, but the present invention is not limited to thereto.

[0314]

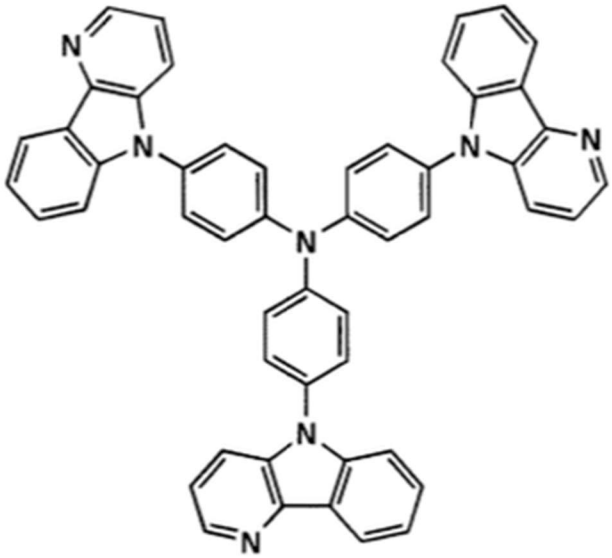
[Formula 4]



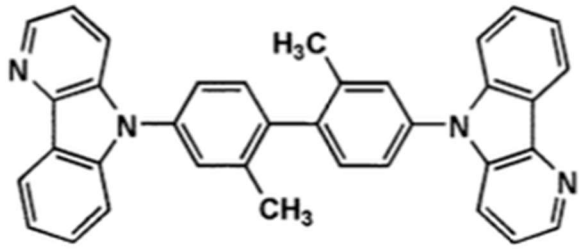
[0315]

[Formula 5]

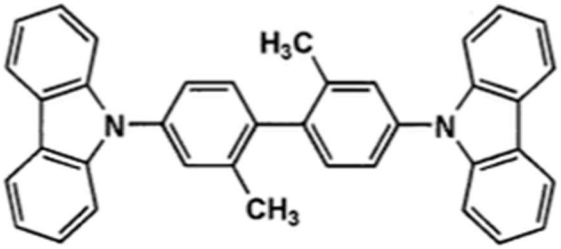
H−12



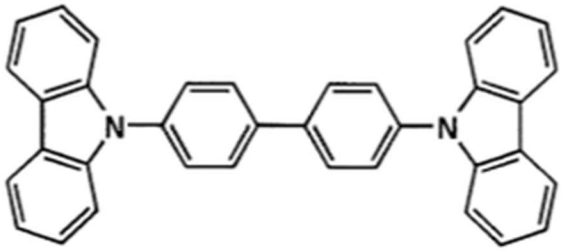
H−13



H−14



H−15



[0316]

The light emission host used in the present invention can be a low molecular compound, a high molecular weight compound with repeating units, or a low molecular compound with a polymerizable group such as a vinyl group or an epoxy group (deposition polymerizable light emission host).

[0317]

As the light emission host, a compound that has a hole transport ability and an electron transport ability, prevents the light emission wavelength from lengthening, and has a high Tg (glass transition temperature) is preferable.

[0318]

As specific examples of light emission hosts, the compounds described in the following literature are suitable. For example, Patent Appl. Pub. Nos. JP 2001-257076, JP 2002-308855, JP 2001-313179, JP 2002-319491, JP 2001-357977, JP 2002-334786, JP 2002-8860, JP 2002-334787, JP 2002-15871, JP 2002-334788, JP 2002-43056, JP 2002-334789, JP 2002-75645, JP 2002-338579, JP 2002-105445, JP 2002-343568, JP 2002-141173, JP 2002-352957, JP 2002-203683, JP 2002-363227, JP 2002-231453, JP 2003-3165, JP 2002-234888, JP 2003-27048, JP 2002-255934, JP 2002-260861, JP 2002-280183, JP 2002-299060, JP 2002-302516, JP 2002-305083, JP 2002-305084, JP 2002-308837, and the like.

[0319]

In addition, a plurality of known host compounds may be used in combination. Also, by using a plurality of dopant compounds, it is possible to mix different light emissions, thereby obtaining any desired light emission color. White light emission is possible by adjusting the type and doping amount of phosphorescent compounds, and can be applied to illumination and backlighting.

[0320]

The color emitted by the organic EL device of the present invention is determined by the color measured with a spectroradiometer CS-1000 (Konica Minolta Sensing) and applied to the CIE chromaticity coordinates in FIG. 4.16 on page 108 of "Shinhen Shikisai Kagaku Handbook [The New Handbook of Color Science]" (The Color Science Association of Japan (Ed.), University of Tokyo Press, 1985).

[0321]

The color emission layer can be formed as a film by depositing the above compound with a known thin film deposition method such as vacuum deposition, spin coating, casting, LB, and inkjet. The thickness of the color emission layer is not particularly restricted but is normally in the range of 5 nm to 5 μm and preferably 5 to 200 nm. The light emission layer can be a single-layer structure comprising one, two, or more of these phosphorescent compounds or host compounds, or a laminated structure comprising a plurality of layers of the same composition or different compositions.

[0322]

(Hole transport layer)

The hole transport layer comprises a hole transport material having the function of transporting holes, and in a broad sense, hole injection layers and electron blocking layers are both included in hole transport layers. A single or a plurality of hole transport layers can be provided.

[0323]

The hole transport material can be either organic or inorganic, with either hole injection or transport or electron barrier properties. Examples include triazole derivatives, oxadiazole derivatives, imidazole derivatives, polyarylalkane derivatives, pyrazoline derivatives and pyrazolone derivatives, phenylenediamine derivatives, arylamine derivatives, amino substituted chalcone derivatives, oxazole derivatives, styrylanthracene derivatives, fluorenone derivatives, hydrazone derivatives, stilbene derivatives, silazane derivatives, aniline copolymers, conductive polymer oligomers, and particularly thiophene oligomers.

[0324]

The above materials can be used as the hole transport material, but using a porphyrin compound, an aromatic tertiary amine compound, or a styrylamine compound, especially an aromatic tertiary amine compound, is preferable.

[0325]

Typical examples of the aromatic tertiary amine compounds and styrylamine compounds include N,N,N′,N′-tetraphenyl-4,4′-diaminophenyl; N,N′-diphenyl-N,N′-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD); 2,2-bis(4-di-p-tolylaminophenyl)propane; 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane; N,N,N′,N′-tetra-p -tolyl-4,4′-diaminobiphenyl; 1,1-bis(4-di-p-tolylaminophenyl)-4-phenylcyclohexane; bis(4-dimethylamino-2-methylphenyl)phenylmethane; bis(4-di-p-tolylaminophenyl)phenylmethane; N,N′-diphenyl-N,N′-di(4-methoxyphenyl)-4,4′-diaminobiphenyl; N,N,N′,N′-tetraphenyl-4,4′-diaminodiphenyl ether; 4,4′-bis(diphenylamino)quadriphenyl) quadriphenyl; N,N,N-tri(p-tolyl)amine; 4-(di-p-tolylamino)-4′-[4-(di-p-tolylamino)styryl]stilbene; 4-N,N-diphenylamino-(2-diphenylvinyl)benzene; 3-methoxy-4′-N,N-diphenylamino-stilbenzene; and N-phenylcarbazole; furthermore, compounds having two fused aromatic rings in the molecule as described in the specification of U.S. Patent No. 5,061,569, e.g., 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPD); 4,4′,4″-tris[N-(3-methylphenyl)-N-phenylamino]triphenylamine (MTDATA) with three triphenylamine units linked in a starburst configuration described in Patent Appl. Publication No. JP H4-308688; and the like.

[0326]

In addition, a polymer material in which these materials are introduced into the polymer chain or in which these materials are used as the main chain of the polymer can also be used. Inorganic compounds such as p-type-Si and p-type-SiC can also be used as hole injection materials and hole transport materials.

[0327]

The hole transport layer can be formed by thinning the hole transport material with a known method such as, for example, vacuum deposition, spin coating, casting, printing including inkjet printing, and LB. There is no particular limitation on the thickness of the hole transport layer, which is normally around 5 nm to 5 μm and preferably 5 to 200 nm. The hole transport layer may be a one-layer structure comprising one, two, or more of the above materials.

[0328]

In addition, a hole transport layer with a high p nature doped with impurities can also be used. Examples include those described in Patent Appl. Pub. Nos. JP H4-297076, JP 2000-196140, and JP 2001-102175, and J. Appl. Phys., 95, 5773(2004).

[0329]

(Electron transport layer)

An electron transport layer comprises a material having the function of transporting electrons, and in a broad sense, electron injection layers and hole blocking layers are both included in electron transport layers. The electron transport layer can be a single layer or a plurality of layers.

[0330]

The electron transport material (which also serves as a hole blocking material) used in the single-layer electron transport layer or in the electron transport layer adjacent to the cathode side of the light emission layer in the case of a plurality of layers is required to have only the function of transmitting electrons injected from the cathode to the light emission layer, and any of the conventionally known compounds can be selected and used as the material, e.g., nitro-substituted fluorene derivatives, diphenylquinone derivatives, thiopyran dioxide derivatives, carbodiimides, fluorenylidene methane derivatives, anthraquinodimethane and anthrone derivatives, oxadiazole derivatives, and the like. Furthermore, thiadiazole derivatives in which the oxygen atom of the oxadiazole ring is replaced with a sulfur atom in the above oxadiazole derivatives, and quinoxaline derivatives having a quinoxaline ring known as an electron withdrawing group can also be used as the electron transport material. Also, polymer materials in which these materials are introduced into the polymer chain or in which these materials are used as the main chain of the polymer can also be used.

[0331]

Also, metal complexes of 8-quinolinol derivatives, e.g., tris(8-quinolinol)aluminum (Alq), tris(5,7-dichloro-8-quinolinol)aluminum, tris(5,7-dibromo-8-quinolinol)aluminum, tris(2-methyl-8-quinolinol) aluminum, tris(5-methyl-8-quinolinol)aluminum, bis(8-quinolinol)zinc (Znq), and the like, and metal complexes thereof in which the central metal is replaced by In, Mg, Cu, Ca, Sn, Ga, or Pb can also be used as the electron transport material. In addition, metal-free or metal phthalocyanines, and metal-free and metal phthalocyanines whose ends are substituted with alkyl groups, sulfonic acid groups, or the like can be preferably used as the electron transport material. Distyrylpyrazine derivatives, which are exemplified as materials for the light emission layer, can also be used as the electron transport material, and inorganic semiconductors such as n-type-Si and n-type-SiC can be used as the electron transport material similar to the hole injection layer and the hole transport layer.

[0332]

The electron transport layer can be formed by thinning the electron transport material with a known method such as vacuum deposition, spin coating, casting, printing including inkjet printing, and LB. There is no particular limitation to the thickness of the electron transport layer, which is normally around 5 nm to 5 μm and preferably 5 to 200 nm. The electron transport layer may have a one-layer structure comprising one or more of the above materials.

[0333]

In addition, an electron transport layer with a high n nature doped with impurities can also be used. Examples include those described in Patent Appl. Pub. Nos. JP H4-297076, JP 2000-196140, and JP 2001-102175, and J. Appl. Phys., 95, 5773(2004).

[0334]

As the resin film composing the gas barrier film that an be used in the organic EL element of the present invention, polyesters such as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), polyethylene, polypropylene, cellulose esters such as cellophane, cellulose diacetate, cellulose triacetate, cellulose acetate butyrate, cellulose acetate propionate (CAP), cellulose acetate phthalate (TAC), and cellulose nitrate and derivatives thereof, polyvinylidene chloride, polyvinyl alcohol, polyethylene vinyl alcohol, syndiotactic polystyrene, polycarbonate, norbornene resin, polymethylpentene, polyetherketone, polyimide, polyethersulfone (pes), polysulfones, polyetherketonimide, polyamide, fluororesin, nylon, polymethylmethacrylate, acrylics, polyarylates, and chloro-olefin resins such as ARTON (trade name; manufactured by JSR Corporation) and APEL (trade name; manufactured by Mitsui Chemicals, Inc.) are examples that can be used.

[0335]

The external extraction efficiency of the light emitted from the organic EL device of the present invention at room temperature is preferably at least 1% and more preferably at least 5%. Here, the external extraction quantum efficiency (%) = the number of photons emitted outside the organic EL element / the number of electrons flowing into the organic EL element × 100.

[0336]

A color filter, some other hue improvement filter, or the like may also be used, and a color conversion filter that converts the color emitted from the organic EL element to multicolor using phosphors may also be used. If a color conversion filter is used, λmax of the light emission from the organic EL element is preferably 480 nm or less.

[0337]

(Method for fabricating the organic EL element)

The method for fabricating the organic EL element is described below in detail.

[0338]

The method for fabricating an organic EL element comprising an anode / a hole injection layer / a hole transport layer / a light emission layer / an electron transport layer / an electron injection layer / a cathode is described as an example of the organic EL element.

[0339]

First, the desired electrode material, for example, a thin film comprising an anode material, is formed to a thickness of 1 μm or less, preferably 10-200 nm, on the substrate (gas barrier resin substrate material (film) of the present invention) with a method such as vapor deposition, sputtering, or plasma CVD as described above to produce the anode. Next, organic compound thin films for the hole injection layer, the hole transport layer, the light emission layer, the electron transport layer, the electron injection layer, and the hole blocking layer, which are organic EL element materials, are formed on the anode.

[0340]

The thin film of the organic compound can be produced by vapor deposition, a wet process (spin coating, casting, inkjet, or printing), or the like as described above, but vacuum vapor deposition, spin coating, inkjet, and printing are particularly preferable because a homogeneous film is easily obtained, pinholes are less prone to occur, and the like. In addition, different deposition methods may be applied to each layer. When the vapor deposition method is used for film deposition, the vacuum deposition conditions vary depending on the type of compound used, but in general, it is desirable to select the appropriate conditions in the following ranges: boat heating temperature of 50-450° C, vacuum of 10^{-6}-10^{-2} Pa, deposition rate of 0.01-50 nm/sec, substrate temperature of -50 to +300° C, and film thickness of 0.1 nm to 5 μm, preferably 5-200 nm.

[0341]

After formation of these layers, a thin film comprising cathode material is formed on top of the layers to a thickness of 1 μm or less, preferably in the range of 50-200 nm, by vapor deposition or sputtering, for example, to provide a cathode and obtain the desired organic EL element. In the fabrication of this organic EL element, it is preferable to consistently fabricate from the hole injection layer to the cathode in a single vacuum draw, but it is also acceptable to take the product out and apply different deposition methods in the process. In such cases, care must be taken to ensure that the work is performed under a dry inert gas atmosphere and the like.

[0342]

It is also possible to reverse the fabrication order so as to fabricate the cathode, the electron injection layer, the electron transport layer, the light emission layer, the hole transport layer, the hole injection layer, and the anode in that order. When DC voltage is applied to the multicolor display device thus obtained, luminescence can be observed when a voltage of around 2-40 V is applied with the anode as the + polarity and the cathode as the - polarity. Alternating current voltage may also be applied. The applied AC voltage can be in any waveform.

[0343]

The display device using the organic EL element of the present invention can be used as a display device, a display, and various light-emitting light sources. In display devices and displays, full-color display is possible by using three types of organic EL elements emitting blue, red, and green light.

[0344]

Display devices and displays include TVs, PCs, mobile devices, AV equipment, text broadcasting displays, information displays in automobiles, and the like. In particular, display devices and displays may be used to reproduce still or moving images, and when used as a display device for moving image reproduction, the drive method may be either a simple matrix (passive matrix) method or an active matrix method.

[0345]

Illumination devices using the organic EL element of the present invention include, but are not limited to, home lighting, in-car lighting, backlighting for clocks and liquid crystal, billboard advertisements, traffic signals, light sources for optical storage media, light sources for electrophotographic copiers, light sources for optical communication processors, and light sources for optical sensors.

[0346]

The organic EL element of the present invention may also be used with a resonator structure. Uses of the organic OL element with such a resonator structure include, but are not limited to, light sources for optical storage media, light sources for electrophotographic copiers, light sources for optical communication processors, light sources for optical sensors, and the like. The organic EL element of the present invention can also be made to produce laser oscillation and used in the above applications.

[0347]

The gas barrier resin substrate material coated with a gas barrier layer containing a ceramic film whose residual stress is within a predetermined range according to the present invention has excellent productivity, is stored under severe conditions, is strong against bending and the like, maintains good transparency without deterioration in adhesion, gas barrier properties, or the like, and can be manufactured in a stable manner.

[0348]

[Display Device]

The organic EL element of the present invention may be used as one type of lamp, such as for illumination or an exposure light source, as a projection device of the type that projects images, or as a display device (display) of the type that allows direct viewing of still or moving images. When the organic EL element is used as a display device for moving image playback, the drive method can be either a simple matrix (passive matrix) method or an active matrix method. Also, it is possible to fabricate a full-color display device using three or more organic EL elements of the present invention with different emission colors. Alternatively, one emission color, e.g., white emission light, can be made into BGR using a color filter to create a full-color display. Furthermore, it is possible to convert the organic EL light emission color to other colors using color conversion filters to achieve full color, in which case λmax of the organic EL light emission is preferably 480 nm or less.

[0349]

An example of a display device composed from the organic EL element of the present invention is described with reference to the drawings.

[0350]

FIG. 12 is a schematic drawing showing an example of a display device composed from an organic EL element. The display is of a mobile phone or the like, for example, that displays image information by emitting light from an organic EL element.

[0351]

A display 111 comprises a display section A having a plurality of pixels, a control section B that carries out image scanning of the display section A on the basis of image information, and the like.

[0352]

The control unit B is electrically connected to the display unit A and sends a scanning signal and an image data signal on the basis of external image information to each of the plurality of pixels, and the scanning signals cause the pixels in each scanning line to sequentially emit light according to the image data signals to carry out image scanning and display image information on the display unit A.

[0353]

FIG. 13 is a schematic view of the display section A.

[0354]

The display section A has a wiring section including a plurality of scanning lines 115 and data lines 116, a plurality of pixels 113, and the like on a substrate. The main members of the display unit A are described below. FIG. 12 shows the light emitted by a pixel 113 when extracted in the direction of the white arrow (downward).

[0355]

The scanning lines 115 and the plurality of data lines 116 of the wiring section each comprises a conductive material, and the scanning lines 115 and the data lines 116 are orthogonal to each other in a grid pattern and are connected to the pixels 113 at the intersecting positions (details not shown).

[0356]

When a scanning signal is applied from the scanning line 115, the pixel 113 receives an image data signal from the data line 116 and emits light according to the received image data. By adjacently arranging pixels in the red region, pixels in the green region, and pixels in the blue region, as appropriate, on the same substrate, full-color display is possible.

[0357]

The light emission process of the pixels is described next.

[0358]

FIG. 14 is a schematic diagram of a pixel.

[0359]

The pixel is equipped with an organic EL element 120, a switching transistor 121, a drive transistor 122, a capacitor 123, and the like. Red, green, and blue light emitting organic EL elements are used as the organic EL elements 120 in a plurality of pixels, and these elements can be adjacently arranged on the same substrate to provide full-color display.

[0360]

In FIG. 14, an image data signal is applied from the control section B to the drain of the switching transistor 121 via the data line 116. When a scanning signal is applied to the gate of the switching transistor 121 from the control section B via the scanning line 115, the drive of switching transistor 121 turns on and the image data signal applied to the drain is transmitted to the capacitor 123 and the gate of the drive transistor 122.

[0361]

With the transmission of the image data signal, the capacitor 123 is charged according to the potential of the image data signal and the drive transistor 122 turns on. The drain of the drive transistor 122 is connected to a power line 117 and the source is connected to the electrode of the organic EL element 120, and current is supplied from the power line 117 to the organic EL element 120 according to the potential of the image data signal applied to the gate.

[0362]

When the scanning signal moves to the next scanning line 115 in sequential scanning of the control unit B, the drive of the switching transistor 121 turns off. However, even if the drive of switching transistor 121 turns off, the capacitor 123 retains the potential of the charged image data signal, so the drive of drive transistor 122 retains an on status and the organic EL element 120 continues to emit light until the next scanning signal is applied. When the next scanning signal is applied in sequential scanning, the drive transistor 122 is driven according to the potential of the next image data signal synchronized with the scanning signal, and the organic EL element 120 emits light.

[0363]

In other words, the emission of light from the organic EL element 120 is performed by providing a switching transistor 121 and a drive transistor 122, which are active elements, for the organic EL element 120 in each of the plurality of pixels 113. This light emission method is called the active matrix method.

[0364]

Here, the emission of light from the organic EL element 120 may be emission with a plurality of gradations based on a multi-value image data signal with a plurality of gradation potentials, or the emission of light may be an on/off emission of a predetermined amount of light based on a binary image data signal.

[0365]

The potential of the capacitor 123 may be held continuously until the next scanning signal is applied, or it may be discharged immediately before the next scanning signal is applied.

[0366]

The present invention is not limited to the active matrix method described above, but can also be used for a passive matrix emission drive, in which the organic EL device emits light according to the data signal only when the scanning signal is scanned.

[0367]

FIG. 15 is a schematic diagram of a passive matrix display device. In FIG. 15, a plurality of scanning lines 115 and a plurality of image data lines 116 are provided in a grid pattern opposite each other across a pixel 113.

[0368]

When the scanning signal of the scanning line 115 is applied in sequential scanning, the pixel 113 connected to the applied scanning line 115 emits light according to the image data signal. In the passive matrix method, there are no active elements in the 113 pixels, which reduces manufacturing costs.

[0369]

[Illumination device]

The organic EL materials of the present invention can also be applied to organic EL elements that produce substantially white light emission as an illumination device. White light emission is obtained by mixing a plurality of colors emitted simultaneously with a plurality of light emission materials. The combination of the plurality of emission colors may include three emission peak wavelengths of the three primary colors, i.e., blue [*sic:* red], green, and blue, or two emission peak wavelengths using a complementary color relationship, such as blue and yellow or blue-green and orange.

[0370]

The combination of light-emitting materials to obtain a plurality of light-emitting colors can be either a combination of a plurality of phosphorescent or fluorescent materials (light-emitting dopants), or a combination of a light-emitting material emitting fluorescent or phosphorescent light and a dye material emitting light from the light-emitting material as excitation light, but in the white organic EL element according to the present invention, the method of combining a plurality of light-emitting dopants is preferable.

[0371]

The layer structure of the organic EL element for obtaining a plurality of light emission colors includes a method of having a plurality of emission dopants in one light emission layer, a method of having a plurality of emission layers and having dopants with different light emission wavelengths in each emission layer, a method of forming a matrix of micro-pixels that emit light at different wavelengths, and the like.

[0372]

In the white organic EL element according to the present invention, patterning may be applied using a metal mask, an inkjet printing method, or the like at the time of film deposition if necessary. When patterning, only the electrode may be patterned, the electrode and the light emission layer may be patterned, or all layers of the element may be patterned.

[0373]

The light emitting material used in the light emission layer is not particularly limited, and, for example, in the case of a backlight for a liquid crystal display element, any combination of the platinum complexes according to the present invention and other known light emitting materials can be selected, combined and whitened to match the wavelength range corresponding to the color filter (CF) characteristics.

[0374]

Thus, in addition to the aforementioned display devices and displays, white light emitting organic EL elements are also useful in in various light emitting light sources and display devices such as home lighting and in-car lighting as illumination devices and the backlights of liquid crystal display devices as one type of lamp such as an exposure light source.

[0375]

Other applications include light sources for billboard advertisements, traffic signals, and optical storage media, light sources for electrophotographic copiers, light sources for optical communication processors, light sources for optical sensors, and the like, as well as a wide range of general household appliances and the like that require display devices.

[EMBODIMENTS]

[0376]

The embodiments below are provided to describe the present invention in detail, but the invention is not limited thereto. In the embodiment, "part" or "%" are used to indicate "parts by mass" or "mass %" unless otherwise noted.

[0377]

Embodiment 1

<<Fabrication of a gas barrier thin film laminate>>

[Preparation of Sample 1]

On a resin substrate material (a polyethylene terephthalate (PET) film with a clear hard coat (CHC) layer manufactured by Kimoto Co., Ltd.; PET thickness: 125 μm, CHC thickness: 6 μm), thin films were formed in the following order under the production conditions listed below: first buffer film: 500 nm, first barrier film: 50 nm, second buffer film: 500 nm, second barrier film: 50 nm, third buffer film: 500 nm, third barrier film: 50 nm, fourth buffer film: 500 nm, and Sample 1 was obtained with a total of 7 laminated films.

[0378]

(Buffer film fabrication)

Production was carried out using the atmospheric pressure plasma CVD apparatus shown in FIG. 5 under the below conditions.

[0379]

<Buffer film mixed gas composition>

Discharge gas: nitrogen gas	94.85 volume%
Thin film forming gas: hexamethyldisiloxane	0.15 volume%
Additive gas: oxygen gas	5.0 volume%

<Buffer film formation conditions>

First electrode side	Power source type	Haiden Research Institute	100 kHz (continuous mode)	PHF-6k
	Frequency	100 kHz		
	Output density	10 W/cm^2 (with a voltage Vp of 7 kV)		
	Electrode temp.	120° C		
Second electrode side	Power source type	Pearl Kogyo Co., Ltd.	13.56 MHz	CF-5000-13M
	Frequency	13.56 MHz		
	Output density	5 W/cm^2 (with a voltage Vp of 1 kV)		
	Electrode temp.	90° C		

(Barrier film fabrication)

Fabrication was carried out under the below conditions using the same atmospheric pressure plasma CVD apparatus.

[0380]

<Barrier film mixed gas composition>

Discharge gas: nitrogen gas	94.99 volume%
Thin film forming gas: tetraethoxysilane	0.01 volume%
Additive gas: oxygen gas	5.0 volume%

<Buffer film formation conditions>

First electrode side	Power source type	Haiden Research Institute	100 kHz (continuous mode)	PHF-6k
	Frequency	100 kHz		
	Output density	10 W/cm^2 (with a voltage Vp of 7 kV)		
	Electrode temp.	120° C		
Second electrode side	Power source type	Pearl Kogyo Co., Ltd.	13.56 MHz	CF-5000-13M
	Frequency	13.56 MHz		
	Output density	5 W/cm^2 (with a voltage Vp of 2 kV)		
	Electrode temp.	90° C		

[Preparation of Sample 2]

Sample 2 was prepared similarly to Sample 1, except that a contact-type web cleaner (manufactured by Kelva, Sweden) consisting of a cleaning roller, an adhesive roller, and an electrostatic removal bar described in FIG. 1b) was used between the buffer film formation step and the barrier film formation step (at three locations).

[0381]

[Preparation of Sample 3]

Sample 3 was prepared similarly to Sample 1, except that a contact-type foreign matter removal method using the adhesive tape (Cleaning Tape EC-315 manufactured by Sumiron) described in FIG. 1a) was used between the buffer film formation step and the barrier film formation step (at three locations).

[0382]

[Preparation of Sample 4]

Sample 4 was prepared similarly to Sample 1, except that a contact-type foreign matter removal method using the foreign matter removal device using ultrasonic waves (model UVU-F manufactured by Shinko Co., Ltd.) described in FIG. 2 was used between the buffer film formation step and the barrier film formation step (at three locations).

[0383]

[Preparation of Sample 5]

Sample 5 was prepared similarly to Sample 1, except that a contact-type foreign matter removal method using the adhesive tape (Cleaning Tape EC-315 manufactured by Sumiron) described in FIG. 1a) was used between all of the formation steps after formation of the first buffer film and until the formation of the fourth buffer film (at six locations).

[0384]

[Preparation of Sample 6]

Sample 6 was manufactured similarly to Sample 3, except that the method for fabricating the buffer film and the barrier film was changed to the following method.

[0385]

(Buffer film fabrication)

The substrate material was placed in the vacuum chamber of the vacuum deposition equipment, which was degassed to 10^{-4} Pa, then the buffer layer was formed using tetraethoxysilane (TEOS), hydrogen gas, and helium gas at an applied voltage (RF power) of 100 W and a substrate material temperature of 180° C while appropriately adjusting the feed rate of the raw material to achieve an average carbon content of 11.3 atomic number%.

[0386]

(Barrier film fabrication)

The substrate material was placed in the vacuum chamber of the vacuum deposition equipment, which was degassed to 10^{-4} Pa, and then the barrier layer was formed using hexamethyldisiloxane (hereinafter abbreviated as HMDSO), hydrogen gas, and helium gas at an applied voltage (RF power) of 300 W and a substrate material temperature of 180° C.

[0387]

<<Characteristics value measurement>>

The carbon content of the barrier film and the buffer film, as well as the internal stress of the barrier film, were measured for Samples 1-6 fabricated as described above. The water vapor transmission coefficient of the laminate was also measured for each sample in which a gas barrier thin film laminate was formed on a polyethylene terephthalate (PET) film. The measurement method is described below.

[0388]

<Carbon content>

The carbon content of each of the fabricated buffer and ceramic films was measured by XPS (atomic concentration %). Carbon content percentage is the atomic concentration% calculated with the following XPS method and is defined below.

[0389]

Atomic concentration% = number of carbon atoms / total number of atoms × 100

The XPS surface analyzer used in the present invention was an ESCALAB -200R manufactured by VG Scientifics [*sic*: Scientific]. In further detail, Mg was used in the X-ray anode and the output power was 600 W (acceleration voltage: 15 kV, emission current: 40 mA) for the measurement. The energy resolution was set to be 1.5-1.7 eV when defined by the half-value width of the clean [*sic*: normal] Ag 3d5/2 peak.

[0390]

First, the binding energies were measured in the range of 0-1100 eV with a data acquisition interval of 1.0 eV to determine what elements were detected.

[0391]

Next, for all detected elements except for the etching ion species, a narrow scan was performed for the photoelectron peak that gave the maximum intensity with a data acquisition interval of 0.2 eV, and the spectrum of each element was measured.

[0392]

The resulting spectra were transferred to the Common Data Processing System (Ver. 2.3 or later being preferably) manufactured by VAMAS-SCA-JAPAN to avoid differences in the results of content calculation due to differences in measuring equipment or computers, then processing was carried out with the software, and the content of the elements (carbon, oxygen, silicon, titanium, and the like) in each analysis target was found in atomic concentration (at%).

[0393]

Prior to the quantification processing, the count scale was calibrated for each element and smoothed by 5 points. Peak area intensity (cps * eV) with the background removed was used in the quantification process. The Shirley method was used for background processing.

[0394]

<Internal stress>

The internal stress in the ceramic film was measured with the following method. A ceramic film of the same composition and thickness as the film to be measured was formed on a quartz substrate 10 mm wide, 50 mm long, and 0.1 mm thick to a thickness of 1 μm using the same method, and the curl produced in the sample was measured with the thin film property evaluation apparatus MH4000 manufactured by NEC San-ei Instruments with the concave side of the sample facing up.

[0395]

<Water vapor transmission coefficient>

The water vapor transmission coefficient was measured for Samples 1-6 according to the method described in JIS K 7129B. The water vapor transmission coefficient was measured using model WOPET-003 manufactured by Createc GmbH & Co. KG.

[0396]

The reference samples were compared and evaluated using the OX-TRAN2/21/L type oxygen transmission coefficient analyzer and the PERMATRAN-W3/33G type water vapor transmission coefficient analyzer manufactured by MOCON up to the 10^{-2} order, and then the MOCON equipment was calibrated as the reference and extrapolated up to the 10^{-7} order by simulation (40° C, 90% RH).

[0397]

The results obtained above are shown in Table 1.

[0398]

[Table 1]

Sample no.	Ceramic layers						Foreign matter removal means		Water vapor transmission coefficient ($g/m^2/day$)	Notes
	Buffer film			Barrier film						
	Formation method	Film composition	Carbon content (atomic no. %)	Formation method	Film composition	Carbon content (atomic no.%)	Compressive stress (MPa)	Removal method	Removal location		
1	*A	SiO_xC_y	12.6	*A	SiO_2	< 0.1	3.0	–	–	0.0124	Comparative example
2	*A	SiO_xC_y	12.6	*A	SiO_2	< 0.1	3.0	Adhesive roller	*1	0.0011	Present invention
3	*A	SiO_xC_y	12.6	*A	SiO_2	< 0.1	3.0	Adhesive tape	*1	0.0009	Present invention
4	*A	SiO_xC_y	12.6	*A	SiO_2	< 0.1	3.0	Ultrasonic cleaner	*1	0.0014	Present invention
5	*A	SiO_xC_y	12.6	*A	SiO_2	< 0.1	3.0	Adhesive tape	*2	0.0005	Present invention
6	*B	SiO_xC_y	12.6	*B	SiO_2	< 0.1	3.0	Adhesive tape	*1	0.0036	Present invention

*A: Atmospheric pressure plasma method
*B: Vacuum plasma method
*1: After buffer film formation
*2: After all layers formed except topmost

[0399]

The results shown in Table 1 clearly indicate that the samples of the present invention prepared by applying the foreign matter removal method have superior moisture vapor barrier properties compared to the comparative example.

[0400]

Embodiment 2

<<Fabrication of the organic EL device>>

Using Samples 1-6 prepared in Embodiment 1 as organic EL display substrates, organic EL devices 101-106 were respectively fabricated according to the following method.

[0401]

Each sample was first cleaned in an ultrasonic cleaner using the following solution for the following time and dried (120° C).

[0402]

(Ultrasonic cleaning)

Surfactant 7% aqueous solution	15 min
Ultrapure water	5 min
Organic alkali (Semico Clean 56 (manufactured by Furuuchi Chemical Corporation)	15 min
Ultrapure water	5 min
Ultrapure water	5 min
2-propanol	15 min

(ITO film fabrication)

Each cleaned sample was then introduced into the vacuum chamber, a patterned deposition mask was placed on the ceramic film formation side of the sample, and an anode comprising a 0.2-μm-thick ITO film was formed by DC magnetron sputtering (conditions: substrate support temperature 250° C, oxygen pressure 1×10^{-3} Pa) using an ITO target (indium:tin = 95:5 (molar ratio)) with an SnO_2 content of 10 mass%.

[0403]

The surface resistance of the anode was 10 Ω/sq. The anode substrate formed with the anode was placed in a cleaning vessel and ultrasonically cleaned with isopropyl alcohol, followed by oxygen plasma treatment.

[0404]

(Fabrication of the organic EL element)

Next, a PEDOT-PSS (polyethylene dioxythiophene-polystyrenesulfonic acid doped; BAYTRON manufactured by Bayer AG) layer was formed on the ITO transparent electrode side of the resulting resin substrate with ITO film by spin coating to a dry thickness of 40 nm.

[0405]

The transparent support substrate was fixed to a substrate holder of a commercially available vacuum deposition device.

[0406]

After the vacuum chamber was depressurized to 4×10^{-4} Pa, a tantalum resistance heating boat containing m-MTDATXA was energized and heated, and a 40 nm hole transport layer was deposited on the transparent support substrate at a deposition rate of 0.1 nm/sec.

[0407]

Then, each of the light emission layers was laminated and formed as shown below using each composition of light emission layers A and B and intermediate layers 1 and 2 [*sic*: 2 not shown below] as shown below.

[0408]

Each light emission layer was formed by placing the host compound and the dopants in the following proportions in a tantalum resistance heating boat, energizing and heating the boat, and depositing each light emission layer at a deposition rate of 0.1 nm/sec to the thickness indicated.

[0409]

Light emission layer A	CDBP:Ir-15 (3%)	25 nm
Intermediate layer 1	L-98	3nm
Light emission layer B	CDBP:Ir-16 (8%)	10 nm

For the light emission layers, CDBP:Ir-15 (3%) 25 nm indicates a 25-nm deposited film that contains 3 mass% of Ir-15 as the dopant to CDBP as the host.

[0410]

Next, 10 nm of L-98 was deposited thereon as a hole blocking layer.

[0411]

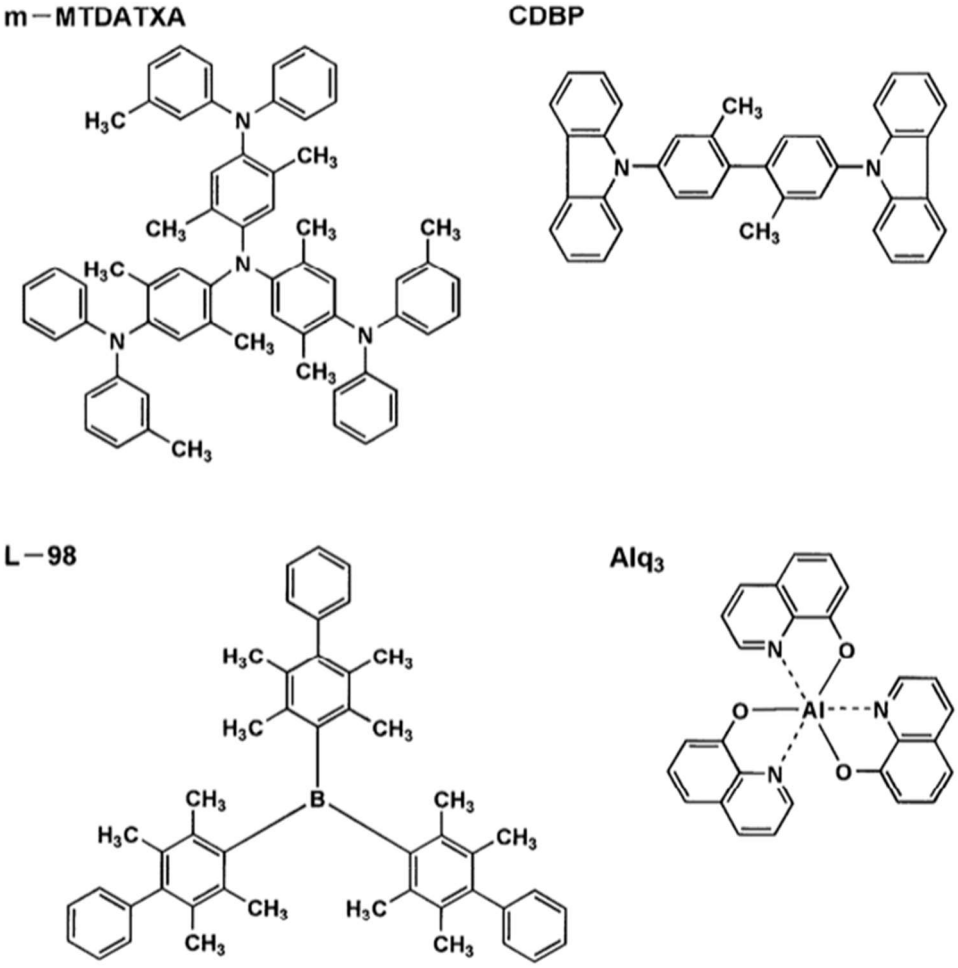
Further, an electron transport layer with a thickness of 35 nm was deposited on the hole blocking layer at a deposition rate of 0.1 nm/sec by electrifying and heating a heating boat containing Alq3. The substrate temperature at the time of deposition was room temperature.

[0412]

0.5 nm of lithium fluoride was then deposited as the cathode buffer layer (electron injection layer), and 110 nm of aluminum was deposited to form the cathode, resulting in an organic EL element.

[0413]

[Formula 6]



[0414]

The same resin substrate samples used for the respective substrates were used as the respective sealing materials on the layers of the organic EL element with the structure shown in FIG. 10(a), and the ceramic film formation side facing the cathode was bonded to the periphery via an ultraviolet ray-curable epoxy adhesive (XNR-5570) manufactured by Nagase ChemteX Corporation. The adhesive was cured by irradiating the substrate side with a halogen lamp at 6 J/cm^2 for a total of 3 minutes.

[0415]

Thus the organic EL devices 101-106 were fabricated.

[0416]

<<Evaluation of the organic EL devices>>

After the fabricated organic EL devices 101-106 were stored at 60° C and 90% RH for 500 hours, a magnified image was taken at 50× to evaluate the occurrence of dark spots, and the organic ELE devices fabricated using the samples of the present invention did not show any dark spots, but faint dark spots were observed to occur in the organic EL device 101, which used the comparative example Sample 1. As described above, it can be understood that the organic EL devices using the gas barrier resin substrate material of the present invention maintain excellent moisture vapor barrier performance compared to the comparative example.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0417]

[FIG. 1] A schematic configuration drawing showing an example of a contact-type foreign material removal device.

[FIG. 2] A schematic configuration drawing showing an example of a non-contact-type foreign matter removal device that uses ultrasonic waves.

[FIG. 3] A cross-section drawing showing a typical example of a gas barrier resin substrate material of the present invention.

[FIG. 4] A schematic drawing showing an example of a jet-type atmospheric pressure plasma discharge treatment device useful in the present invention.

[FIG. 5] A schematic drawing showing an example of an atmospheric pressure plasma discharge treatment device that treats a substrate material between opposing electrodes and is useful for the present invention.

[FIG. 6] A perspective drawing showing an example of the structure of a conductive metal base material of the roll rotating electrode shown in FIG. 5 and a dielectric coated thereon.

[FIG. 7] A perspective drawing showing an example of the structure of a conductive metal base material of a rectangular cylindrical electrode and a dielectric coated thereon.

[FIG. 8] A schematic configuration drawing showing an example of the method for manufacturing a gas barrier thin film laminate of the present invention.

[FIG. 9] A cross-sectional configuration drawing showing an example of an organic EL device in which the gas barrier thin film laminate of the present invention is formed on a cathode and sealed.

[FIG. 10] A cross-sectional configuration drawing showing the organic EL device in which an organic EL element formed on the gas barrier resin substrate material of the present invention is covered with another sealing film for adhesive sealing.

[FIG. 11] Showing an example of an organic EL device in which the organic EL element is sealed using a glass sealing can.

[FIG. 12] A schematic drawing showing an example of a display device composed from an organic EL element.

[FIG. 13] A schematic view of the display section A.

[FIG. 14] A schematic diagram of a pixel.

[FIG. 15] A schematic diagram of a passive matrix display device.

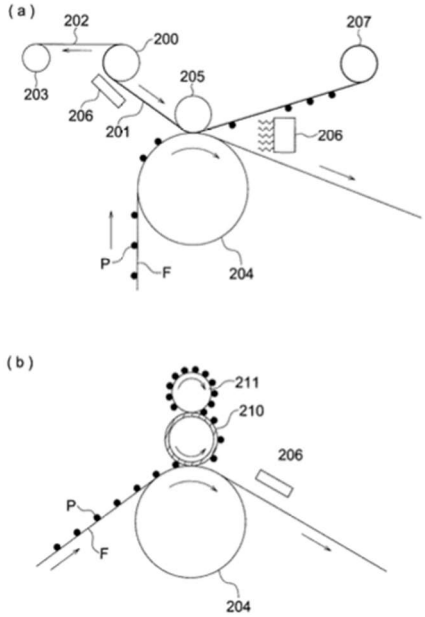
[DESCRIPTION OF THE REFERENTIAL NUMBERS]

[0418]

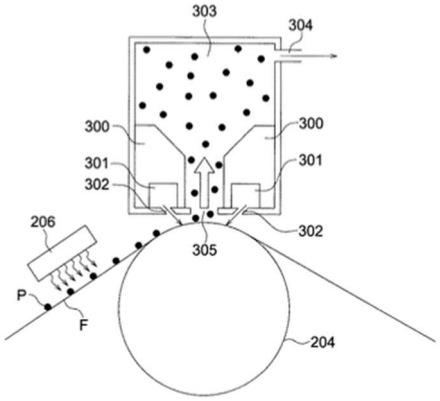
1: resin substrate material
3: adhesion film
4: ceramic film
5: protective film
10: plasma discharge treatment device
11: first electrode
12: second electrode
21: first power source
30: plasma discharge treatment device
32: discharge space
35: roll rotating electrode
35a: roll electrode
35A: metal base material
35B: dielectric
36: rectangular fixed electrode group

40: electric field application means
41: first power source
42: second power source
50: gas supply means
51: gas generation device
52: air supply port
53: air discharge port
60: electrode temperature regulation means
G: thin film forming gas
G°: gas in a plasma state
G′: treatment exhaust gas
101: gas barrier resin substrate material
102: organic EL layer
103: cathode
104: glass sealing can
105: barium oxide
107: adhesive
111: display
113: pixel
115: scanning line
116: data line
117: power source line
120: organic EL element
121: switching transistor
122: drive transistor
123: capacitor
201: adhesive tape
206: static elimination device
210: cleaning roller
211: adhesion roller
300: pressure head part
301: ultrasonic wave generator
303: vacuum head part
F: gas barrier film
P: foreign matter

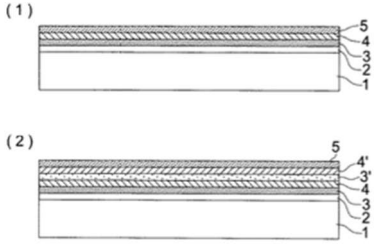
[FIG. 1]



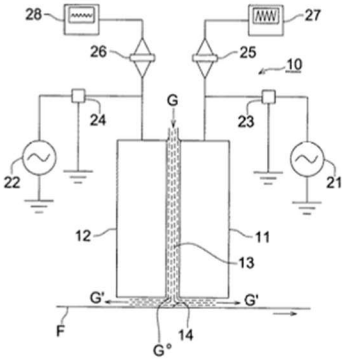
[FIG. 2]



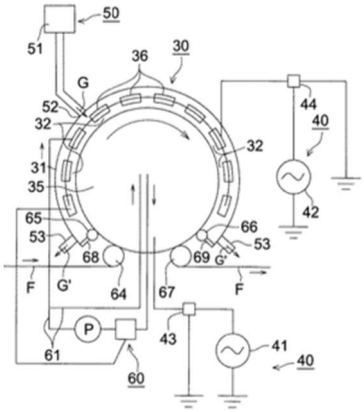
[FIG. 3]



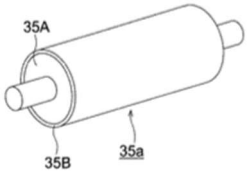
[FIG. 4]



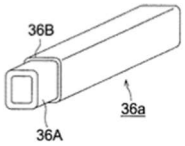
[FIG. 5]



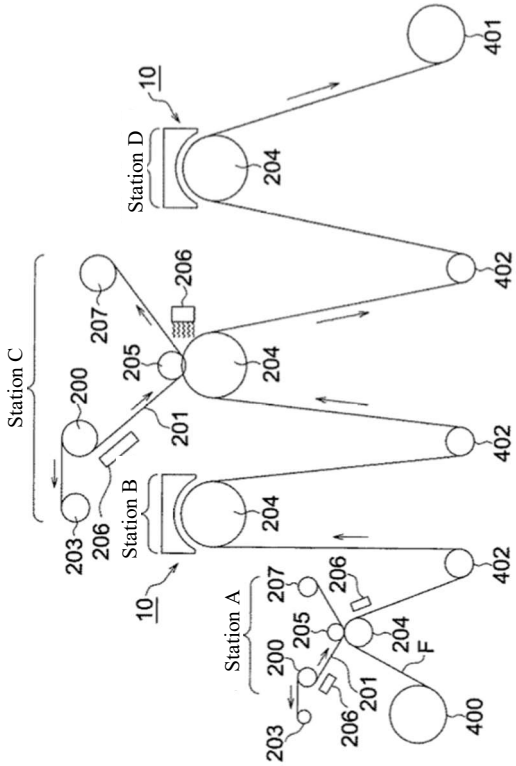
[FIG. 6]



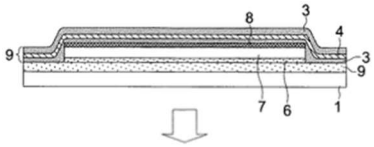
[FIG. 7]



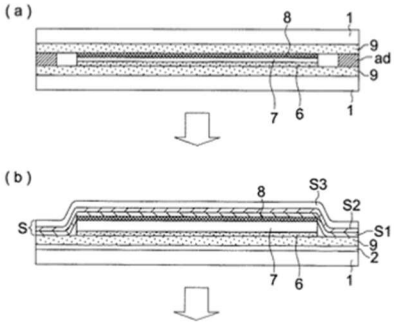
[FIG. 8]



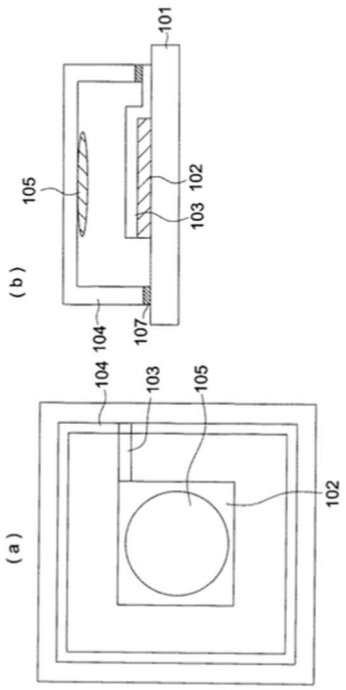
[FIG. 9]



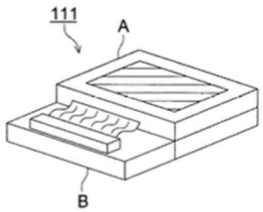
[FIG. 10]



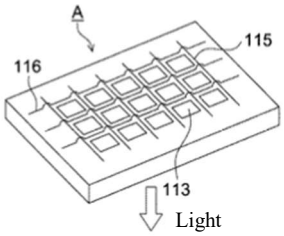
[FIG. 11]



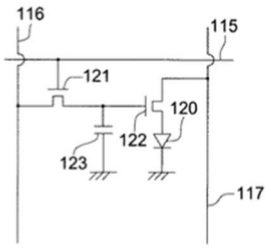
[FIG. 12]



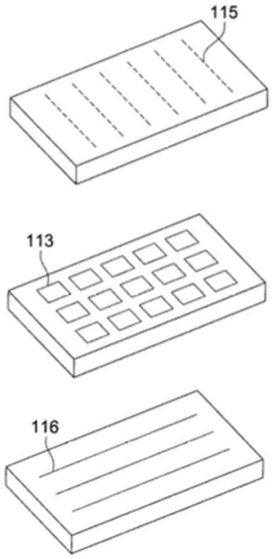
[FIG. 13]



[FIG. 14]



[FIG. 15]



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(51) Int. Cl.			FI			Theme code (for reference)
H05B	33/02	(2006.01)	H05B	33/02		
H01L	51/50	(2006.01)	H05B	33/14	A	
H05B	33/10	(2006.01)	H05B	33/10		

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