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(72) Inventors:
• **Kumaki, Daisuke**
Tokyo 157-0074 (JP)
• **Seo, Satoshi**
c/oSemiconductor Energy Lab. Co., Ltd
Kanagawa-ken 243-0036 (JP)

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(71) Applicant: **SEMICONDUCTOR ENERGY
LABORATORY CO., LTD.**
Atsugi-shi, Kanagawa-ken 243-0036 (JP)

(74) Representative: **Grünecker, Kinkeldey,
Stockmair & Schwanhäusser**
Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

(54) **Light-emitting element, display device, and electronic appliance**

(57) The present invention provides a light-emitting element having a structure in which the drive voltage is comparatively low and a light-emitting element in which the increase in the drive voltage over time is small. Further, the present invention provides a display device in which the drive voltage and the increase in the drive voltage over time are small and which can resist long-term use. A layer in contact with an electrode in a light-emitting

element is a layer containing a P-type semiconductor or a hole-generating layer such as an organic compound layer containing a material having electron-accepting properties. The light-emitting layer (104) is sandwiched between the hole-generating layers (102,103), and an electron-generating layer (105) is sandwiched between the light-emitting layer (104) and the hole-generating layer on a cathode side (103).

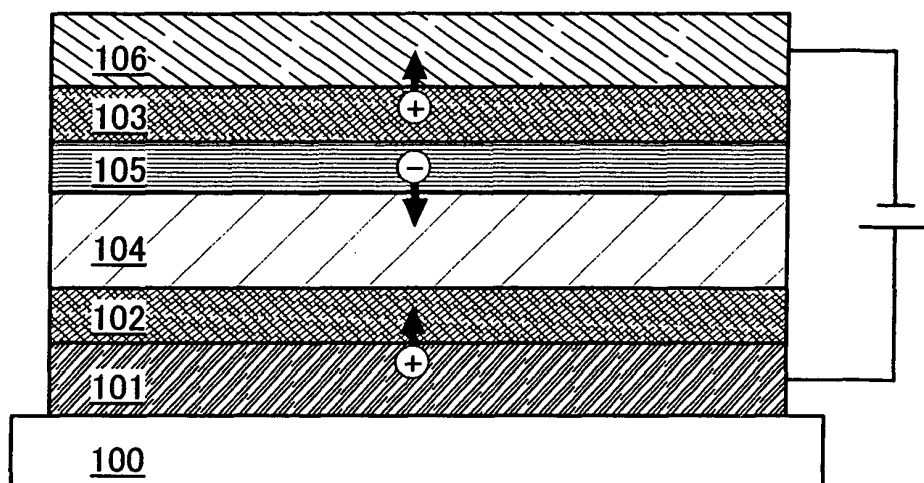


FIG. 1

Description**BACKGROUND OF THE INVENTION**

5 1. Field of the Invention

[0001] The present invention relates to a light-emitting element which sandwiches a thin film containing a light-emitting material between electrodes and which emits light by applying current. Moreover, the present invention relates to a display device and an electronic appliance which use the light-emitting element.

10 2. Related Art

[0002] A display using a thin film light-emitting element of a self-light-emitting type, which emits light by itself when current is applied, has been extensively developed.

[0003] This thin film light-emitting element emits light by connecting an electrode to a single-layer or multilayer thin film formed using one or both of organic compound and inorganic compound and by applying current. Such a thin film light-emitting element is expected to reduce the power consumption, occupy smaller space, and increase the visibility, and the market is also expected to expand further.

[0004] It has become possible to manufacture an element which emits light more efficiently than before by dividing the function for each layer of a light-emitting element having a multilayer structure (for example, see Reference 1: Applied Physics Letters, Vol. 51, No. 12, 913-915 (1987) by C. W. Tang et al.).

[0005] A thin film light-emitting element having a multilayer structure has a light-emitting laminated body sandwiched between an anode and a cathode. The light-emitting laminated body comprises a hole-injecting layer, a hole-transporting layer, a light-emitting layer, an electron-transporting layer, an electron-injecting layer, and the like. Among these layers, the hole-injecting layer, the hole-transporting layer, the electron-transporting layer, and the electron-injecting layer are not always employed depending on the element structure.

[0006] The hole-injecting layer in the light-emitting laminated body as above is formed by selecting a material which can inject holes comparatively easily from a metal electrode into a layer mainly containing organic compound. The electron-transporting layer in the light-emitting laminated body is formed by selecting a material being superior in electron-transporting properties. Thus, each layer in the light-emitting laminated body is formed by selecting a material superior in each function.

[0007] However, a material which can inject electrons comparatively easily from an electrode into a material mainly containing organic compound, or a material mainly containing organic compound which can transport electrons at a predetermined mobility or more are very limited. As is clear from the limitation on the material, the injection of the electrons from the electrode into the layer mainly containing the organic compound is originally rare to occur. This causes the problem that the drive voltage increases drastically over time.

SUMMARY OF THE INVENTION

[0008] Consequently, it is an object of the present invention to provide a light-emitting element having a structure in which the increase in the drive voltage over time is small.

[0009] Further, it is an object of the present invention to provide a display device in which the drive voltage is low and the increase in the drive voltage over time is small and which can resist long-term use.

[0010] These objects are achieved by a light emitting element as set forth in claim 1.

[0011] In detail, these objects are achieved by a light-emitting element comprising an anode and a cathode; a first layer between the anode and the cathode, said first layer generating holes; a second layer between the anode and the cathode, said second layer generating holes and contacting the cathode; a third layer between the first layer and the second layer, said third layer including a light emitting material; and a fourth layer between the second layer and the third layer, said fourth layer generating electrons.

[0012] This enables the increase in the drive voltage over time to be small.

[0013] Further developments of the invention are the subject matter of the dependent claims.

[0014] In a light-emitting element having a structure according to the present invention, the increase in the drive voltage over time can be suppressed.

[0015] Further, a display device in which the increase in the drive voltage over time is small and which can resist long-term use can be provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] In the accompanying drawings:

FIG 1 shows a light-emitting element according to the present invention;
 FIG 2 shows a light-emitting element according to the present invention;
 FIG 3 shows a light-emitting element according to the present invention;
 FIG 4 shows a light-emitting element according to the present invention;
 FIGS. 5A to 5E show a process for manufacturing a thin film light-emitting element according to the present invention;
 FIGS. 6A to 6C show a process for manufacturing a thin film light-emitting element according to the present invention;
 FIGS. 7A and 7B show an example of a structure of a display device according to the present invention;
 FIGS. 8A and 8B are a top view and a cross-sectional view of a light-emitting device according to the present invention;
 FIGS. 9A to 9E show examples of electronic appliances to which the present invention can be applied;
 FIGS. 10A to 10C show examples of a structure of a display device according to the present invention;
 FIGS. 11A and 11F show examples of a pixel circuit of a display device according to the present invention;
 FIG 12 shows an example of a protective circuit of a display device according to the present invention;
 FIG 13 is a graph showing the voltage-luminance characteristic of an element in Embodiment 1;
 FIG 14 is a graph showing the voltage-current characteristic of an element in Embodiment 1;
 FIG 15 is a graph showing the voltage-luminance characteristic of an element in Embodiment 2;
 FIG 16 is a graph showing the current density-luminance characteristic of an element in Embodiment 2;
 FIG. 17 is a graph showing the voltage-current characteristic of an element in Embodiment 2;
 FIG 18 is a graph showing the change of voltage of an element over time in Embodiment 2;
 FIG 19 is a graph showing the change of luminance of an element over time in Embodiment 2;
 FIG 20 is a graph showing the voltage-luminance characteristic of an element in Embodiment 3;
 FIG 21 is a graph showing the voltage-current characteristic of an element in Embodiment 3;
 FIGS. 22A to 22C show absorption spectra of a complex material containing α -NPD and molybdenum oxide;
 FIGS. 23A to 23C show absorption spectra of a complex material containing DNTPD and molybdenum oxide;
 FIG 24 is a graph showing a relation between an optical distance and current efficiency; and
 FIG 25 is a graph showing an optical distance and a light-emission spectrum.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Embodiment Modes and Embodiments are hereinafter described with reference to the drawings. However, since the present invention can be carried out with many different modes, it is to be understood by those skilled in the art that the modes and details can be modified without departing from the scope of the present invention. Therefore, the present invention is not construed as being limited to the description of the following Embodiment Modes and Embodiments.

[Embodiment Mode 1]

[0018] The present embodiment mode describes the structure of a light-emitting element of the present invention with reference to FIGS. 1 and 2. In a light-emitting element according to the present invention, a light-emitting layer 104 containing a light-emitting material and an electron-generating layer 105 are stacked, and the light-emitting layer 104 and the electron-generating layer 105 are sandwiched between a first hole-generating layer 102 and a second hole-generating layer 103. The first hole-generating layer 102 and the second hole-generating layer 103 are further sandwiched between an anode 101 and a cathode 106, and stacked over an insulator 100 such as a substrate or an insulating film. Over the insulator 100 such as the substrate or the insulating film, the anode 101, the first hole-generating layer 102, the light-emitting layer 104, the electron-generating layer 105, the second hole-generating layer 103, and the cathode 106 are stacked in order (FIG 1). Alternatively, the order may be opposite: the cathode 106, the second hole-generating layer 103, the electron-generating layer 105, the light-emitting layer 104, the first hole-generating layer 102, and the anode 101 are stacked in order (FIG 2).

[0019] The first hole-generating layer 102 and the second hole-generating layer 103 may be formed either with different materials or with the same material. For example, a layer containing both of a hole-transporting material and an electron-accepting material which can receive electrons from the hole-transporting material, a P-type semiconductor layer, or a layer containing a P-type semiconductor is used. As the hole-transporting material, for example, an aromatic amine compound (having a bond of a benzene ring with nitrogen), phthalocyanine (abbreviated to H₂Pc), or a phthalocyanine compound such as copper phthalocyanine (abbreviated to CuPc) or vanadyl phthalocyanine (abbreviated to VOPc) can be used. The aromatic amine compound is, for example, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (abbreviated

to α -NPD), 4,4'-bis[N-(3-methylphenyl)-N-phenyl-amino]-biphenyl (abbreviated to TPD), 4,4',4"-tris(N,N-diphenyl-amino)-triphenylamine (abbreviated to TDATA), 4,4',4"-tris[N-(3-methylphenyl)-N-phenyl-amino]-triphenylamine (abbreviated to MTDATA), 4,4'-bis(N-(4-(N,N-di-m-tolylamino)phenyl)-N-phenylamino)biphenyl (abbreviated to DNTPD), 1,3,5-tris[N,N-di(m-tolyl)amino]benzene (abbreviated to m-MTDAB), or 4,4',4"-tris(N-carbazolyl)triphenylamine (abbreviated to TCTA). As the electron-accepting material which can receive electrons from the hole-transporting material, for example, vanadium oxide, molybdenum oxide, 7,7,8,8,-tetracyanoquinodimethane (abbreviated to TCNQ), 2,3-dicyanophenanthroquinone (abbreviated to DCNNQ), 2,3,5,6-tetrafluoro-7,7,8,8,-tetracyanoquinodimethane (abbreviated to F₄-TCNQ), or the like is given. The electron-accepting material is selected which can receive electrons in accordance with the combination with the hole-transporting material. Further, metal oxide such as molybdenum oxide, vanadium oxide, ruthenium oxide, cobalt oxide, nickel oxide, or copper oxide can be used as the P-type semiconductor.

[0020] As the electron-generating layer 105, a layer containing both of an electron-transporting material and an electron donating material which can donate electrons to the electron-transporting material, an N-type semiconductor layer, or a layer containing an N-type semiconductor can be used. As the electron-transporting material, for example, the following can be used; a metal complex having a quinoline skeleton or a benzoquinoline skeleton such as tris(8-quinolinolato)aluminum (abbreviated to Alq₃), tris(4-methyl-8-quinolinolato)aluminum (abbreviated to Almq₃), bis(10-hydroxybenzo[h]-quinolinolato)beryllium (abbreviated to BeBq₂), or bis(2-methyl-8-quinolinolato)-4-phenylphenolato-aluminum (abbreviated to BAlq). Besides, a metal complex having an oxazole or thiazole ligand such as bis[2-(2-hydroxyphenyl)benzoxazolate]zinc (abbreviated to Zn(BOX)₂) or bis[2-(2-hydroxyphenyl)benzothiazolate]zinc (abbreviated to Zn(BTZ)₂) can be used. In addition to the metal complex, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (abbreviated to PBD), 1,3-bis[5-(p-tert-butylphenyl)-1,3,4-oxadiazole-2-yl]benzene (abbreviated to OXD-7), 3-(4-tert-butylphenyl)-4-phenyl-5-(4-biphenyl)-1,2,4-triazole (abbreviated to TAZ), 3-(4-tert-butylphenyl)-4-(4-ethylphenyl)-5-(4-biphenyl)-1,2,4-triazole (abbreviated to p-EtTAZ), bathophenanthroline (abbreviated to BPhen), bathocuproin (abbreviated to BCP), or the like can be used. As the electron donating material which can donate electrons to the electron-transporting material, for example, alkali metal such as lithium or cesium, magnesium, alkali-earth metal such as calcium, or rare-earth metal such as erbium or ytterbium can be used. The electron donating material which can donate electrons is selected in accordance with the combination with the electron-transporting material. Further, a metal compound such as metal oxide can be used as the N-type semiconductor, and for example zinc oxide, zinc sulfide, zinc selenide, titanium oxide, or the like can be used.

[0021] The light-emitting layer 104 containing the light-emitting material is divided into two types. One of them is a layer in which a light-emitting material to be a luminescence center is diffused in a layer formed with a material having a wider energy gap than the light-emitting material. The other one is a layer consisting of a light-emitting material. The former structure is preferred because the concentration quenching is difficult to occur. As the light-emitting material to be the luminescence center, the following can be employed; 4-dicyanomethylene-2-methyl-6-[2-(1,1,7,7-tetramethyl-9-julolidyl)ethenyl]-4H-pyran (abbreviation: DCJT); 4-dicyanomethylene-2-tert-butyl-6-[2-(1,1,7,7-tetramethyl-julolidine-9-yl)ethenyl]-4H-pyran; perfluoranthene; 2,5-dicyano-1,4-bis[2-(10-methoxy-1,1,7,7-tetramethyl-julolidine-9-yl)ethenyl]benzene, N,N'-dimethylquinacridone (abbreviated to DMQd), coumarin 6, coumarin 545T, tris(8-quinolinolato)aluminum (abbreviated to Alq₃), 9,9'-bianthryl, 9,10-diphenylanthracene (abbreviated to DPA), 9,10-bis(2-naphthyl)anthracene (abbreviated to DNA), 2,5,8,11-tetra-tert-butylperylene (abbreviated to TBP), or the like. As the material to be a base material in the case of forming the layer in which the light-emitting material is diffused, the following can be used; an anthracene derivative such as 9,10-di(2-naphthyl)-2-tert-butylanthracene (abbreviated to t-BuDNA), a carbazole derivative such as 4,4'-bis(N-carbazolyl)biphenyl (abbreviated to CBP), or a metal complex such as tris(8-quinolinolato)aluminum (abbreviated to Alq₃), tris(4-methyl-8-quinolinolato)aluminum (abbreviated to Almq₃), bis(10-hydroxybenzo[h]-quinolinolato)beryllium (abbreviated to BeBq₂), bis(2-methyl-8-quinolinolato)-4-phenylphenolato-aluminum (abbreviated to BAlq), bis[2-(2-hydroxyphenyl)pyridinato]zinc (abbreviated to Znpp₂), or bis[2-(2-hydroxyphenyl)benzoxazolate]zinc (abbreviated to ZnBOX). As the material which can constitute the light-emitting layer 104 singularly, tris(8-quinolinolato)aluminum (abbreviated to Alq₃), 9,10-bis(2-naphthyl)anthracene (abbreviated to DNA), or bis(2-methyl-8-quinolinolato)-4-phenylphenolato-aluminum (abbreviated to BAlq) or the like can be used.

[0022] The light-emitting layer 104 may be formed either in a single-layer structure or a multilayer structure. A hole-transporting layer may be provided between the first hole-generating layer 102 and the layer in which the light-emitting material is diffused in the light-emitting layer 104. Further, an electron-transporting layer may be provided between the electron-generating layer 105 and the layer in which the light-emitting material is diffused in the light-emitting layer 104. These layers are not necessarily provided. Alternatively, only one of the hole-transporting layer and the electron-transporting layer may be provided. The materials of the hole-transporting layer and the electron-transporting layer conform to those of the hole-transporting layer in the hole-generating layer and the hole-transporting layer in the electron-generating layer respectively; therefore, the description is omitted here. Refer to the description of those layers.

[0023] The anode 101 is preferably formed with metal, alloy, an electrically conductive compound each of which has high work function (work function of 4.0 eV or more), or mixture of these. As a specific example of the anode material, the following can be used; ITO (indium tin oxide), ITO containing silicon, IZO (indium zinc oxide) in which zinc oxide

(ZnO) is mixed by 2 to 20% into indium oxide, gold (Au), platinum (Pt), nickel (Ni), tungsten (W), chromium (Cr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), palladium (Pd), or metal nitride such as TiN. Meanwhile, as the cathode material used for forming the cathode 106, it is preferable to use metal, alloy, an electrically conductive compound each of which has low work function (work function of 3.8 eV or less), or mixture of these. As the specific example of the cathode material, the following can be used; an element belonging to group 1 or 2 in the periodic table; alkali metal such as Li or Cs, Mg, or alkali-earth metal such as Ca or Sr. In addition, alloy containing the above element such as Mg:Ag or Al:Li, a compound containing the above element such as LiF, CsF, or CaF₂, or transition metal containing rare-earth metal can also be used. Further, a multilayer containing the above element and another metal (including alloy) such as Al, Ag, or ITO can be used.

[0024] In addition to the anode 101, the first hole-generating layer 102, the light-emitting layer 104, the electron-generating layer 105, the second hole-generating layer 103, and the cathode 106, the light-emitting layer may have a hole-injecting layer 107 between the anode 101 and the first hole-generating layer 102 (FIGS. 3 and 4). A phthalocyanine compound is effective for the hole-injecting layer 107. For example, phthalocyanine (abbreviated to H₂-Pc), copper phthalocyanine (abbreviated to Cu-Pc), or the like can be used.

[0025] The above material is just an example, and the material can be selected appropriately by a practitioner as long as the advantage of the present invention is obtained.

[0026] In the light-emitting element having the above structure according to the present invention, holes are injected from the second hole-generating layer 103 into the second electrode by applying voltage. In addition, electrons are injected from the electron-generating layer 105 into the light-emitting layer 104. Further, holes are injected from the first hole-generating layer 102 into the light-emitting layer 104. Then, the injected electrons and holes are recombined in the light-emitting layer, and light emission is obtained when the excited light-emitting material returns to the ground state. Here, in the light-emitting element according to the present invention, the electrons are not injected from the electrode into the layer mainly containing the organic compound but injected from the layer mainly containing the organic compound into the layer mainly containing the organic compound. The electrons are difficult to be injected from the electrode into the layer mainly containing the organic compound. In the conventional light-emitting element, the drive voltage has increased when the electrons are injected from the electrode into the layer mainly containing the organic compound. However, since the light-emitting element according to the present invention does not have such a process, the light-emitting element having low drive voltage can be provided. Moreover, it is already known from the experiment that the drive voltage increases over time more drastically when the light-emitting element has higher drive voltage; therefore, the light-emitting element having low drive voltage also serves as a light-emitting element in which the increase in the drive voltage over time is small.

[Embodiment Mode 2]

[0027] Another embodiment mode of the present invention is described. The present embodiment mode describes an example of improving the characteristic of a viewing angle of a light-emitting element and a display device by appropriately adjusting the thicknesses of the first hole-generating layer 102 and the second hole-generating layer 103. Since the multilayer structure and the material of the light-emitting element in the present embodiment mode are the same as those in Embodiment Mode 1, the description is omitted here. Refer to Embodiment Mode 1.

[0028] Light emitted from the light-emitting element include light directly emitted from the light-emitting layer 104 and light emitted after being reflected once or multiple times. The light directly emitted and the light emitted after being reflected interfere in accordance with the relation between their phases so that they are intensified or attenuated with each other. Therefore, the light emitted from the light-emitting element is light which has been combined as a result of the interference.

[0029] The phase of light reflected when entering a medium having high refractive index from a medium having low refractive index is inverted. For this reason, in the light-emitting element having the structure shown in Embodiment Mode 1, the phase of light is inverted when the light is reflected at the interface between the electrode such as the anode 101 or the cathode 106 and the layer in contact with the electrode. When the light reflected at the electrode interferes with the light emitted from the light-emitting layer, it is possible to decrease the change of the spectrum shape which occurs depending on the angle of viewing a surface from which light is extracted and to increase the current efficiency of the light-emitting element, provided that the optical distance (refractive index $\times$ physical distance) between the light-emitting layer and the electrode satisfies $(2m-1)\lambda/4$ (m is a natural number of 1 or more and λ is a center wavelength of the light emitted from the light-emitting layer). The current efficiency shows the luminance with respect to the flowed current. When the current efficiency is higher, predetermined luminance can be obtained even with a smaller amount of current. Moreover, the deterioration of the element tends to be little.

[0030] Since the reflection is small between films whose gap of refractive index is small, the reflections except the reflection at the interface between the electrode and the film in contact with the electrode are ignorable. Therefore, in this embodiment mode, attention is paid only to the reflection between the electrode and the film in contact with the

electrode.

[0031] In the case of a light-emitting element in which light is extracted from the side of the anode 101, the light is reflected at the cathode 106. For this reason, in order to increase the current efficiency of the light-emitting element and to decrease the change of the spectrum shape which occurs depending on the angle of viewing the surface from which the light is extracted, the optical distance (refractive index $\times$ physical distance) from the light-emission position to the surface of the cathode 106 needs to be $(2m-1)\lambda/4$ (m is a natural number of 1 or more and λ is a center wavelength of the light emitted from the light-emitting layer).

[0032] The light-emitting layer 104 may be formed in a single-layer structure with a layer containing a light-emitting material, or may be formed in a multilayer structure including a layer such as an electron-transporting layer or a hole-transporting layer and a layer containing a light-emitting material. The layer containing the light-emitting material may be a layer in which a light-emitting material to be a luminescence center is diffused or may be a layer consisting of a light-emitting material.

[0033] A plurality of layers formed with different materials are provided between the light-emission position and the cathode 106. In this embodiment mode, the plurality of layers correspond to the electron-generating layer 105 and the second hole-generating layer 103. A part of the layer containing the light-emitting material that corresponds to a half thickness thereof can be regarded as a layer positioned between the light-emission position and the cathode 106. In the case of forming the light-emitting layer with a plurality of layers, more layers formed with different materials may be included. In such a structure, the optical distance from the light-emission position to the cathode 106 can be calculated by multiplying the thicknesses and the refractive indexes of the respective films and summing up the products. The total is set so as to be $(2m-1)\lambda/4$ (m is a natural number of 1 or more and λ is a center wavelength of the light emitted from the light-emitting layer). That is to say, the following formula (1) is satisfied. In the formula (1), the layer containing the light-emitting material is assumed to be 1 and the cathode 106 is assumed to be j (j is an integer number of 4 or more), and the layers existing between the layer containing the light-emitting material and the cathode 106 are denoted with numerals in order from the layer containing the light-emitting material. Moreover, the refractive index n and the thickness d with a certain numeral given thereto indicate the refractive index and the thickness of the layer to which the same numeral is given (that is, n_1 is the refractive index of the layer containing the light-emitting material and d_j is the thickness of the cathode).

[0034]

$$\sum_{k=2}^{j-1} n_k d_k \leq \frac{(2m-1)\lambda}{4} \leq n_1 d_1 + \sum_{k=2}^{j-1} n_k d_k \quad (\text{Formula 1})$$

[0035] Here, it is necessary to adjust the film thickness in order to satisfy the formula (1). Since the layer mainly containing the organic compound has low electron mobility, the drive voltage increases when the electron-transporting material and the electron-generating layer 105 in which electrons serve as the carrier are thick. Consequently, in this embodiment mode, the thickness of the second hole-generating layer 103 in which the mobility is comparatively high in the layer mainly containing the organic compound is adjusted, whereby the formula (1) is satisfied without drastically increasing the drive voltage.

[0036] In the case of a light-emitting element in which light is extracted from the side of the cathode 106, the light is reflected at the anode 101. Therefore, in order to increase the current efficiency of the light-emitting element and to decrease the change of the spectrum shape which occurs depending on the angle of viewing the surface from which the light is extracted, the optical distance (refractive index $\times$ physical distance) from the light-emission position to the surface of the anode 101 may be set to $(2m-1)\lambda/4$ (m is a natural number of 1 or more and λ is a center wavelength of the light emitted from the light-emitting layer).

[0037] The light-emitting layer 104 may be formed either in a single-layer structure of the layer containing the light-emitting material or in a multilayer structure including the layer containing the light-emitting material and the layer such as the electron-transporting layer or the hole-transporting layer. The layer containing the light-emitting material may be a layer in which the light-emitting material to be the light-emission center is diffused, or a layer consisting of the light-emitting material. However, in any one of the above-mentioned structures, the layer containing the light-emitting material has a certain degree of thickness and an infinite number of the luminescence centers exist; therefore, it is impossible to determine the exact position where the light emission occurs. Accordingly, in this embodiment mode, a position of a part of the film containing the light-emitting material that corresponds to a half thickness thereof is regarded as the position where the light-emission occurs.

[0038] One or a plurality of layers are provided between the position where the light-emission occurs and the anode 101. In this embodiment mode, the layer corresponds to the first hole-generating layer 102. Further, it can be said that a part of the layer containing the light-emitting material that corresponds to a half thickness thereof is also the layer

located between the position where the light-emission occurs and the anode 101. Moreover, more layers may be included in the case where the light-emitting layer is formed with a plurality of layers. In such a structure, the optical distance from the light-emission position to the anode 101 can be calculated by multiplying the thicknesses and the refractive indexes of the respective films and summing up the products. That is to say, the following formula (2) is satisfied. In the formula (2), the layer containing the light-emitting material is assumed to be 1 and the anode 101 is assumed to be j (j is an integer number of 4 or more), and the layers existing between the layer containing the light-emitting material and the anode 101 are denoted with numerals in order from the layer containing the light-emitting material. Moreover, the refractive index n and the thickness d with a certain numeral given thereto indicate the refractive index and the thickness of the layer to which the same numeral is given (that is, n_1 is the refractive index of the layer containing the light-emitting material and d_j is the thickness of the anode).

[0039]

$$\sum_{k=2}^{j-1} n_k d_k \leq \frac{(2m-1)\lambda}{4} \leq n_1 d_1 + \sum_{k=2}^{j-1} n_k d_k \quad (\text{Formula 2})$$

[0040] Here, it is necessary to adjust the film thickness in order to satisfy the formula (2). In this embodiment mode, the formula (2) can be satisfied without drastically increasing the drive voltage, by adjusting the thickness of the first hole-generating layer 102 in which the mobility is comparatively high in the layer mainly containing the organic compound.

[0041] In the case of the structure in which light is extracted from both of the anode 101 and the cathode 106, both of the formulas (1) and (2) may be satisfied.

[0042] With the structure of the light-emitting element shown in this embodiment mode, it is possible to provide a light-emitting element in which the change of the light-emission spectrum which occurs depending on the angle of viewing the surface from which the light is extracted is decreased.

[0043] The present embodiment mode can be combined with Embodiment Mode 1.

[Embodiment Mode 3]

[0044] This embodiment mode describes a display device according to the present invention shown in Embodiment Mode 1 or Embodiment Mode 2 while showing its manufacturing method with reference to FIGS. 5A to 6C. Although this embodiment mode shows an example of manufacturing an active matrix display device, a light-emitting element of the present invention is also applicable for a passive matrix display device.

[0045] First, a first base insulating layer 51a and a second base insulating layer 51b are formed over a substrate 50, and then a semiconductor layer is formed over the second base insulating layer 51b (FIG 5A).

[0046] As a material of the substrate 50, glass, quartz, plastic (such as polyimide, acrylic, polyethylene terephthalate, polycarbonate, polyacrylate, or polyethersulfone), or the like can be used. These substrates may be used after being polished by CMP or the like as necessary. In this embodiment mode, a glass substrate is used.

[0047] The first base insulating layer 51a and the second base insulating layer 51b are provided in order to prevent an element which adversely affects the characteristic of the semiconductor film such as alkali metal or alkali-earth metal in the substrate 50 from diffusing into the semiconductor layer. As the material of these base insulating layers, silicon oxide, silicon nitride, silicon oxide containing nitrogen, silicon nitride containing oxygen, or the like can be used. In this embodiment mode, the first base insulating layer 51a is formed with silicon nitride, and the second base insulating layer 51b is formed with silicon oxide. Although the base insulating layer is formed in a two-layer structure including the first base insulating layer 51a and the second base insulating layer 51b in this embodiment mode, the base insulating layer may be formed in a single-layer structure or a multilayer structure including three or more layers. The base insulating layer is not necessary when the diffusion of the impurity from the substrate does not lead to a significant problem.

[0048] In this embodiment mode, the semiconductor layer formed subsequently is obtained by crystallizing an amorphous silicon film with a laser beam. The amorphous silicon film is formed in 25 to 100 nm thick (preferably 30 to 60 nm thick) over the second base insulating layer 51 b by a known method such as a sputtering method, a reduced-pressure CVD method, or a plasma CVD method. After that, heat treatment is conducted for one hour at 500°C for dehydrogenation.

[0049] Next, the amorphous silicon film is crystallized with a laser irradiation apparatus to form a crystalline silicon film. In this embodiment mode, an excimer laser is used at the laser crystallization. After the emitted laser beam is shaped into a linear beam spot using an optical system, the amorphous silicon film is irradiated with the linear beam spot. Thus, the crystalline silicon film is formed which is to be used as the semiconductor layer.

[0050] Alternatively, the amorphous silicon film can be crystallized by another method such as a method in which the crystallization is conducted only by heat treatment or a method in which heat treatment is conducted using a catalyst element for inducing the crystallization. As the element for inducing the crystallization, nickel, iron, palladium, tin, lead,

cobalt, platinum, copper, gold, or the like is given. By using such an element, the crystallization is conducted at lower temperature in shorter time than the crystallization only by the heat treatment; therefore, the damage to the glass substrate is suppressed. In the case of crystallizing only by the heat treatment, a quartz substrate which can resist the high temperature is preferably used as the substrate 50.

[0051] Subsequently, a small amount of impurity elements are added to the semiconductor layer as necessary in order to control the threshold, which is so-called channel doping. In order to obtain the required threshold, an impurity showing N-type or P-type (such as phosphorus or boron) is added by an ion-doping method or the like.

[0052] After that, as shown in FIG 5A, the semiconductor layer is patterned into a predetermined shape so that an island-shaped semiconductor layer 52 is obtained. The patterning is conducted by etching the semiconductor layer using a mask. The mask is formed in such a way that a photo resist is applied to the semiconductor layer and the photo resist is exposed and baked so that a resist mask having a desired mask pattern is formed over the semiconductor layer.

[0053] Next, a gate insulating layer 53 is formed so as to cover the semiconductor layer 52. The gate insulating layer 53 is formed in 40 to 150 nm thick with an insulating layer containing silicon by a plasma CVD method or a sputtering method. In this embodiment mode, silicon oxide is used.

[0054] Then, a gate electrode 54 is formed over the gate insulating layer 53. The gate electrode 54 may be formed with an element selected from the group consisting of tantalum, tungsten, titanium, molybdenum, aluminum, copper, chromium, and niobium, or may be formed with an alloy material or a compound material which contains the above element as its main component. Further, a semiconductor film typified by a poly-crystalline silicon film doped with an impurity element such as phosphorus may be used. Ag-Pd-Cu alloy may also be used.

[0055] Although the gate electrode 54 is formed with a single layer in this embodiment mode, the gate electrode 54 may have a multilayer structure including two or more layers of, for example, tungsten as a lower layer and molybdenum as an upper layer. Even in the case of forming the gate electrode in the multilayer structure, the above-mentioned material is preferably used. The combination of the above materials may also be selected appropriately. The gate electrode 54 is processed by etching with the use of a mask formed with a photo resist.

[0056] Subsequently, impurities are added to the semiconductor layer 52 at high concentration using the gate electrode 54 as the mask. According to this step, a thin film transistor 70 comprising the semiconductor layer 52, the gate insulating layer 53, and the gate electrode 54 is formed.

[0057] The manufacturing process of the thin film transistor is not limited in particular, and may be modified appropriately so that a transistor having a desired structure can be manufactured.

[0058] Although this embodiment mode employs a top-gate thin film transistor using the crystalline silicon film obtained by the laser crystallization, a bottom-gate thin film transistor using an amorphous semiconductor film can also be applied to a pixel portion. Not only silicon but also silicon germanium can be used for the amorphous semiconductor. In the case of using silicon germanium, the concentration of germanium preferably ranges from approximately 0.01 to 4.5 atomic%.

[0059] Moreover, a microcrystal semiconductor (semi-amorphous semiconductor) film which includes crystal grains each having a diameter of 0.5 to 20 nm in the amorphous semiconductor may also be used. The microcrystal having the crystal with a diameter of 0.5 to 20 nm is also referred to as a so-called microcrystal (μc).

[0060] Semi-amorphous silicon (also referred to as SAS), which belongs to the semi-amorphous semiconductor, can be obtained by decomposing silicide gas according to glow discharging. As typical silicide gas, SiH_4 is given. Besides, Si_2H_6 , SiH_2Cl_2 , SiHCl_3 , SiCl_4 , SiF_4 , or the like can be used. By using the silicide gas after diluting the silicide gas with hydrogen or hydrogen and one or plural kinds of noble gas selected from the group consisting of helium, argon, krypton, and neon, SAS can be easily formed. The silicide gas is preferably diluted with the dilution ratio of 1:10 to 1:1000. The reaction to form the film by the decomposition according to glow discharging may be conducted at the pressure ranging from 0.1 to 133 Pa. The electric power for forming the glow discharging may be supplied at high frequency in the range of 1 to 120 MHz, preferably 13 to 60 MHz. The substrate heat temperature is preferably 300°C or less, preferably in the range of 100 to 250°C.

[0061] The raman spectrum of thus formed SAS shifts to the side of lower wavenumber than 520 cm^{-1} . According to X-ray diffraction, diffraction peaks of a silicon crystal lattice are observed at (111) and (220). As a terminating agent of a dangling bond, hydrogen or halogen is added by at least 1 atomic% or more. As the impurity element in the film, the impurity in the air such as oxygen, nitrogen, and carbon is desirably $1 \times 10^{20} \text{ cm}^{-3}$ or less, and especially, the concentration of oxygen is $5 \times 10^{19} \text{ cm}^{-3}$ or less, preferably $1 \times 10^{19} \text{ cm}^{-3}$ or less. The mobility of a TFT manufactured with this film is $\mu=1$ to $10 \text{ cm}^2/\text{Vsec}$.

[0062] This SAS may be used after being crystallized further with a laser beam.

[0063] Subsequently, an insulating film (hydride film) 59 is formed with silicon nitride so as to cover the gate electrode 54 and the gate insulating layer 53. After forming the insulating film (hydride film) 59, heat treatment for approximately 1 hour at 480°C is conducted so as to activate the impurity element and to hydrogenate the semiconductor layer 52.

[0064] Subsequently, a first interlayer insulating layer 60 is formed so as to cover the insulating film (hydride film) 59. As a material for forming the first interlayer insulating layer 60, silicon oxide, acrylic, polyimide, siloxane, a low-k material, or the like is preferably used. In this embodiment mode, a silicon oxide film is formed as the first interlayer insulating

layer. In this specification, siloxane is a material whose skeletal structure includes a bond of silicon and oxygen and which has an organic group containing at least hydrogen (such as an alkyl group or an aryl group), a fluoro group, or the organic group containing at least hydrogen and the fluoro group as the substituent (FIG 5B).

[0065] Next, contact holes that reach the semiconductor layer 52 are formed. The contact holes can be formed by etching with a resist mask until the semiconductor layer 52 is exposed. Either wet etching or dry etching can be applied. The etching may be conducted once or multiple times depending on the condition. When the etching is conducted multiple times, both of the wet etching and the dry etching may be conducted (FIG 5C).

[0066] Then, a conductive layer is formed so as to cover the contact holes and the first interlayer insulating layer 60. A connection portion 61a, a wiring 61b, and the like are formed by processing the conductive layer into a desired shape. This wiring may be a single layer of aluminum, copper, or the like. In this embodiment mode, the wiring is formed in a multilayer structure of molybdenum/aluminum/molybdenum in order from the bottom. Alternatively, a structure of titanium/aluminum/titanium or titanium/titanium nitride/aluminum/titanium is also applicable (FIG 5D).

[0067] A second interlayer insulating layer 63 is formed so as to cover the connection portion 61a, the wiring 61b, and the first interlayer insulating layer 60. As the material of the second interlayer insulating layer 63, an applied film having self-flattening properties such as a film of acrylic, polyimide, siloxane, or the like is preferable. In this embodiment mode, the second interlayer insulating layer 63 is formed with siloxane (FIG 5E).

[0068] Next, an insulating layer may be formed with silicon nitride over the second interlayer insulating layer 63. This is to prevent the second interlayer insulating layer 63 from being etched more than necessary in a later step of etching a pixel electrode. Therefore, the insulating layer is not necessary in particular when the difference of the etching rate is large between the pixel electrode and the second interlayer insulating layer. Next, a contact hole penetrating the second interlayer insulating layer 63 to reach the connection portion 61a is formed.

[0069] Next, after a light-transmitting conductive layer is formed so as to cover the contact hole and the second interlayer insulating layer 63 (or the insulating layer), the light-transmitting conductive layer is processed to form the anode 101 of the thin film light-emitting element. Here, the anode 101 electrically contacts the connection portion 61a.

As the material of the anode 101, it is preferable to use metal, alloy, an electrically conductive compound, or mixture of these each of which has high work function (work function of 4.0 eV or more). For example, ITO (indium tin oxide), ITO containing silicon (ITSO), IZO (indium zinc oxide) in which zinc oxide (ZnO) is mixed by 2 to 20% into indium oxide, zinc oxide, GZO (gallium zinc oxide) in which gallium is contained in zinc oxide, gold (Au), platinum (Pt), nickel (Ni), tungsten (W), chromium (Cr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), palladium (Pd), or metal nitride such as TiN can be used. In this embodiment mode, the anode 101 is formed with ITSO (FIG 6A).

[0070] Next, an insulating layer formed with an organic material or an inorganic material is formed so as to cover the second interlayer insulating layer 63 (or the insulating layer) and the anode 101. Subsequently, the insulating layer is processed so as to partially expose the anode 101, thereby forming a partition wall 65. As the material of the partition wall 65, a photosensitive organic material (such as acrylic or polyimide) is preferable. Besides, a non-photosensitive organic material or inorganic material may also be used. Further, the partition wall 65 may be used as a black matrix by making the partition wall 65 black in such a way that a black pigment or dye such as titanium black or carbon nitride is diffused into the material of the partition wall 65 with the use of a diffuse material. It is desirable that the partition wall 65 has a tapered shape in its end surface toward the first electrode with its curvature changing continuously (FIG 6B).

[0071] Next, a light-emitting laminated body 66 is formed so as to cover a part of the anode 101 that is exposed from the partition wall 65. In this embodiment mode, the light-emitting laminated body 66 may be formed by an evaporating method or the like. The light-emitting laminated body 66 is formed with the first hole-generating layer 102, the light-emitting layer 104, the electron-generating layer 105, and the second hole-generating layer 103 stacked in order.

[0072] The first hole-generating layer 102 and the second hole-generating layer 103 may be formed with either different materials or the same material. For example, a layer containing both of a hole-transporting material and an electron-accepting material which can receive electrons from the hole-transporting material, a P-type semiconductor layer, or a layer containing a P-type semiconductor is used. As the hole-transporting material, for example, an aromatic amine compound (having a bond of a benzene ring with nitrogen), phthalocyanine (abbreviated to H2Pc), or a phthalocyanine compound such as copper phthalocyanine (abbreviated to CuPc) or vanadyl phthalocyanine (abbreviated to VOPc) can be used. The aromatic amine compound is, for example, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (abbreviated to α -NPD), 4,4'-bis[N-(3-methylphenyl)-N-phenyl-amino]-biphenyl (abbreviated to TPD), 4,4',4"-tris(N,N-diphenyl-amino)-triphenylamine (abbreviated to TDATA), 4,4',4"-tris[N-(3-methylphenyl)-N-phenyl-amino]-triphenylamine (abbreviated to MTDATA), or 4,4'-bis(N-(4-(N,N-di-m-tolylamino)phenyl)-N-phenylamino)biphenyl (abbreviated to DNTPD). As the electron-accepting material which can receive electrons from these hole-transporting materials, for example, the following can be used; molybdenum oxide, vanadium oxide, 7,7,8,8,-tetracyanoquinodimethane (abbreviated to TCNQ), 2,3-dicyanonaphthoquinone (abbreviated to DCNNQ), 2,3,5,6-tetrafluoro-7,7,8,8,-tetracyanoquinodimethane (abbreviated to F4-TCNQ), or the like. The electron-accepting material is selected which can receive electrons in accordance with the combination with the hole-transporting material. Further, molybdenum oxide, vanadium oxide, ruthenium oxide, cobalt oxide, nickel oxide, or copper oxide can be used as the P-type semiconductor. It is to be noted that the materials

mentioned above are just examples, and a practitioner can select appropriately. Concerning the hole-transporting material and the electron-accepting material which can receive electrons from the hole-transporting material, the mixture ratio of the electron-accepting material to the hole-transporting material is preferably 0.5 or more, more preferably in the range of 0.5 to 2, in molar ratio. In this embodiment mode, the first hole-generating layer and the second hole-generating layer use α -NPD as the electron-transporting material and use molybdenum oxide (MoO_3) as the electron-accepting material which can receive electrons from α -NPD. α -NPD and MoO_3 are deposited by a co-evaporating method so that the mass ratio is α -NPD: MoO_3 =4:1 (which corresponds to 1 in molar ratio). In this embodiment mode, the first hole-generating layer is formed in 50 nm thick and the second hole-generating layer is formed in 20 nm thick.

[0073] When the light-emitting layer 104 is formed with a layer in which a light-emitting material to be the light-emission center is diffused in the layer containing the material having larger energy gap than the light-emitting material, the following material can be used as the light-emitting material to be the luminescence center; 4-dicyanomethylene-2-methyl-6-[2-(1,1,7,7-tetramethyl-9-julolidyl)ethenyl]-4H-pyran (abbreviation: DCJT); 4-dicyanomethylene-2-*t*-butyl-6-[2-(1,1,7,7-tetramethyl-julolidine-9-yl)ethenyl]-4H-pyran; perfluoranthene; 2,5-dicyano-1,4-bis[2-(10-methoxy-1,1,7,7-tetramethyl-julolidine-9-yl)ethenyl]benzene, N,N'-dimethylquinacridone (abbreviated to DMQd), coumarin 6, coumarin 545T, tris (8-quinolinolato)aluminum (abbreviated to Alq_3), 9,9'-bianthryl, 9,10-diphenylanthracene (abbreviated to DPA), 9,10-bis(2-naphthyl)anthracene (abbreviated to DNA), 2,5,8,11-tetra-*t*-butylperylene (abbreviated to TBP), or the like. As the material to be a base material in which the light-emitting material is diffused, the following can be used; an anthracene derivative such as 9,10-di(2-naphthyl)-2-*tert*-butylanthracene (abbreviated to *t*-BuDNA), a carbazole derivative such as 4,4'-bis(N-carbazolyl)biphenyl (abbreviated to CBP), or a metal complex such as tris(8-quinolinolato)aluminum (abbreviated to Alq_3), tris (4-methyl-8-quinolinolato)aluminum (abbreviated to Almq_3), bis(10-hydroxybenzo[h]-quinolinolato)beryllium (abbreviated to BeBq_2), bis(2-methyl-8-quinolinolato)-4-phenylphenolato-aluminum (abbreviated to BALq), bis[2-(2-hydroxyphenyl)pyridinato]zinc (abbreviated to Znpp_2), or bis[2-(2-hydroxyphenyl)benzoxazolate]zinc (abbreviated to ZnBOX). As the material which can constitute the light-emitting layer 104 singularly, tris(8-quinolinolato)aluminum (abbreviated to Alq_3), 9,10-bis(2-naphthyl)anthracene (abbreviated to DNA), bis(2-methyl-8-quinolinolato)-4-phenylphenolato-aluminum (abbreviated to BALq), or the like can be used.

[0074] The light-emitting layer 104 may be formed either in a single-layer structure or a multilayer structure. Moreover, a hole-transporting layer may be provided between the first hole-generating layer 102 and the layer in which the light-emitting material is diffused in the light-emitting layer 104 (or the layer containing the light-emitting material). Further, an electron-transporting layer may be provided between the electron-generating layer 105 and the layer in which the light-emitting material is diffused in the light-emitting layer 104 (or the layer containing the light-emitting material). These layers are not always necessary to be provided, and only one or both of the hole-transporting layer and the electron-transporting layer may be provided. The materials of the hole-transporting layer and the electron-transporting layer conform to those of the hole-transporting layer in the hole-generating layer and the electron-transporting layer in the electron-generating layer; therefore, the description is omitted here. Refer to the description of those layers.

[0075] In this embodiment mode, the hole-transporting layer, the layer in which the light-emitting material is diffused, and the electron-transporting layer are formed as the light-emitting layer 104 over the hole-generating layer 102. α -NPD is deposited in 10 nm thick as the hole-transporting layer, Alq and coumarin 6 are deposited in 35 nm thick with their mass ratio of 1:0.005 as the layer in which the light-emitting material is diffused, and Alq is deposited in 10 nm thick as the electron-transporting layer.

[0076] As the electron-generating layer 105, a layer containing both of an electron-transporting material and an electron-donating material which can donate electrons to the electron-transporting material, an N-type semiconductor layer, or a layer containing an N-type semiconductor can be used. As the electron-transporting material, for example, the following can be employed; a material containing a metal complex which has a quinoline skeleton or a benzoquinoline skeleton such as tris(8-quinolinolato)aluminum (abbreviated to Alq_3), tris(4-methyl-8-quinolinolato)aluminum (abbreviated to Almq_3), bis(10-hydroxybenzo[h]-quinolinolato)beryllium (abbreviated to BeBq_2), or bis(2-methyl-8-quinolinolato)-4-phenylphenolato-aluminum (abbreviated to BALq). Besides, metal containing a metal complex which has an oxazole or thiazole ligand such as bis[2-(2-hydroxyphenyl)benzoxazolate]zinc (abbreviated to Zn(BOX)_2) or bis[2-(2-hydroxyphenyl)benzothiazolate]zinc (abbreviated to Zn(BTZ)_2) can be used. In addition to the metal complex, the following can be employed; 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (abbreviated to PBD), 1,3-bis[5-(*p*-*tert*-butylphenyl)-1,3,4-oxadiazole-2-yl]benzene (abbreviated to OXD-7), 3-(4-*tert*-butylphenyl)-4-phenyl-5-(4-biphenyl)-1,2,4-triazole (abbreviated to TAZ), 3-(4-*tert*-butylphenyl)-4-(4-ethylphenyl)-5-(4-biphenyl)-1,2,4-triazole (abbreviated to *p*-Et-TAZ), bathophenanthroline (abbreviated to BPhen), bathocuproin (abbreviated to BCP), or the like. As the electron-donating material which can donate electrons to the electron-transporting material, for example, alkali metal such as lithium or cesium, magnesium, alkali-earth metal such as calcium, or rare-earth metal such as erbium or ytterbium can be used. The electron-donating material which can donate electrons is selected in accordance with the combination with the electron-transporting material. Further, zinc oxide, zinc sulfide, zinc selenide, titanium oxide, or the like can be used as the N-type semiconductor.

[0077] The mixture ratio between the electron-transporting material and the electron-donating material which can

donate electrons to the electron-transporting material is approximately 1:0.5 to 1:2, preferably 1:1, in molar ratio. The electron-transporting material is formed with Alq and the electron-donating material which can donate electrons to Alq is formed with lithium (Li) in the electron-generating layer in this embodiment mode. Deposition is conducted by the co-evaporating method so that Alq:Li=1:0.01 in mass ratio. The film thickness is set to 10 nm.

[0078] The light-emitting element which emits light with a different emission wavelength may be formed for each pixel to conduct the color display. Typically, light-emitting elements corresponding to the respective colors of R (red), G (green), and B (blue) are formed. Even in this case, the color purity can be increased and the pixel portion can be prevented from having a mirror surface (reflection) by providing, at a side of the pixel from which the light is emitted, a filter (colored layer) which transmits light of the emission wavelength. By providing the filter (colored layer), a circular polarizing plate which has been required conventionally can be omitted and the loss of the light emitted from the light-emitting element can be suppressed. Moreover, the change of the tone of color when viewing the pixel portion (display screen) obliquely can be reduced.

[0079] The light-emitting element can have a structure in which light of a single color or a white color is emitted. In the case of using the light-emitting element of the white color, a filter (colored layer) to transmit the light of a particular wavelength is provided at a side of the pixel from which the light is emitted. Thus, the color display can be conducted.

[0080] In order to form a light-emitting layer which emits the white light, the white light can be obtained by stacking, for example, Alq₃, Alq₃ partially doped with Nile red, which is pigment for red light emission, Alq₃, p-EtTAZ, and TPD (aromatic diamine) sequentially according to an evaporating method.

[0081] Moreover, the light-emitting layer may be formed not only with a singlet-excited light-emitting material but also with a triplet-excited light-emitting material containing a metal complex and the like. For example, among a red light-emitting pixel, a green light-emitting pixel, and a blue light-emitting pixel, the red light-emitting pixel, which has a comparatively short half-life period, is formed with the triplet excited light-emitting material, and the others are formed with the singlet-excited light-emitting material. Because of the high emission efficiency, the triplet-excited light-emitting material has the characteristic that the power consumption is low to obtain the same luminance. That is to say, in the case of applying the triplet-excited light-emitting material to the red pixel, the amount of current flowing to the light-emitting element is small; therefore, the reliability can be enhanced. For lower power consumption, the red light-emitting pixel and the green light-emitting pixel may be formed with the triplet-excited light-emitting material, and the blue light-emitting pixel may be formed with the singlet-excited light-emitting material. By forming the green light-emitting element, to which human visibility is high, also with the triplet-excited light-emitting material, lower power consumption can be achieved.

[0082] As an example of the triplet-excited light-emitting material, the following can be employed; a material using a metal complex as dopant, such as a metal complex containing platinum, which is one of third transition elements, as metal center or a metal complex containing iridium as metal center. The triplet-excited light-emitting material is not limited to these compounds, and other compounds which have the above structure and contain an element belonging to any one of groups 8 to 10 in the periodic table as metal center can be used.

[0083] The light-emitting element formed with the above material emits light by applying bias in a forward direction. A pixel of a display device formed using the light-emitting element can be driven by a simple matrix method or an active matrix method. In any way, the respective pixels emit light by applying bias in the forward direction at a particular timing and do not emit light for a certain period. The reliability of the light-emitting element can be increased by applying bias in a reverse direction in this non-emission period. The light-emitting element has deterioration modes in which light-emission intensity decreases under a certain drive condition or the luminance seems to decrease because a non-emission region expands within the pixel. However, when alternately driving is conducted by applying bias in the forward and reverse directions, the progress of the deterioration can be slowed down and the reliability of the light-emitting device can be enhanced.

[0084] Subsequently, the cathode 106 is formed so as to cover the light-emitting laminated body 66. Accordingly, a light-emitting element 93 comprising the anode 101, the light-emitting laminated body 66, and the cathode 106 can be manufactured. As the cathode material used for forming the cathode 106, it is preferable to use metal, alloy, an electrically conductive compound, mixture of these, or the like each of which has low work function (work function of 3.8 eV or less). As a specific example of the cathode material, the following can be given; an element belonging to group 1 or 2 in the periodic table, that is, alkali metal such as Li or Cs, Mg, alkali-earth metal such as Ca or Sr, alloy containing these elements such as Mg:Ag or Al:Li, or a compound containing these elements such as LiF, CsF, or CaF₂. In addition, the cathode can also be formed with a transition metal containing rare-earth metal. Further, a multilayer containing the above element and another metal (including alloy) such as Al, Ag, or ITO can be used. In this embodiment mode, the cathode is formed with aluminum.

[0085] In the light-emitting element having the above structure, the drive voltage is low and the increase in the drive voltage over time is small.

[0086] The electrode in electrical contact with the connection portion 61a is the anode 101 in this embodiment mode; however, the electrode in electrical contact with the connection portion 61a may be the cathode 106. In this case, the light-emitting laminated body 66 may be formed by stacking the second hole-generating layer 103, the electron-generating

layer 105, the light-emitting layer 104, and the first hole-generating layer 102 in order, and the anode 101 may be formed over the light-emitting laminated body 66.

[0087] After that, a silicon oxynitride film is formed as a second passivation film by a plasma CVD method. In the case of using the silicon oxynitride film, a silicon oxynitride film manufactured with SiH_4 , N_2O , and NH_3 by a plasma CVD method, a silicon oxynitride film manufactured with SiH_4 and N_2O by a plasma CVD method, or a silicon oxynitride film manufactured with gas in which SiH_4 and N_2O are diluted with Ar by a plasma CVD method is preferably formed.

[0088] As a first passivation film, a silicon oxynitride hydride film manufactured with SiH_4 , N_2O , and H_2 is also applicable. The structure of the first passivation film is not limited to the single-layer structure, and the first passivation film may be formed in a single-layer structure or a multilayer structure of another insulating layer containing silicon. A multilayer film of a carbon nitride film and a silicon nitride film, a multilayer film of styrene polymer, a silicon nitride film, or a diamond-like carbon film may be formed instead of the silicon oxynitride film.

[0089] Subsequently, in order to protect the light emitting element from the deterioration-promoting material such as moisture, the display portion is sealed. In the case of using a counter substrate for sealing, the counter substrate and an element substrate are pasted together by an insulating sealing material so as to expose an external connection portion. The space between the counter substrate and the element substrate may be filled with inert gas such as dry nitrogen, or the sealing material may be applied to the whole surface of the pixel portion for pasting the counter substrate. It is preferable to use an ultraviolet curable resin or the like as the sealing material. A drying agent or particles for keeping the gap between the substrates uniform may be mixed into the sealing material. Subsequently, a flexible wiring substrate is pasted to the external connection portion, thereby completing the display device.

[0090] An example of the structure of the thus manufactured display device is described with reference to FIGS. 7A and 7B. Although the shapes are different, the same parts having the same function are denoted with the same reference numerals and the description to such parts may be omitted. In this embodiment mode, the thin film transistor 70 having the LDD structure connects to the light-emitting element 93 via the connection portion 61a.

[0091] In FIG 7A, the anode 101 is formed with a light-transmitting conductive film and has a structure in which light emitted from the light-emitting laminated body 66 is extracted to the side of the substrate 50. A reference numeral 94 denotes a counter substrate, which is to be fixed to the substrate 50 with a sealing material or the like after forming the light-emitting element 93. By filling the space between the counter substrate 94 and the element with a light-transmitting resin 88 or the like and sealing the space, it is possible to prevent the light-emitting element 93 from deteriorating due to the moisture. Further, the resin 88 desirably has moisture-absorption properties. In addition, it is more desirable that a drying agent 89 having high light-transmitting properties is diffused in the resin 88 because the effect of moisture can be suppressed further.

[0092] In FIG 7B, the anode 101 and the cathode 106 are both formed with a light-transmitting conductive film and have a structure in which light can be extracted toward both of the substrate 50 and the counter substrate 94. In this structure, it is possible to prevent the screen from becoming transparent by providing a polarizing plate 90 outside the substrate 50 and the counter substrate 94, whereby increasing the visibility. A protective film 91 is preferably provided outside the polarizing plate 90.

[0093] Either an analog video signal or a digital video signal may be used in the display device having the display function according to the present invention. The digital video signal includes a video signal using voltage and a video signal using current. When the light-emitting element emits light, the video signal inputted into the pixel uses the constant voltage or the constant current. When the video signal uses the constant voltage, the voltage applied to the light-emitting element or the current flowing in the light-emitting element is constant. On the other hand, when the video signal uses the constant current, the voltage applied to the light-emitting element or the current flowing in the light-emitting element is constant. The light-emitting element to which the constant voltage is applied is driven by the constant voltage, and the light-emitting element in which the constant current flows is driven by the constant current. The constant current flows in the light-emitting element driven by the constant current without being affected by the change of the resistance of the light-emitting element. Either method may be employed in the light-emitting display device and its driving method of the present invention.

[0094] In the display device according to the present invention manufactured by the method in this embodiment mode, the drive voltage is low and the increase in the drive voltage over time is small.

[Embodiment Mode 4]

[0095] This embodiment mode describes an external view of a panel of a light-emitting device corresponding to one aspect of the present invention with reference to FIGS. 8A and 8B. FIG 8A is a top view of a panel in which a transistor and a light-emitting element formed over a substrate are sealed by a sealing material formed between the substrate and a counter substrate 4006. FIG 8B corresponds to a cross-sectional view of FIG 8A. The structure of the light-emitting element mounted in this panel is a structure in which a layer in contact with an electrode is a hole-generating layer and a light-emitting layer is sandwiched between the hole-generating layers. Moreover, in the light-emitting element, an

electron-generating layer is provided between the hole-generating layer on a cathode side and the light-emitting layer.

[0096] A sealing material 4005 is provided so as to surround a pixel portion 4002, a signal line driver circuit 4003, and a scanning line driver circuit 4004 which are provided over a substrate 4001. In addition, the counter substrate 4006 is provided over the pixel portion 4002, the signal line driver circuit 4003, and the scanning line driver circuit 4004. Therefore, the pixel portion 4002, the signal line driver circuit 4003, and the scanning line driver circuit 4004 are sealed together with a filling material 4007 by the substrate 4001, the sealing material 4005, and the counter substrate 4006.

[0097] The pixel portion 4002, the signal line driver circuit 4003, and the scanning line driver circuit 4004 provided over the substrate 4001 have a plurality of thin film transistors. FIG 8B shows a thin film transistor 4008 included in the signal line driver circuit 4003 and a thin film transistor 4010 included in the pixel portion 4002.

[0098] The light-emitting element 4011 is connected electrically to the thin film transistor 4010.

[0099] Further, a lead wiring 4014 corresponds to a wiring for supplying a signal or a power source voltage to the pixel portion 4002, the signal line driver circuit 4003, and the scanning line driver circuit 4004. The lead wiring 4014 is connected to a connection terminal 4016 via a lead wiring 4015a and a lead wiring 4015b. The connection terminal 4016 is electrically connected to a terminal of a flexible print circuit (FPC) 4018 via an anisotropic conductive film 4019.

[0100] As the filling material 4007, in addition to inert gas such as nitrogen or argon, an ultraviolet curable resin or a thermoset resin can be used. For example, polyvinyl chloride, acrylic, polyimide, an epoxy resin, a silicon resin, polyvinyl butyral, or ethylene vinylene acetate can be used.

[0101] It is to be noted that the display device according to the present invention includes in its category the panel in which the pixel portion having the light-emitting element is formed and a module in which an IC is mounted in the panel.

[0102] In the panel and the module having the structure shown in this embodiment mode, the drive voltage is low and the increase in the drive voltage over time is small.

[Embodiment Mode 5]

[0103] As an electronic appliance according to the present invention to which a module, for example the module which has been exemplified in Embodiment Mode 4, is mounted, the following is given; a camera such as a video camera or a digital camera, a goggle type display (head mount display), a navigation system, a sound reproduction device (car audio component or the like), a computer, a game machine, a mobile information terminal (a mobile computer, a mobile telephone, a mobile game machine, an electronic book, or the like), an image reproduction device equipped with a recording medium (specifically a device which reproduces the recording medium such as a digital versatile disc (DVD) and which is equipped with a display for displaying the image), or the like. FIGS. 9A to 9E show specific examples of these electronic appliances.

[0104] FIG 9A shows a light-emitting display device, which corresponds to, for example, a television receiving device or a monitor of a personal computer. The light-emitting display device according to the present invention includes a case 2001, a display portion 2003, speaker portions 2004, and the like. In the light-emitting display device according to the present invention, the drive voltage of the display portion 2003 is low and the increase in the drive voltage of the display portion 2003 over time is small. In the pixel portion, a polarizing plate or a circular polarizing plate is preferably provided in the pixel portion to enhance the contrast. For example, films are preferably provided in order of a quarter wave-plate, a half wave-plate, and a polarizing plate to a sealing substrate. Further, an anti-reflection film may be provided over the polarizing plate.

[0105] FIG 9B shows a mobile phone including a main body 2101, a case 2102, a display portion 2103, an audio input portion 2104, an audio output portion 2105, operation keys 2106, an antenna 2108, and the like. In the display portion 2103 of the mobile phone according to the present invention, the drive voltage is low and the increase in the drive voltage over time is small.

[0106] FIG 9C shows a computer including a main body 2201, a case 2202, a display portion 2203, a keyboard 2204, an external connection port 2205, a pointing mouse 2206, and the like. In the display portion 2203 of the computer according to the present invention, the drive voltage is low and the increase in the drive voltage over time is small. Although FIG 9C shows a laptop computer, the present invention is also applicable for a desktop computer in which a hard disk is integrated with a display portion.

[0107] FIG 9D shows a mobile computer including a main body 2301, a display portion 2302, a switch 2303, operation keys 2304, an infrared port 2305, and the like. In the display portion 2302 of the mobile computer according to the present invention, the drive voltage is low and the increase in the drive voltage over time is small.

[0108] FIG 9E shows a mobile game machine including a case 2401, a display portion 2402, speaker portions 2403, operation keys 2404, an recording medium insert portion 2405, and the like. In the display portion 2402 of the mobile game machine according to the present invention, the drive voltage is low and the increase in the drive voltage over time is small.

[0109] As thus described, the present invention is applicable in a wide range, and can be used in electronic appliances of every field.

[Embodiment Mode 6]

[0110] FIGS. 10A to 10C show examples of bottom emission, dual emission, and top emission, respectively. The structure whose manufacturing process has been described in Embodiment Mode 2 corresponds to the structure of FIG 10C. FIGS. 10A and 10B show the structures in which a first interlayer insulating layer 900 in FIG 10C is formed with a material having self-flattening properties and a wiring to be connected with a thin film transistor 901 and the anode 101 of the light-emitting element are formed over the same interlayer insulating layer. In FIG 10A, the anode 101 in the light-emitting element is formed with a light-transmitting material, and light is emitted toward a lower part of the light-emitting device, which is called a bottom-emission structure. In FIG 10B, the cathode 106 is formed with a light-transmitting material such as ITO, ITSO, or IZO, and light is extracted from both sides, which is called a dual-emission structure. When a film is formed with aluminum or silver thickly, the film does not transmit light; however, the film transmits light when the film is formed thinly. Therefore, by forming the cathode 106 with aluminum or silver in such a thickness that light can pass therethrough, dual emission can be achieved.

[0111] [Embodiment Mode 7]

[0112] This embodiment mode describes a pixel circuit and a protective circuit in the panel and the module shown in Embodiment Mode 4, and their operations. FIGS. 5A to 6C show cross section of a driver TFT 1403 and a light-emitting element 1405 in FIGS. 11A to 11F.

[0113] A pixel shown in FIG 11A includes a signal line 1410 and power source lines 1411 and 1412 in a column direction and a scanning line 1414 in a row direction. The pixel further includes a switching TFT 1401, the driver TFT 1403, a current control TFT 1404, a capacitor element 1402, and the light-emitting element 1405.

[0114] A pixel shown in FIG 11C has the same structure as that in FIG 11A except that a gate electrode of the driver TFT 1403 is connected to the power source line 1412 provided in the row direction. In other words, the pixels shown in FIGS. 11A and 11C have the same equivalent circuit diagram. However, in the case of arranging the power source line 1412 in the column direction (FIG 11A) and in the case of arranging the power source line 1412 in the row direction (FIG 11C), each power source line is formed of a conductive film having a different layer. Here, attention is paid to a wiring connected to the gate electrode of the driver TFT 1403, and the structure is shown separately in FIGS. 11A and 11C in order to show that the layers for manufacturing these wirings are different.

[0115] As the characteristic of the pixels shown in FIGS. 11A and 11C, the driver TFT 1403 and the current control TFT 1404 are connected serially within the pixel, and it is preferable to set the channel length L (1403) and the channel width W (1403) of the driver TFT 1403, and the channel length L (1404) and the channel width W (1404) of the current control TFT 1404 so as to satisfy $L(1403)/W(1403):L(1404)/W(1404)=5$ to $6000:1$.

[0116] The driver TFT 1403 operates in a saturation region and serves to control the current value of the current flowing into the light-emitting element 1405. The current control TFT 1404 operates in a linear region and serves to control the current supply to the light-emitting element 1405. Both TFTs preferably have the same conductivity type in the manufacturing step, and the TFTs are n-channel type TFTs in this embodiment mode. The driver TFT 1403 may be either an enhancement type or a depletion type. Since the current control TFT 1404 operates in the linear region according to the present invention having the above structure, slight fluctuation of V_{gs} of the current control TFT 1404 does not affect the current value of the light-emitting element 1405. That is to say, the current value of the light-emitting element 1405 can be determined by the driver TFT 1403 operating in the saturation region. With the above structure, the unevenness of the luminance of the light-emitting element due to the variation of the characteristic of the TFT can be improved, thereby providing a display device in which the image quality is enhanced.

[0117] In the pixels shown in FIGS. 11A to 11D, the switching TFT 1401 is to control the input of the video signal to the pixel, and the video signal is inputted into the pixel when the switching TFT 1401 is turned on. Then, the voltage of the video signal is held in the capacitor element 1402. Although FIGS. 11A and 11C show the structure in which the capacitor element 1402 is provided, the present invention is not limited to this. When the gate capacitor and the like can cover the capacitor holding the video signal, the capacitor element 1402 is not necessarily provided.

[0118] A pixel shown in FIG 11B has the same pixel structure as that in FIG 11A except that a TFT 1406 and a scanning line 1414 are added. In the same way, a pixel shown in FIG 11D has the same pixel structure as that in FIG 11C except that the TFT 1406 and the scanning line 1414 are added.

[0119] Switching of the TFT 1406 is controlled by the additionally provided scanning line 1414. When the TFT 1406 is turned on, the charge held in the capacitor element 1402 is discharged, thereby turning off the current control TFT 1404. In other words, by the provision of the TFT 1406, a state can be produced compellingly in which the current is not flowed to the light-emitting element 1405. For this reason, the TFT 1406 can be referred to as an eraser TFT. Consequently, in the structures shown in FIGS. 11B and 11D, a lighting period can be started at the same time as or just after the start of a writing period without waiting for the writing of the signal into all the pixels; therefore the duty ratio can be increased.

[0120] In a pixel shown in FIG 11E, the signal line 1410 and the power source line 1411 are arranged in the column direction, and the scanning line 1414 is arranged in the row direction. Further, the pixel includes the switching TFT 1401, the driver TFT 1403, the capacitor element 1402, and the light-emitting element 1405. A pixel shown in FIG 11F has the

same pixel structure as that shown in FIG 7E except that the TFT 1406 and a scanning line 1415 are added. In the structure shown in FIG 11F, the duty ratio can also be increased by the provision of the TFT 1406.

[0121] As thus described, various pixel circuits can be employed. In particular, in the case of forming a thin film transistor with an amorphous semiconductor film, the semiconductor film for the driver TFT 1403 is preferably large. Therefore, in the above pixel circuit, a top emission type is preferable in which light from the light emitting layer is emitted from the side of the sealing substrate.

[0122] Such an active matrix light-emitting device can be driven at low voltage when the pixel density increases, because the TFTs are provided in each pixel. Therefore, it is considered that the active matrix light-emitting device is advantageous.

[0123] Although this embodiment mode describes the active matrix light-emitting device in which the respective TFTs are provided in each pixel, a passive matrix light-emitting device can also be formed in which TFTs are provided for each column. Since the TFTs are not provided in each pixel in the passive matrix light-emitting device, high aperture ratio can be obtained. In the case of a light-emitting device in which light is emitted to both sides of the electroluminescent layer, the transmissivity of the passive matrix display device is increased.

[0124] In the display device further comprising such pixel circuits according to the present invention, the drive voltage is low and the increase in the drive voltage over time is small. Moreover, the display device has the respective characteristics.

[0125] Subsequently, a case is described in which a diode is provided as a protective circuit to the scanning line and the signal line with the use of an equivalent circuit shown in FIG 11E.

[0126] In FIG 12, the switching TFTs 1401 and 1403, the capacitor element 1402, and the light-emitting element 1405 are provided in a pixel portion 1500. Diodes 1561 and 1562 are provided to the signal line 1410. In the similar way to the switching TFTs 1401 and 1403, the diodes 1561 and 1562 are manufactured based on the above embodiment modes, and have a gate electrode, a semiconductor layer, a source electrode, a drain electrode, and the like. The diodes 1561 and 1562 are operated as the diode by connecting the gate electrode with the drain electrode or the source electrode.

[0127] Common potential lines 1554 and 1555 connecting with the diodes are formed with the same layer as the gate electrode. Therefore, in order to connect with the source electrode or the drain electrode of the diode, it is necessary to form a contact hole in the gate insulating layer.

[0128] A diode provided to the scanning line 1414 has the similar structure.

[0129] As thus described, according to the present invention, a protective diode to be provided to an input stage can be manufactured simultaneously. The position at which the protective diode is formed is not limited to this, and the diode may also be provided between the driver circuit and the pixel.

[0130] In the display device having such protective circuits according to the present invention, the increase in the drive voltage over time is small and the reliability as the display device can be enhanced.

[Embodiment 1]

[0131] This embodiment shows measurement data of a light-emitting element according to the present invention.

[0132] First, a manufacturing method of a light-emitting element in this embodiment is described. The light-emitting element in this embodiment conforms to the structure of the light-emitting element shown in Embodiment Mode 1. In this embodiment, a glass substrate is used as the insulator 100. ITO containing silicon is formed over the glass substrate by a sputtering method, thereby forming the anode 101. The thickness of the anode 101 is set to 110 nm.

[0133] Subsequently, the first hole-generating layer 102 is formed with molybdenum oxide and α -NPD by co-evaporating molybdenum oxide and α -NPD over the anode 101. Here, the thickness of the first hole-generating layer 102 is set to 50 nm.

[0134] Next, the light-emitting layer 104 is formed over the first hole-generating layer 102. The light-emitting layer 104 is formed in a three-layer structure in which a hole-transporting layer, a layer where a light-emitting material is diffused, and an electron-transporting layer are stacked in order from the side of the first hole-generating layer 102. The hole-transporting layer is formed with α -NPD in 10 nm thick by a vacuum evaporating method. The layer in which the light-emitting material is diffused is formed with Alq₃ and coumarin 6 in 35 nm thick by a co-evaporating method. The electron-transporting layer is formed with only Alq₃ in 10 nm thick by a vacuum evaporating method. The layer in which the light-emitting material is diffused is adjusted so that the proportion between Alq₃ and coumarin 6 is 1:0.005 in mass ratio.

[0135] Subsequently, the electron-generating layer 105 is formed with Alq₃ and lithium in 10 nm thick by co-evaporating Alq₃ and lithium over the light-emitting layer 104. Alq₃ and lithium are adjusted so that the mass ratio between Alq₃ and lithium is 1:0.01.

[0136] Next, the second hole-generating layer 103 is formed with molybdenum oxide and α -NPD by co-evaporating molybdenum oxide and α -NPD over the electron-generating layer 105. Here, the thickness of the first hole-generating layer 102 is set to 20 nm. The molar ratio between α -NPD and molybdenum oxide is 1: 1.

[0137] The cathode 106 is formed with aluminum in 100 nm thick over the second hole-generating layer 105.

[0138] When voltage is applied to the light-emitting element having the above structure according to the present invention, holes are injected from the second hole-generating layer 103 to the second electrode. Moreover, electrons are injected from the electron-generating layer 105 to the light-emitting layer 104. Further, holes are injected from the first hole-generating layer 102 to the light-emitting layer 104. Then, the injected holes and electrons are recombined in the light-emitting layer, thereby providing light from coumarin 6.

[0139] FIG 13 shows the voltage-luminance characteristic of the thus manufactured light-emitting element of this embodiment, while FIG 14 shows the voltage-current characteristic thereof. In FIG 13, the horizontal axis shows the voltage (V), and the vertical axis shows the luminance (cd/m^2). In FIG 14, the horizontal axis shows the voltage (V), and the vertical axis shows the current (mA).

[0140] Thus, the light-emitting element in this embodiment exhibits superior characteristic.

[0141] FIG 22A shows the absorption spectrum of a complex material containing α -NPD and molybdenum oxide used as the hole-generating layer in this embodiment. FIG 22B shows the absorption spectrum of only α -NPD and FIG 22C shows the absorption spectrum of only molybdenum oxide. As is known from the figures, the absorption spectrum of the complex material containing α -NPD and molybdenum oxide has a peak which does not appear in the other absorption spectra of only α -NPD and only molybdenum oxide. It is considered that this peak results from the generation of holes by interaction of α -NPD and molybdenum oxide.

[Embodiment 2]

[0142] This embodiment describes a manufacturing method of four light-emitting elements having different mixture proportions between a hole-transporting material and an electron-accepting material which shows electron-accepting properties to the hole-transporting material in a hole-generating layer. The four light-emitting elements are denoted by a light-emitting element (1), a light-emitting element (2), a light-emitting element (3), and a light-emitting element (4). Moreover, this embodiment describes the characteristics of these elements.

[0143] First, the manufacturing method of the light-emitting element in this embodiment is described. In this embodiment, the light-emitting element conforms to the structure of the light-emitting element shown in Embodiment Mode 1. In this embodiment, a glass substrate is used as the insulator 100. ITO containing silicon is formed over the glass substrate by a sputtering method, thereby forming the anode 101. The thickness of the anode 101 is set to 110 nm.

[0144] Subsequently, the first hole-generating layer 102 is formed with molybdenum oxide over the anode 101 by a vacuum evaporating method. Here, the thickness of the first hole-generating layer 102 is set to 5 nm.

[0145] Next, the light-emitting layer 104 is formed over the first hole-generating layer 102. The light-emitting layer 104 is formed in a three-layer structure in which a hole-transporting layer, a layer where a light-emitting material is diffused, and an electron-transporting layer are stacked in order from the side of the first hole-generating layer 102. The hole-transporting layer is formed with α -NPD in 55 nm thick by a vacuum evaporating method. The layer in which the light-emitting material is diffused is formed with Alq_3 and coumarin 6 in 35 nm thick by a co-evaporating method. The electron-transporting layer is formed with only Alq_3 in 10 nm thick by a vacuum evaporating method. The layer in which the light-emitting material is diffused is adjusted so that the proportion between Alq_3 and coumarin 6 is 1:0.005 in mass ratio.

[0146] Subsequently, the electron-generating layer 105 is formed with Alq_3 and lithium in 10 nm thick by co-evaporating Alq_3 and lithium over the light-emitting layer 104. Alq_3 and lithium are adjusted so that the mass ratio between Alq_3 and lithium is 1:0.01.

[0147] Next, the second hole-generating layer 103 is formed with molybdenum oxide and α -NPD by co-evaporating molybdenum oxide and α -NPD over the electron-generating layer 105. Here, the light-emitting element (1) is adjusted so that the molar ratio of α -NPD to molybdenum oxide is 0.5 ($=\alpha\text{-NPD/molybdenum oxide}$). The light-emitting element (2) is adjusted so that the molar ratio of α -NPD to molybdenum oxide is 1.0 ($=\alpha\text{-NPD/molybdenum oxide}$). The light-emitting element (3) is adjusted so that the molar ratio of α -NPD to molybdenum oxide is 1.5 ($=\alpha\text{-NPD/molybdenum oxide}$). The light-emitting element (4) is adjusted so that the molar ratio of α -NPD to molybdenum oxide is 2.0 ($=\alpha\text{-NPD/molybdenum oxide}$). The thickness of the second hole-generating layer 102 is set to 20 nm.

[0148] The cathode 106 is formed with aluminum in 100 nm thick over the second hole-generating layer 103.

[0149] When voltage is applied to the light-emitting element having the above structure according to the present invention, holes are injected from the second hole-generating layer 103 to the second electrode. Moreover, electrons are injected from the electron-generating layer 105 to the light-emitting layer 104. Further, holes are injected from the first hole-generating layer 102 to the light-emitting layer 104. Then, the injected holes and electrons are recombined in the light-emitting layer, thereby providing light from coumarin 6.

[0150] FIG 15 shows the voltage-luminance characteristic of the light-emitting element in the present embodiment. FIG 16 shows the current density-luminance characteristic thereof, and FIG 17 shows the voltage-current characteristic thereof. In FIG 15, the horizontal axis shows the voltage (V) and the vertical axis shows the luminance (cd/m^2). In FIG 16, the horizontal axis shows the current density (mA/cm^2) and the vertical axis shows the luminance (cd/m^2). In FIG 17, the horizontal axis shows the voltage (V) and the vertical axis shows the current (mA). In FIGS. 15 to 17, $\blacktriangle$ shows

the characteristic of the light-emitting element (1), • shows the characteristic of the light-emitting element (2), o shows the characteristic of the light-emitting element (3), and ■ shows the characteristic of the light-emitting element (4).

[0151] It is to be understood from FIGS. 15 to 17 that all of the light-emitting elements operate well. In the light-emitting elements (2) to (4) in which the molar ratio of α -NPD to molybdenum oxide (= α -NPD/molybdenum oxide) ranges from 1 to 2, high luminance is obtained by applying any voltage and high current value is also obtained. Thus, the light-emitting element can be obtained which operates at lower drive voltage by adjusting the molar ratio of α -NPD to molybdenum oxide (= α -NPD/molybdenum oxide) to be in the range of 1 to 2.

[0152] Next, a result of a continuously lighting test of the light-emitting elements of the present embodiment is described. After the light-emitting element manufactured as above is sealed under nitrogen atmosphere, the continuously lighting test is conducted at normal temperature in the following way.

[0153] As is clear from FIG 16, the current density of 26.75 mA/cm² is required when the light is emitted with the luminance of 3000 cd/m² in an initial state of the light-emitting element of the present invention. In this embodiment, the current of 26.75 mA/cm² keeps to be flowed for a certain period of time, and data are collected on the change of the voltage required to flow the current of 26.75 mA/cm² over time and the change of the luminance over time. FIGS. 18 and 19 show the collected data. In FIG 18, the horizontal axis shows the passed time (hour), while the vertical axis shows the voltage (V) required for flowing the current of 26.75 mA/cm². In FIG 19, the horizontal axis shows the passed time (hour), while the vertical axis shows the luminance (any unit of measure). It is to be noted that the luminance (any unit of measure) is a relative value to the initial luminance expressed by assuming that the initial luminance be 100. The relative value is obtained in such a way that the luminance at a particular time is divided by the initial luminance and multiplied by 100.

[0154] It is to be understood from FIG 18 that after 100 hours have passed, the voltage required for flowing the current having the current density of 26.75 mA/cm² is only approximately 1 V higher than that in the initial state. This indicates that the light-emitting element of the present invention is a superior element in which the increase in the drive voltage over time is small.

[0155] In the light-emitting elements shown in Embodiments 1 and 2, layers serving as the hole-injecting layer, the hole-transporting layer, the electron-transporting layer, and the like are formed in addition to the layer serving as the light-emitting layer. However, these layers are not always necessary. Further, in Embodiments 1 and 2, after the layer serving as the light-emitting layer is formed, the electron-generating layer is formed, and then the hole-generating layer is formed. However, the manufacturing method of the light-emitting element according to the present invention is not limited to this. For example, after the hole-generating layer is formed, the electron-generating layer may be formed, and then the layer serving as the light-emitting layer may be formed.

[Embodiment 3]

[0156] This embodiment shows measurement data of a light-emitting element according to the present invention which uses a different material from Embodiment 1.

[0157] First, a method for manufacturing a light-emitting element in this embodiment is described. The light-emitting element in this embodiment conforms to the structure of the light-emitting element shown in Embodiment Mode 1. In this embodiment, a glass substrate is used as the insulator 100. ITO containing silicon is formed over the glass substrate by a sputtering method, thereby forming the anode 101 in 110 nm thick.

[0158] Subsequently, the first hole-generating layer 102 is formed with molybdenum oxide and DNTPD by co-evaporating molybdenum oxide and DNTPD over the anode 101. Here, the thickness of the first hole-generating layer 102 is set to 50 nm. The mass ratio between DNTPD and molybdenum oxide is set to 2:1.

[0159] Next, the light-emitting layer 104 is formed over the first hole-generating layer 102. The light-emitting layer 104 has a three-layer structure including a hole-transporting layer, a layer in which a light-emitting material is diffused, and an electron-transporting layer in order from the side of the first hole-generating layer 102. The hole-transporting layer is formed with α -NPD in 10 nm thick by a vacuum evaporating method. The layer in which the light-emitting material is diffused is formed with Alq₃ and coumarin 6 in 35 nm thick by a co-evaporating method. The electron-transporting layer is formed with only Alq₃ in 10 nm thick by a vacuum evaporating method. It is to be noted that the layer in which the light-emitting material is diffused is adjusted so that the proportion between Alq₃ and coumarin 6 is 1:0.005 in mass ratio.

[0160] Subsequently, the electron-generating layer 105 is formed with Alq₃ and lithium in 10 nm thick by co-evaporating Alq₃ and lithium over the light-emitting layer 104. The mass ratio between Alq₃ and lithium is adjusted so as to be 1:0.01.

[0161] Next, the second hole-generating layer 103 is formed with molybdenum oxide and DNTPD over the electron-generating layer 105 by co-evaporating molybdenum oxide and DNTPD. Here, the thickness of the first hole-generating layer 102 is set to 20 nm. Further, the mass ratio between DNTPD and molybdenum oxide is adjusted so as to be 4:2.

[0162] The cathode 106 is formed with aluminum over the second hole-generating layer 103. The film thickness is set to 100 nm.

[0163] In the light-emitting element having the above structure according to the present invention, holes are injected from the second hole-generating layer 103 to the second electrode by applying voltage. Further, electrons are injected from the electron-generating layer 105 to the light-emitting layer 104. Moreover, holes are injected from the first hole-generating layer 102 to the light-emitting layer 104. In the light-emitting layer, the injected holes and electrons are recombined, thereby providing light from coumarin 6.

[0164] FIG 20 shows the voltage-luminance characteristic of the thus manufactured light-emitting element of this embodiment. FIG 21 shows the voltage-current characteristic thereof. In FIG 20, the horizontal axis shows the voltage (V), while the vertical axis shows the luminance (cd/m^2). Meanwhile, in FIG 21, the horizontal axis shows the voltage (V), while the vertical axis shows the current (mA).

[0165] Thus, the light-emitting element in this embodiment has superior characteristic.

[0166] FIG 23A shows the absorption spectrum of a complex material containing DNTPD and molybdenum oxide used as the hole-generating layer in this embodiment. FIG 23B shows the absorption spectrum of only DNTPD, and FIG 23C shows the absorption spectrum of only molybdenum oxide. As is clear from the figures, the absorption spectrum of the complex material containing DNTPD and molybdenum oxide has a peak which does not appear in the other absorption spectra of only DNTPD and only molybdenum oxide. It is considered that this is because holes are generated by interaction of DNTPD and molybdenum oxide. [Embodiment 4]

[0167] This embodiment describes an example of controlling a light-emission spectrum and viewing-angle dependence of light emission by changing the thickness of a hole-generating layer, which is a so-called optical design of a light-emitting element with reference to FIGS. 24 and 25.

[0168] First, a method for manufacturing a light-emitting element in this embodiment is described. The light-emitting element in this embodiment conforms to the structure of the light-emitting element shown in Embodiment Mode 1. In this embodiment, a glass substrate is used as the insulator 100. ITO containing silicon is formed over the glass substrate by a sputtering method, thereby forming the anode 101 in 110 nm thick.

[0169] Subsequently, the first hole-generating layer 102 is formed with molybdenum oxide and α -NPD by co-evaporating molybdenum oxide and α -NPD over the anode 101. Here, the thickness of the first hole-generating layer 102 is set to 50 nm. The mass ratio between α -NPD and molybdenum oxide is set to 4:1.

[0170] Next, the light-emitting layer 104 is formed over the first hole-generating layer 102. The light-emitting layer 104 has a three-layer structure including a hole-transporting layer, a layer in which a light-emitting material is diffused, and an electron-transporting layer in order from the side of the first hole-generating layer 102. The hole-transporting layer is formed with α -NPD in 10 nm thick by a vacuum evaporating method. The layer in which the light-emitting material is diffused is formed with Alq_3 and coumarin 6 in 40 nm thick by a co-evaporating method. The electron-transporting layer is formed with only Alq_3 in 10 nm thick by a vacuum evaporating method. It is to be noted that the layer in which the light-emitting material is diffused is adjusted so that the proportion between the Alq_3 and coumarin 6 is 1:0.01 in mass ratio.

[0171] Subsequently, the electron-generating layer 105 is formed with Alq_3 and lithium in 10 nm thick by co-evaporating Alq_3 and lithium over the light-emitting layer 104. The mass ratio between Alq_3 and lithium is adjusted so as to be 1:0.01.

[0172] Next, the second hole-generating layer 103 is formed with molybdenum oxide and α -NPD by co-evaporating molybdenum oxide and α -NPD over the electron-generating layer 105. Further, the mass ratio between α -NPD and molybdenum oxide is adjusted so as to be 2:1.

[0173] The cathode 106 is formed with aluminum over the second hole-generating layer 103. The film thickness is set to 100 nm.

[0174] In the light-emitting element having the above structure according to the present invention, holes are injected from the second hole-generating layer 103 to the second electrode by applying voltage. Further, electrons are injected from the electron-generating layer 105 to the light-emitting layer 104. Moreover, holes are injected from the first hole-generating layer 102 to the light-emitting layer 104. In the light-emitting layer, the injected holes and electrons are recombined, thereby providing light from coumarin 6.

[0175] In this embodiment, light is extracted from the light-emitting element toward the side of the glass substrate over which the light-emitting element is formed, and the cathode 106 serves as a reflection electrode. Moreover, by changing the thickness of the second hole-generating layer 103, the optical length of light returning after reflecting on the reflection electrode is adjusted. Accordingly, an interference state between the light emitted to the direction of the glass substrate after reflecting on the reflection electrode and light directly emitted from the light-emitting element changes.

[0176] FIG 24 is a graph showing the relation between the current efficiency and the optical distance to the reflection electrode from the layer in which the light-emitting material is diffused, when the optical distance is changed by changing the thickness of the second hole-generating layer 103. Thus, it is to be understood that the emission efficiency changes periodically by changing the optical distance to the reflection electrode from the layer in which the light-emitting material is diffused. By adjusting the optical distance, it is possible to improve or suppress the emission efficiency.

[0177] FIG 25 is a graph showing the change of a light-emission spectrum in the case of changing the thickness of the second hole-generating layer 103 between 140 nm and 280 nm. The thickness of the second hole-generating layer 103 is 140 nm in an element 1, 160 nm in an element 2, 180 nm in an element 3, 200 nm in an element 4, 220 nm in

an element 5, 240 nm in an element 6, 260 nm in an element 7, and 280 nm in an element 8. It is to be understood from the graph that the maximum wavelength and the spectrum shape of the light change when the optical distance to the reflection electrode from the layer in which the light-emitting material is diffused is changed by changing the thickness of the second hole-generating layer 103. Accordingly, it becomes possible to control the color or the color purity of light emitted from the light-emitting element by adjusting the optical distance.

Claims

1. A light-emitting element comprising:

an anode and a cathode;
 a first layer (102) between the anode and the cathode, said first layer (102) generating holes;
 a second layer (103) between the anode and the cathode, said second layer (103) generating holes and contacting the cathode;
 a third layer (104) between the first layer (102) and the second layer (103), said third layer (104) including a light emitting material; and
 a fourth layer (105) between the second layer (103) and the third layer (104), said fourth layer (105) generating electrons.

2. The light-emitting element according to claim 1, wherein:

said first layer (102) including a first P-type semiconductor material;
 said second layer (103) including a second P-type semiconductor material; and
 said fourth layer (105) including an N-type semiconductor material.

3. The light-emitting element according to claim 2, wherein
 said first P-type semiconductor material; and
 said second P-type semiconductor material is the same material.

4. The light-emitting element according to Claim 2 or 3, wherein the first P-type semiconductor material and the second P-type semiconductor material are metal oxide.

5. The light-emitting element according to Claim 2, 3 or 4, wherein each of the first P-type semiconductor material and the second P-type semiconductor material is at least one compound selected from the group consisting of vanadium oxide, molybdenum oxide, cobalt oxide, and nickel oxide.

6. The light-emitting element according to Claim 2, 3, 4 or 5, wherein the N-type semiconductor material is metal oxide.

7. The light-emitting element according to any one of the claims 2 to 6, wherein the N-type semiconductor is at least one compound selected from the group consisting of zinc oxide, zinc sulfide, zinc selenide, and titanium oxide.

8. The light-emitting element according to claim 1, wherein
 said first layer (102) including a first organic compound and a first material having electron-accepting properties to the first organic compound;
 said second layer (103) including a second organic compound and a second material having electron-accepting properties to the second organic compound; and
 said fourth layer (105) including a fourth organic compound and a third material having electron-donating properties to the fourth organic compound.

9. The light-emitting element according to claim 8, wherein said first organic compound and said second organic compound is the same compound and the first material and the second material is the same material.

10. The light-emitting element according to Claim 8 or 9, wherein the fourth organic compound is an organic compound having electron-transporting properties.

11. The light-emitting element according to Claim 8, 9 or 10, wherein the third material include one of alkali metal, alkali-earth metal, and rare-earth metal.

12. The light-emitting element according to any one of the claims 8 to 11, wherein each of the first organic compound and the second organic compound is an organic compound having hole-transporting properties.

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13. The light-emitting element according to any one of the claims 8 to 12, wherein each of the first material and the second material is metal oxide.

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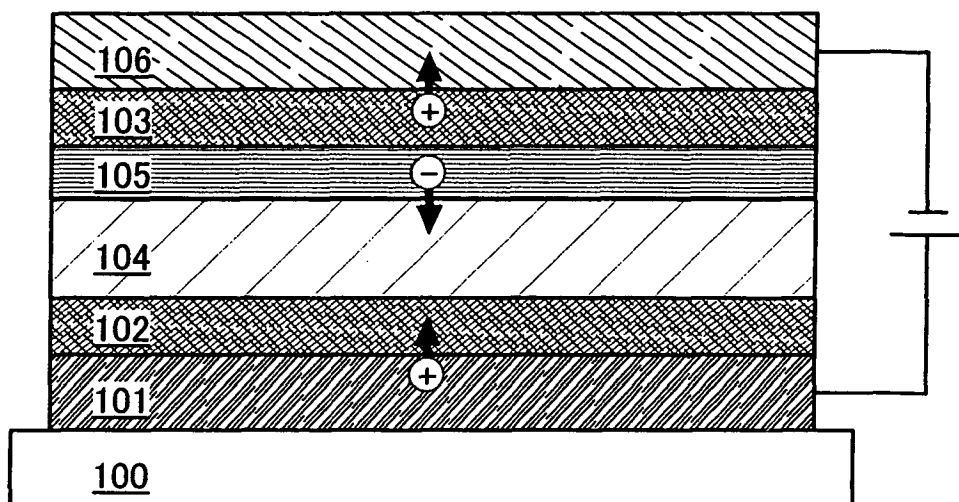


FIG. 1

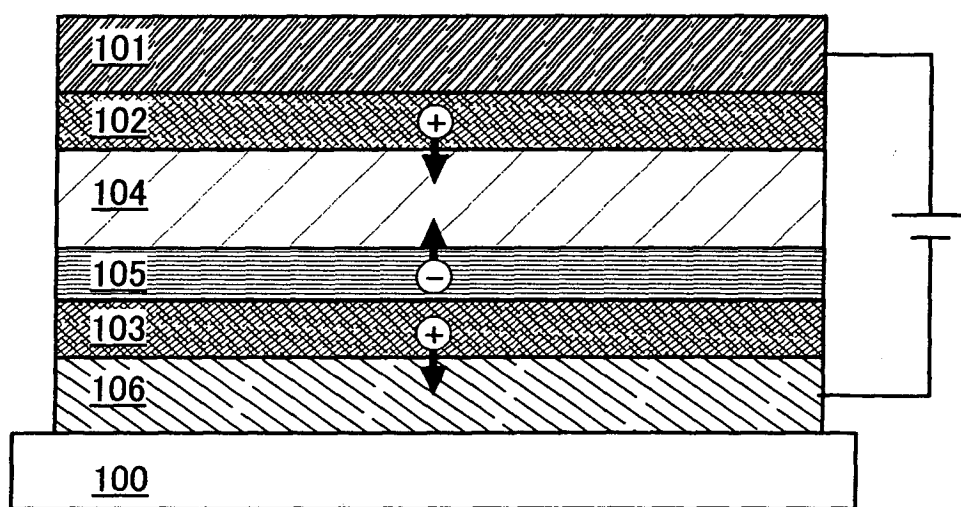


FIG. 2

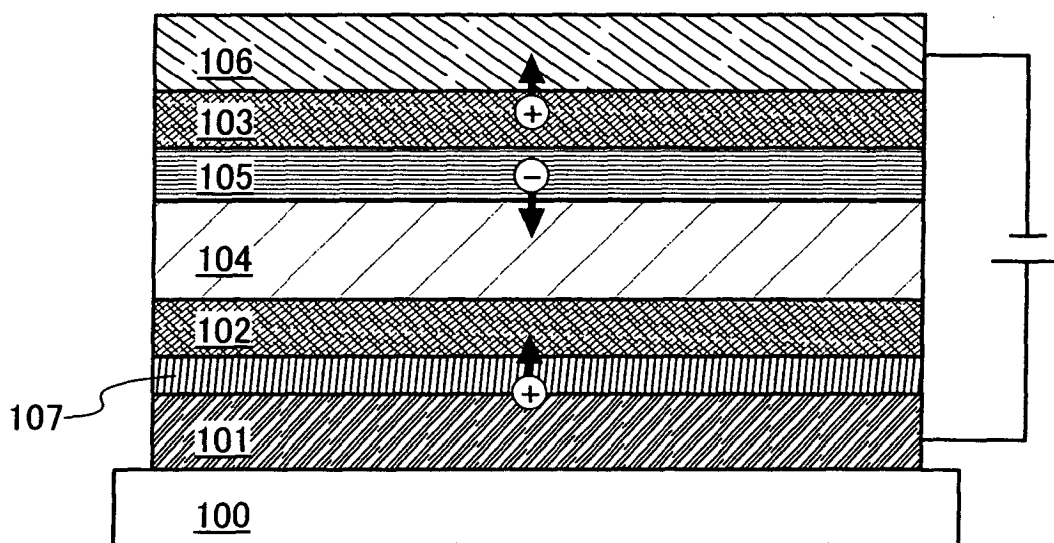


FIG. 3

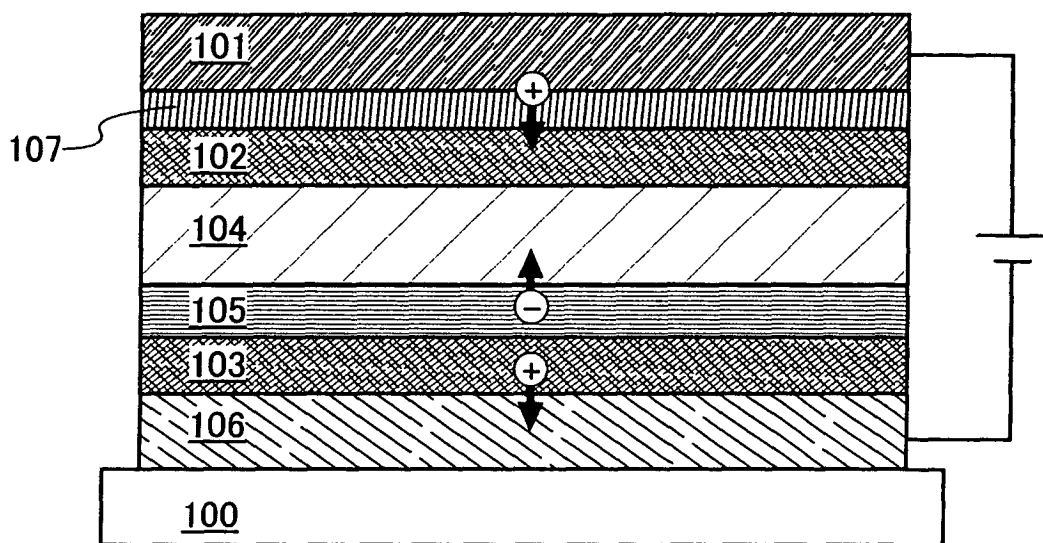


FIG. 4

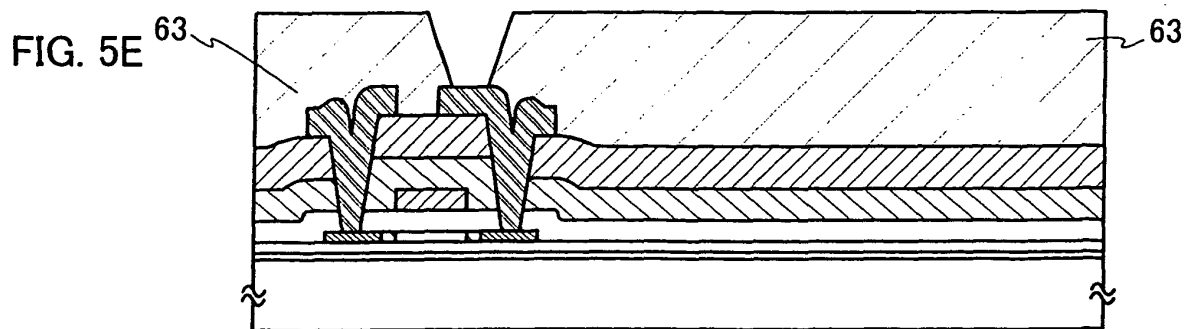
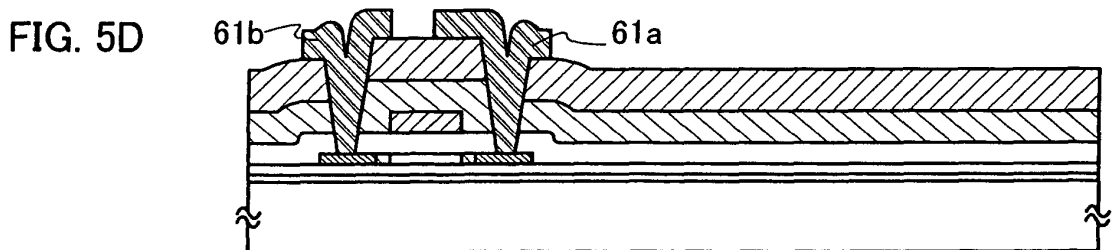
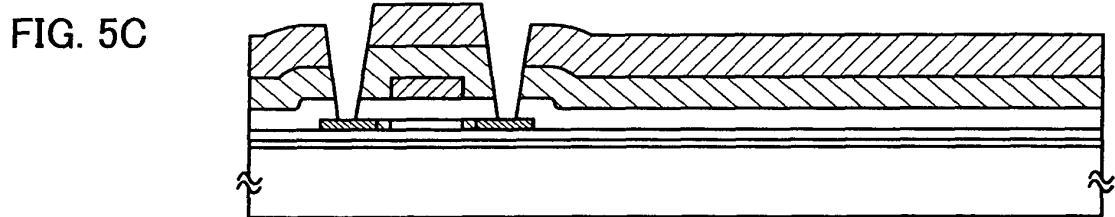
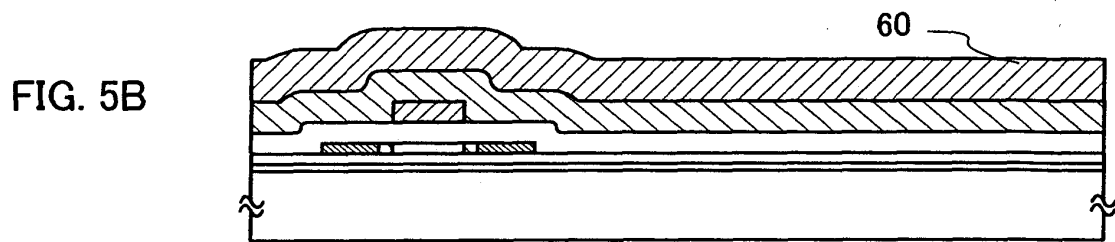
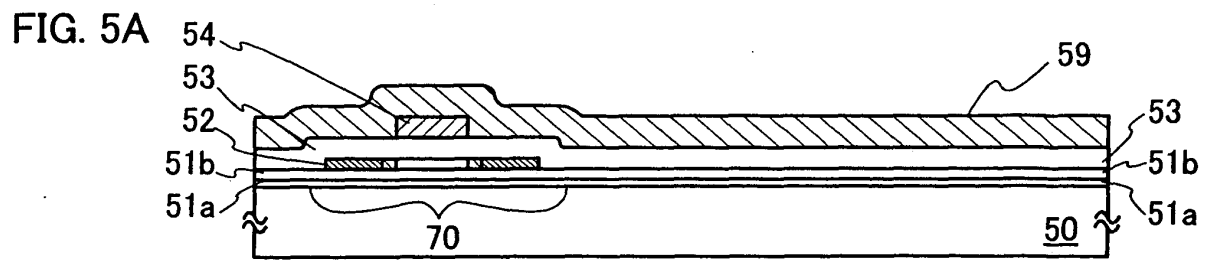


FIG. 6A

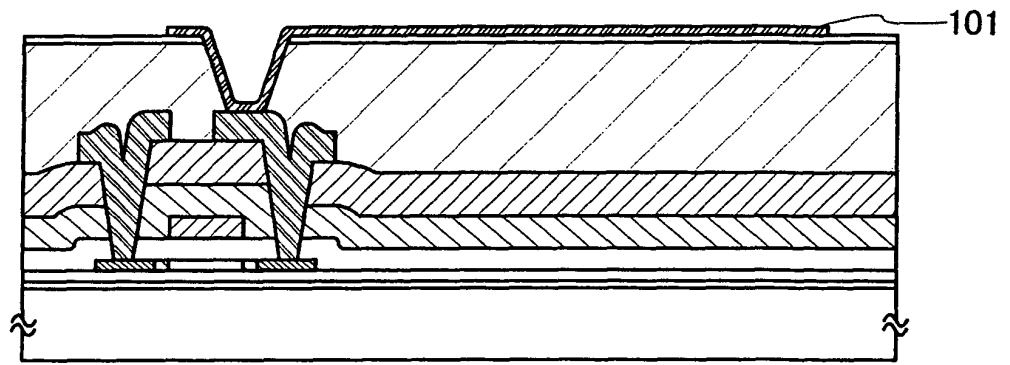


FIG. 6B

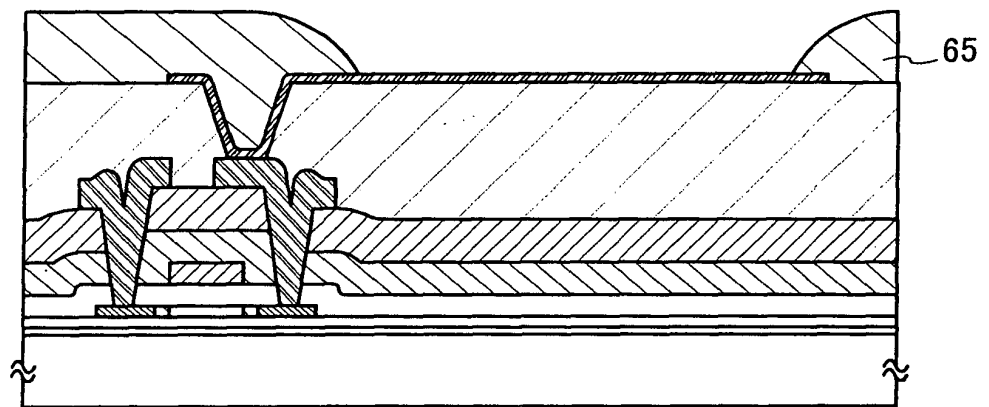


FIG. 6C

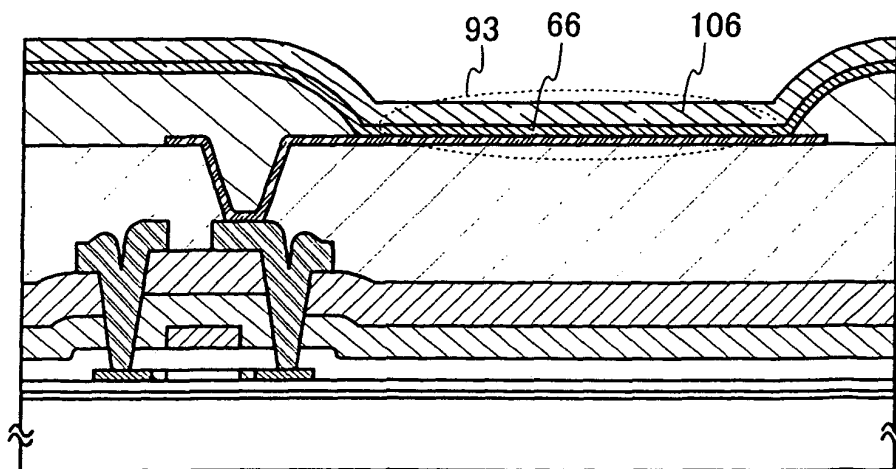


FIG. 7A

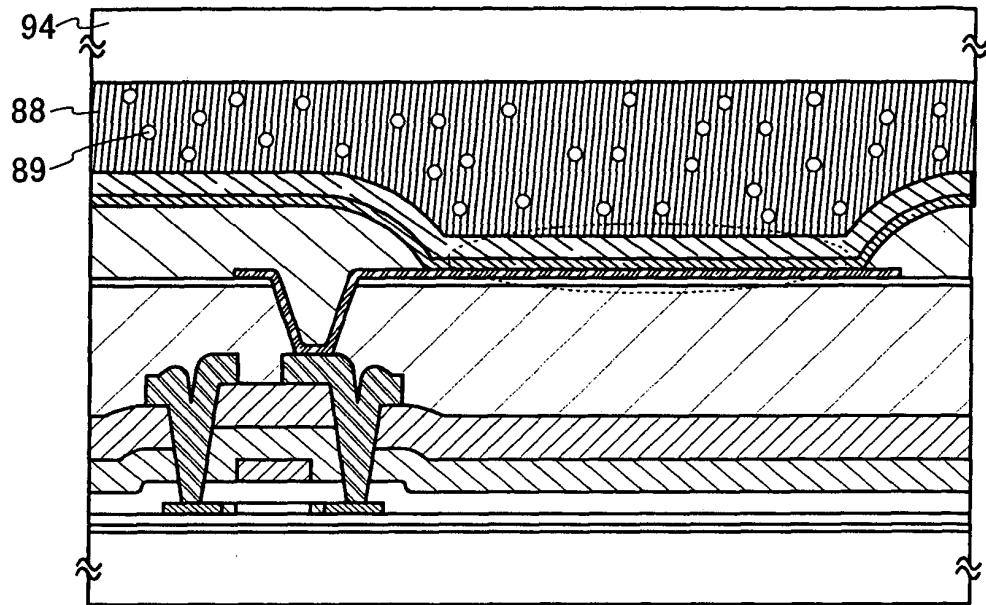


FIG. 7B

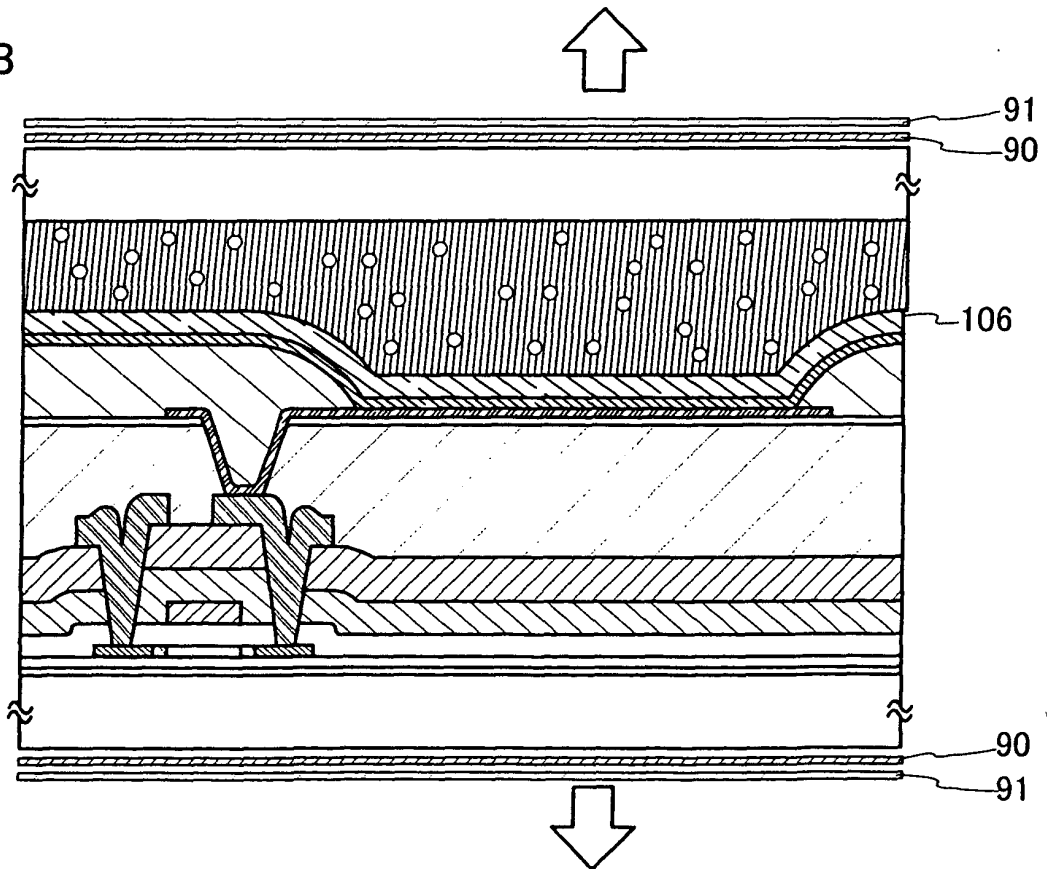


FIG. 8A

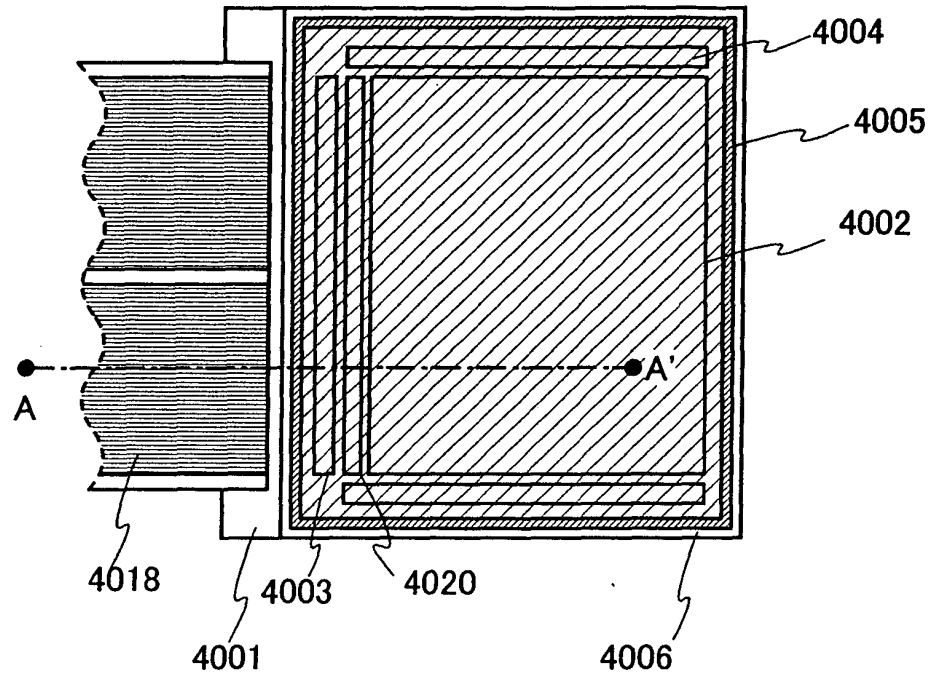


FIG. 8B

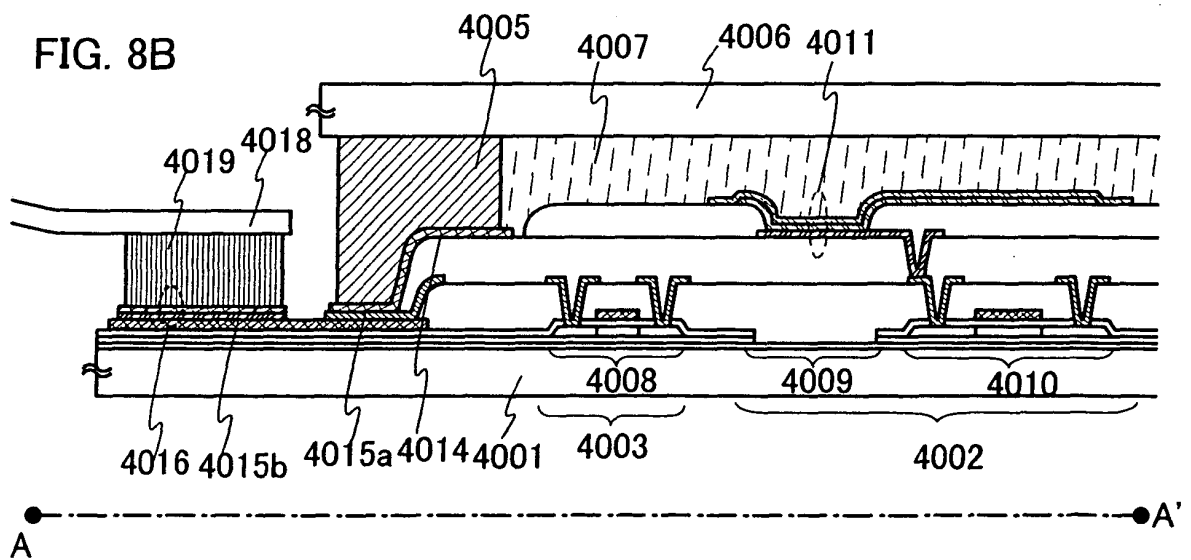


FIG. 9A

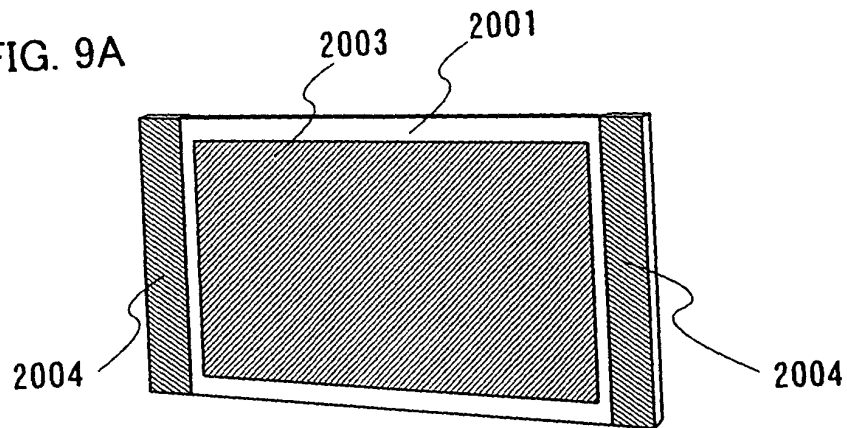


FIG. 9B

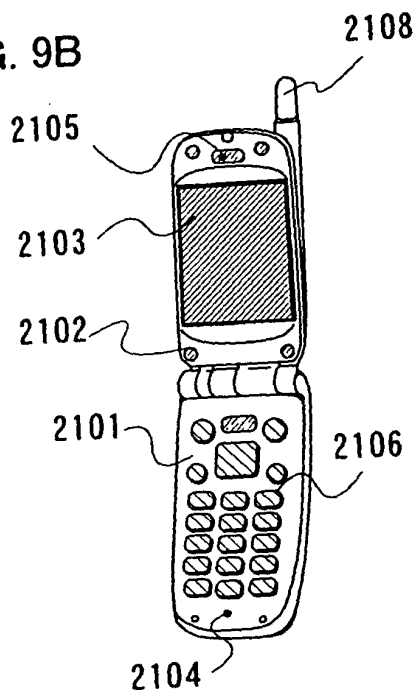


FIG. 9C

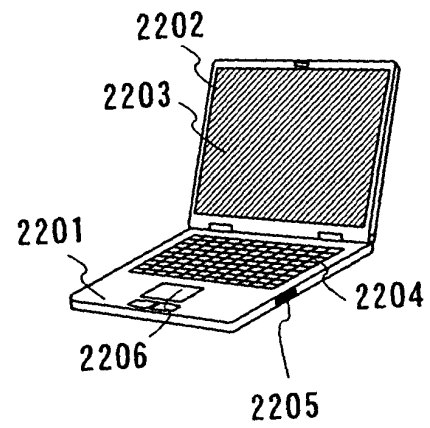


FIG. 9D

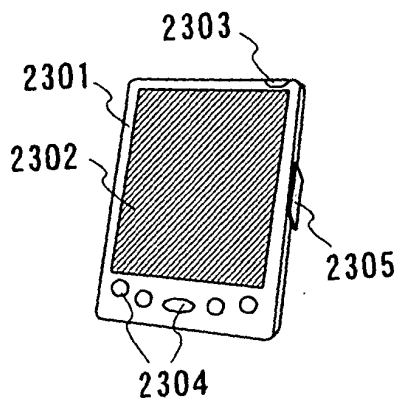


FIG. 9E

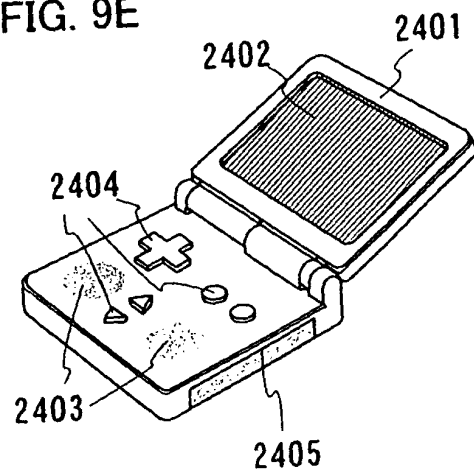


FIG. 10A

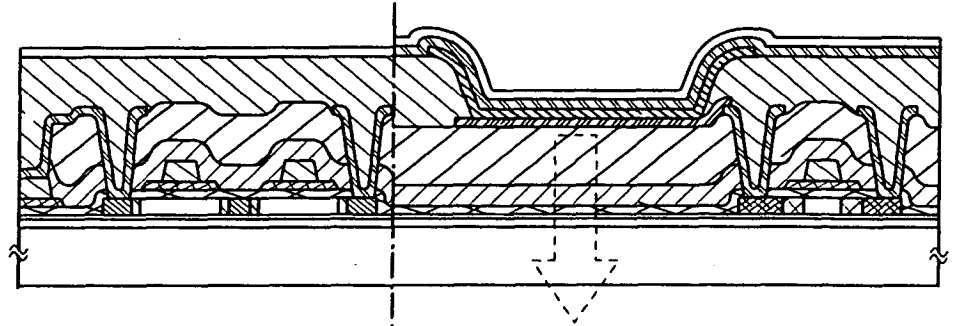


FIG. 10B

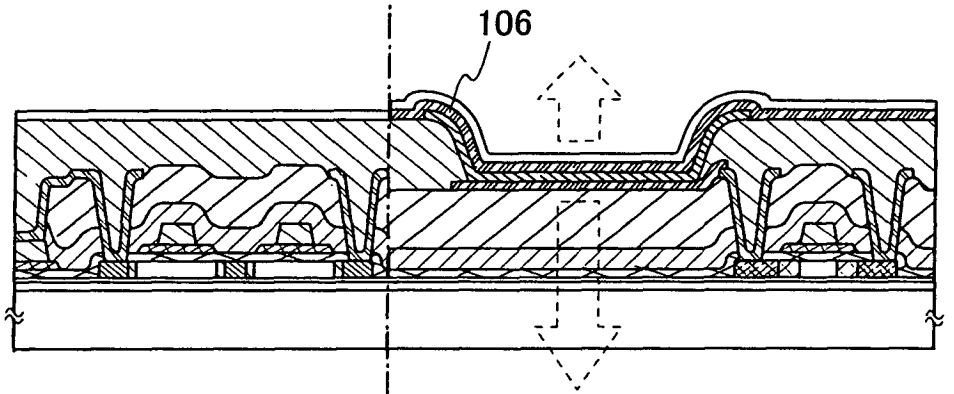


FIG. 10C

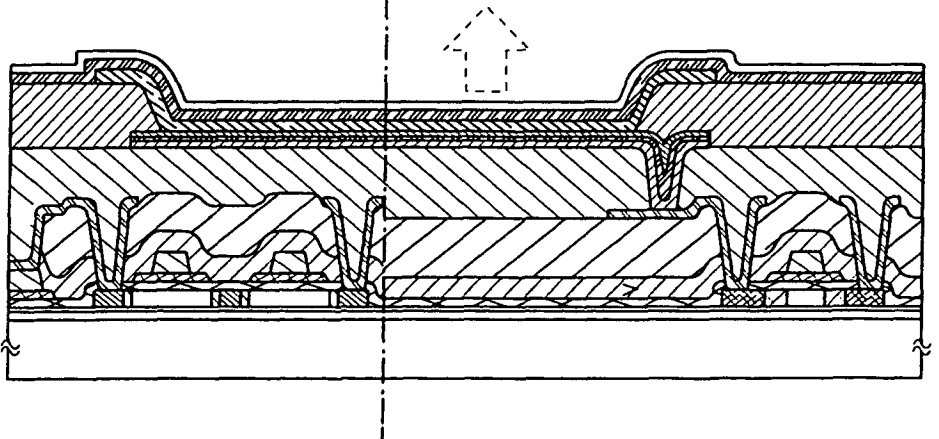


FIG. 11A

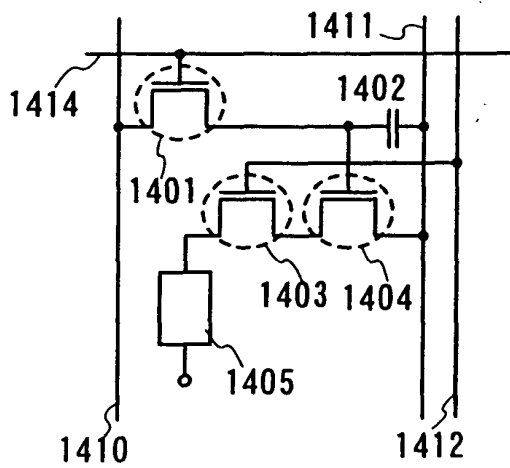


FIG. 11B

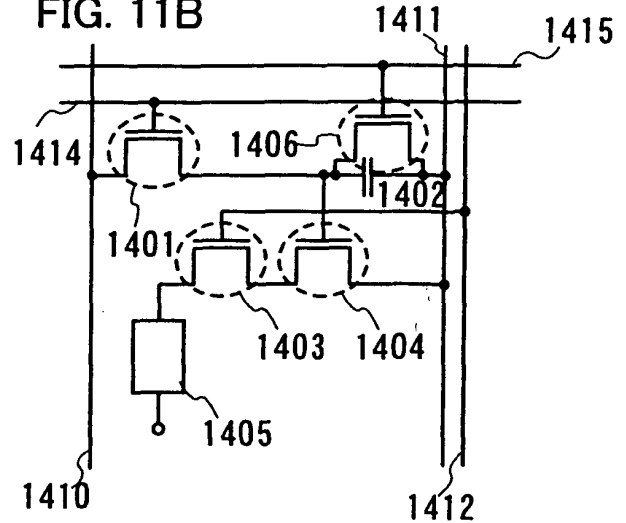


FIG. 11C

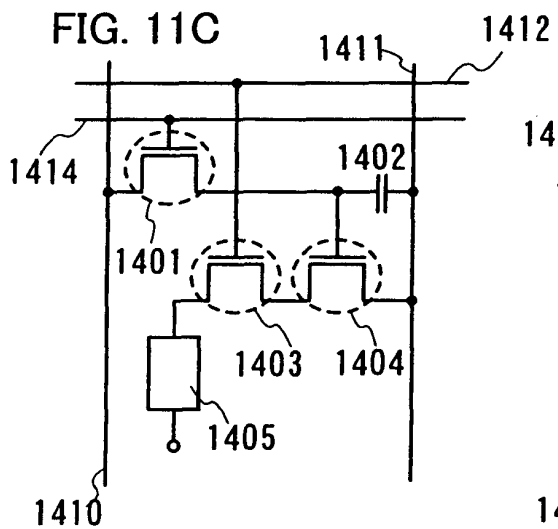


FIG. 11D

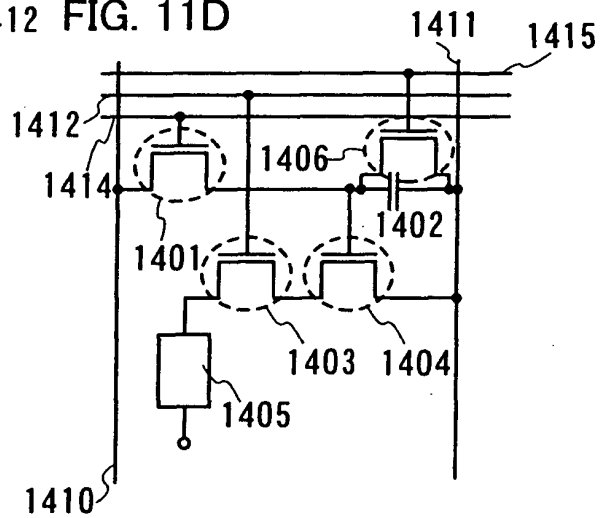


FIG. 11E

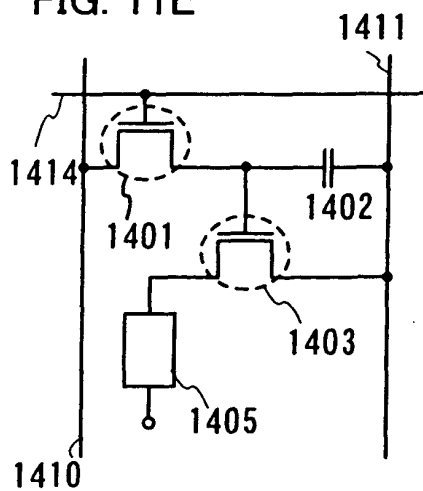
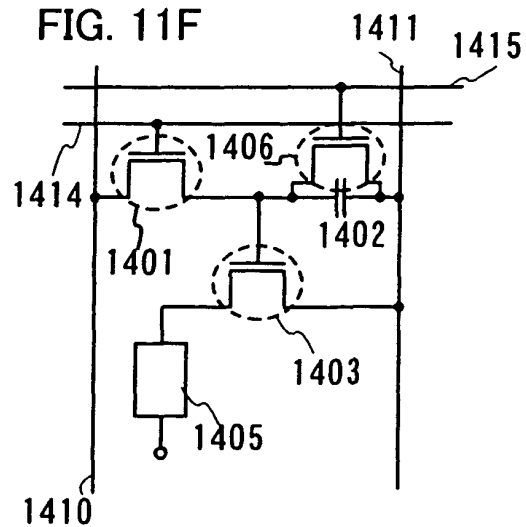


FIG. 11F



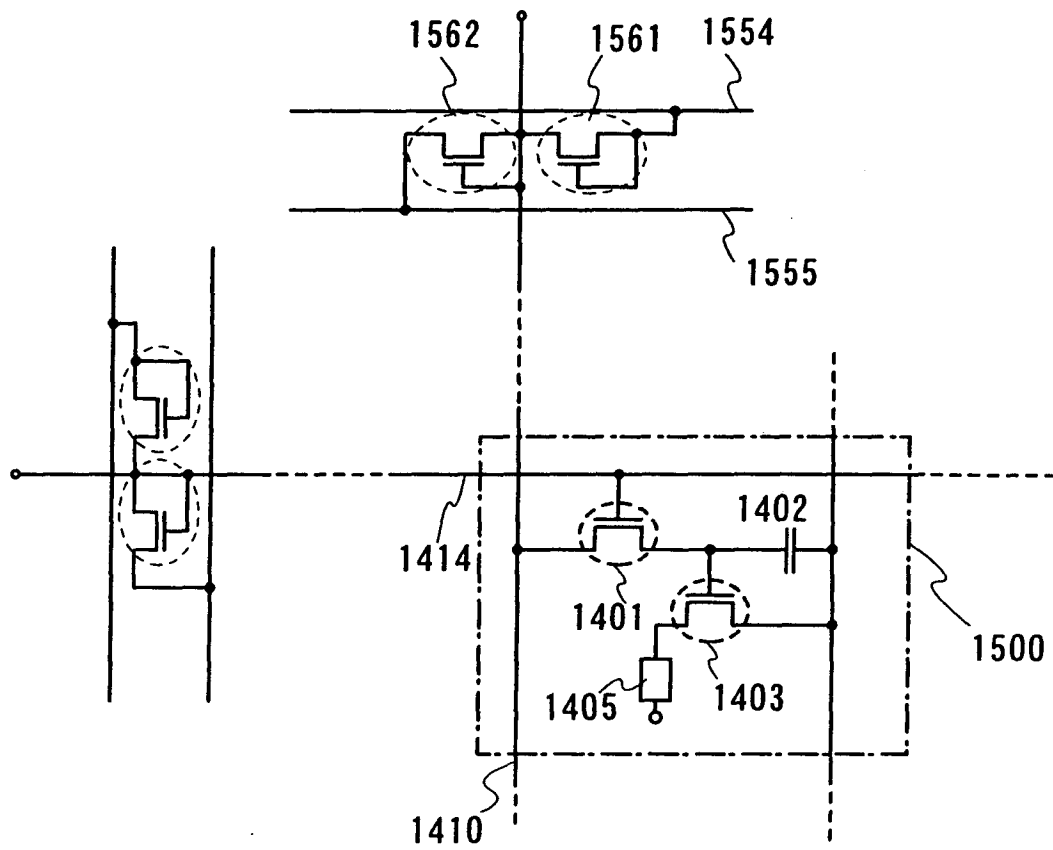


FIG. 12

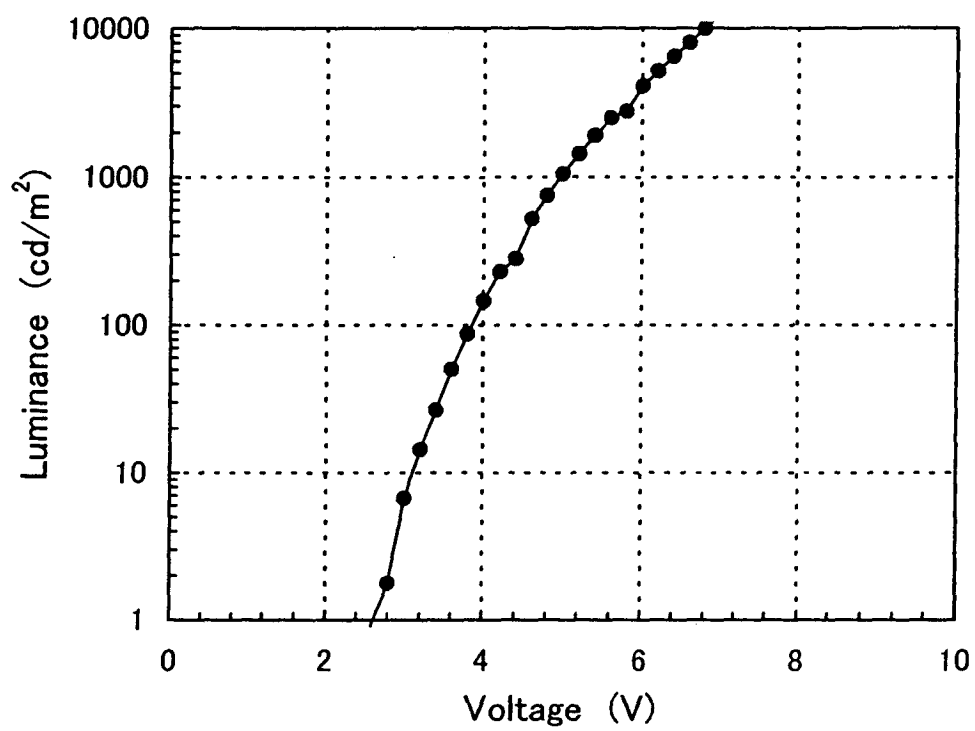


FIG. 13

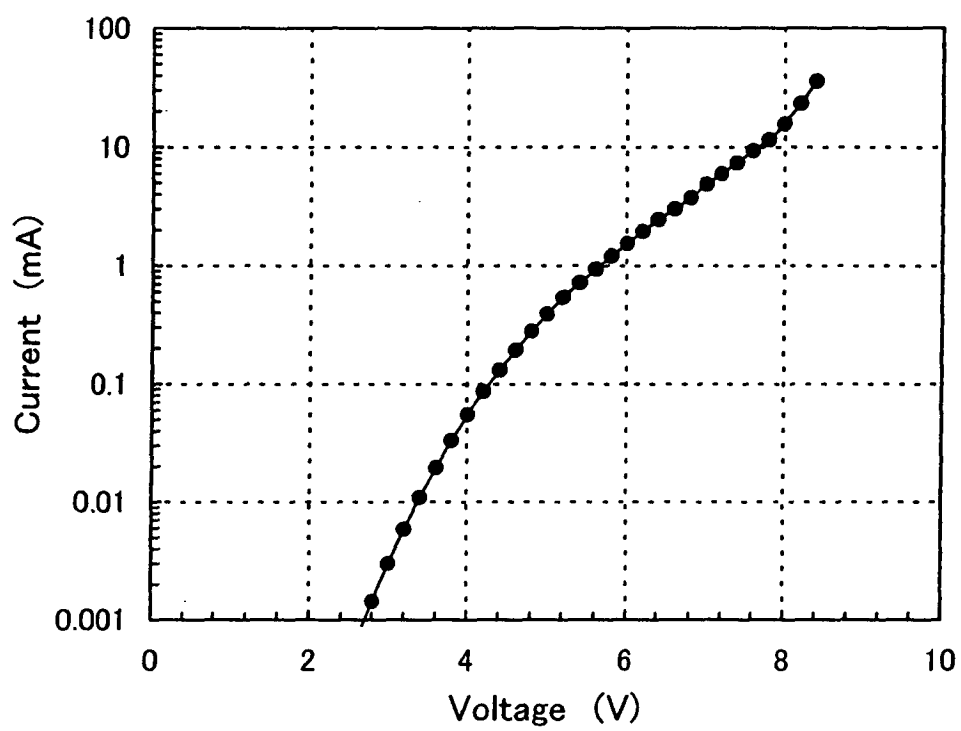


FIG. 14

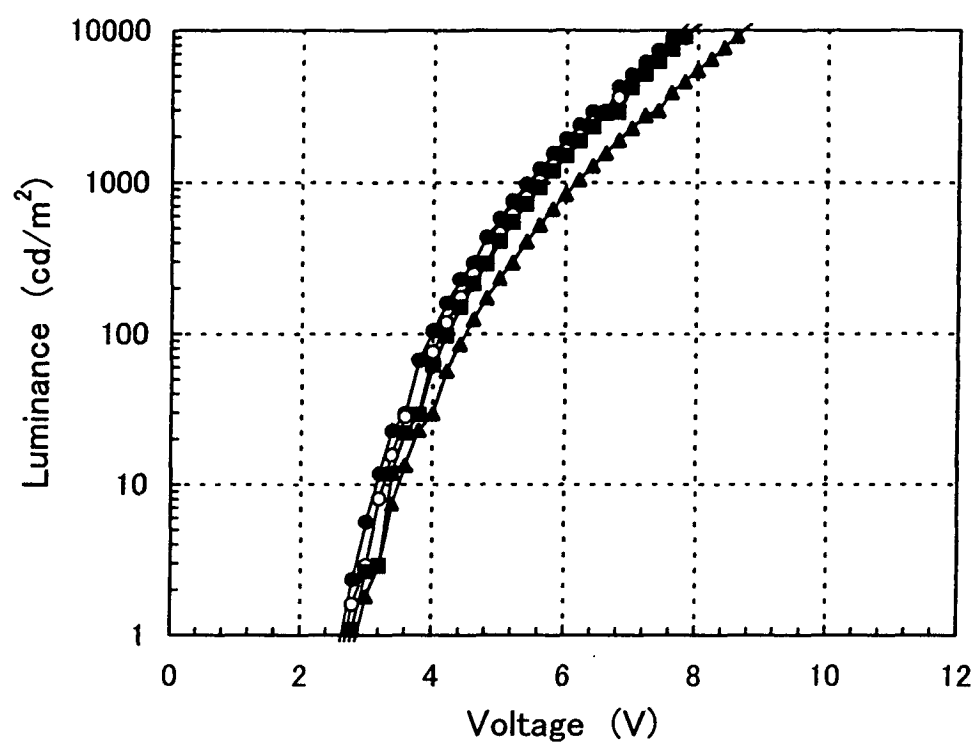


FIG. 15

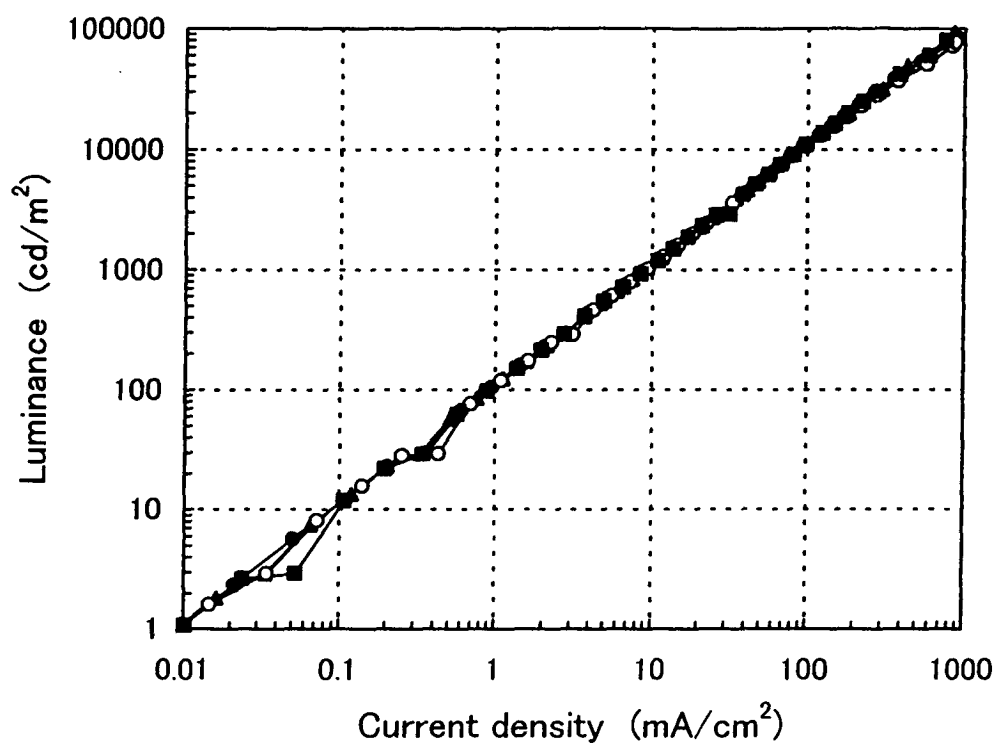


FIG. 16

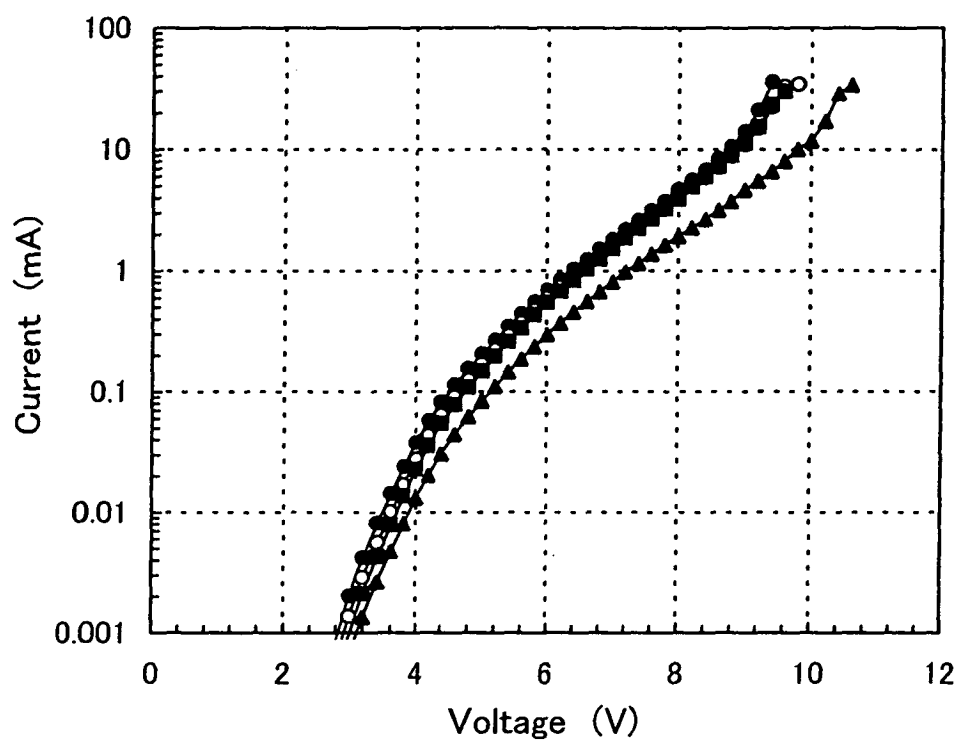


FIG. 17

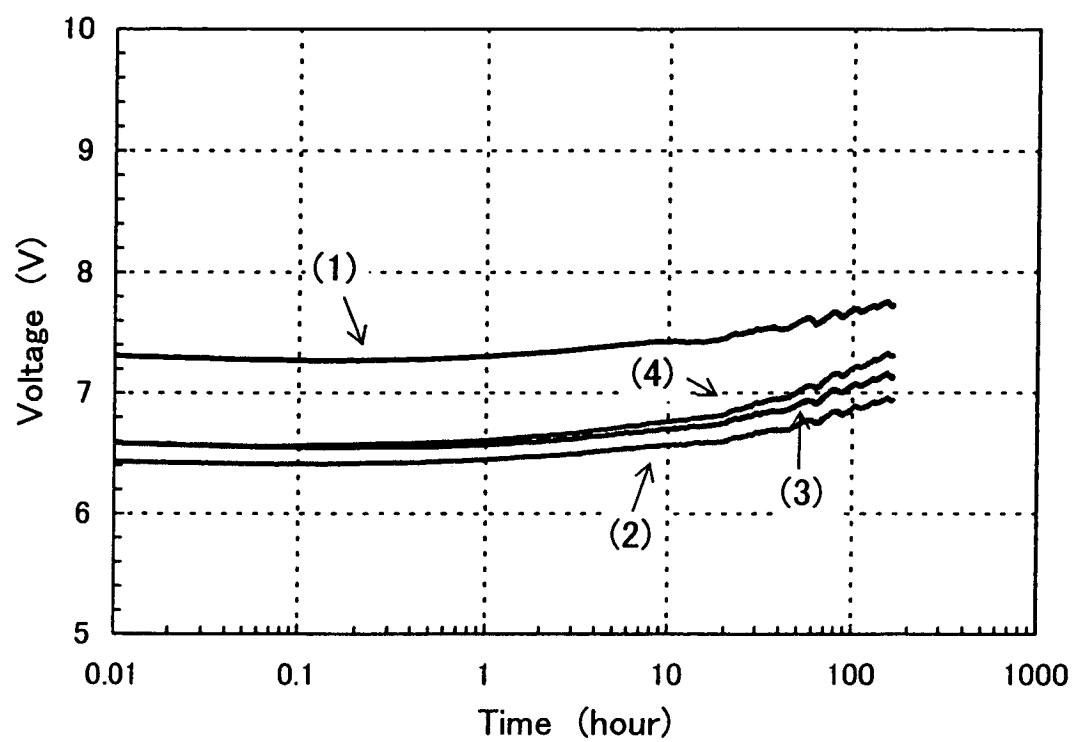


FIG. 18

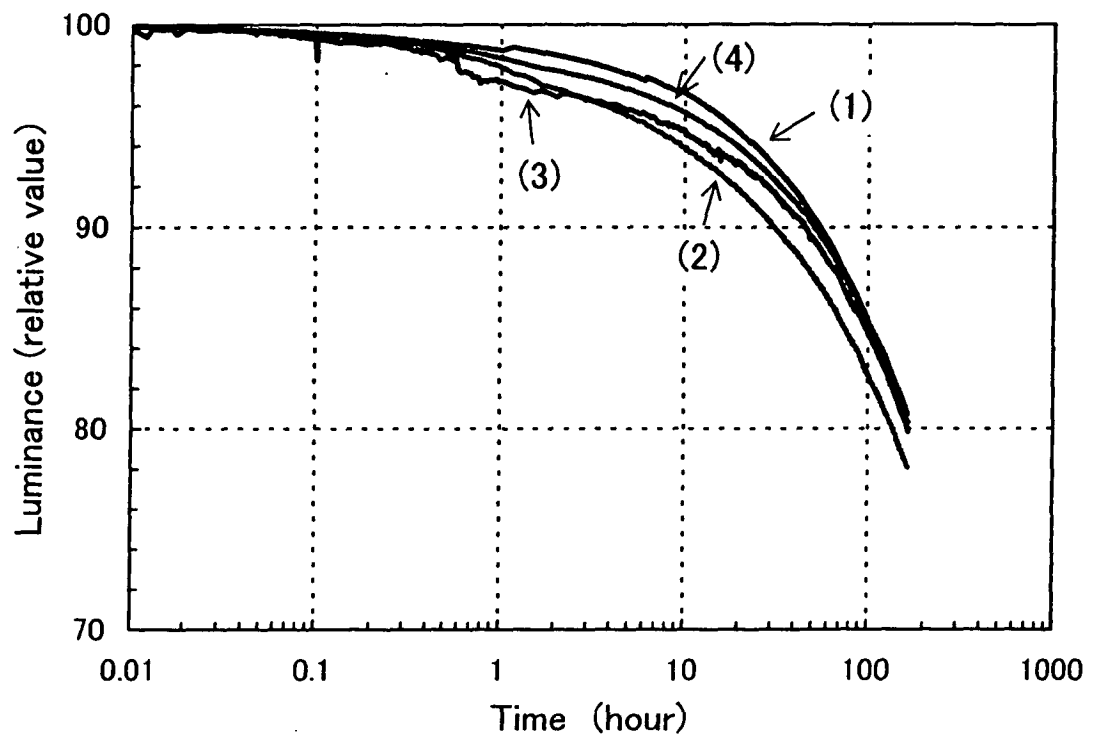


FIG. 19

FIG. 20

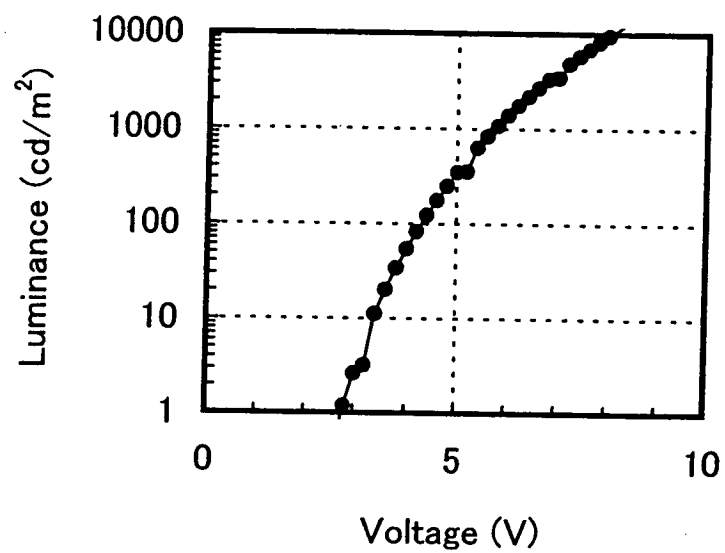


FIG. 21

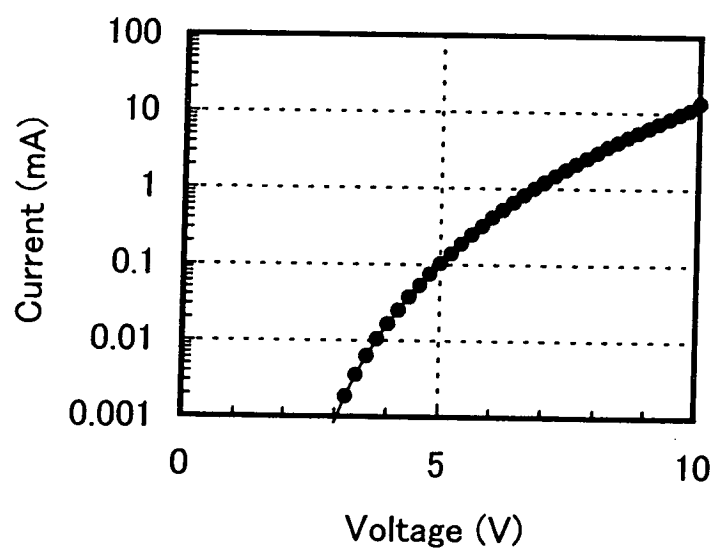


FIG. 22A

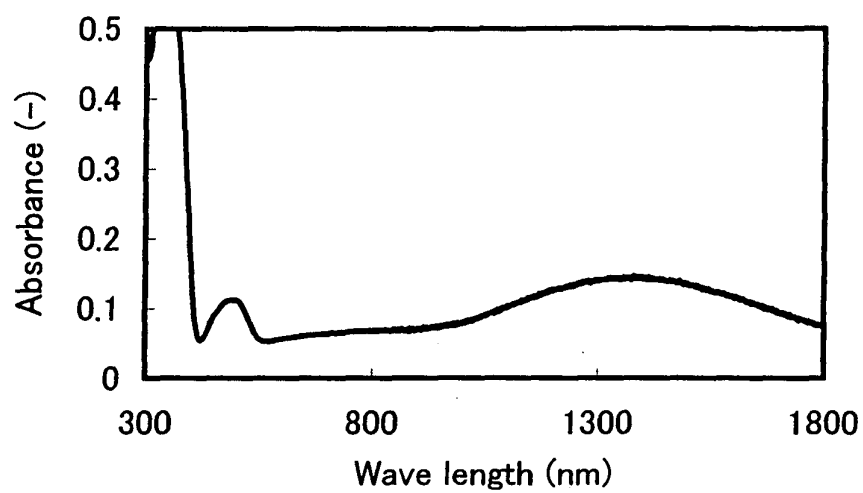


FIG. 22B

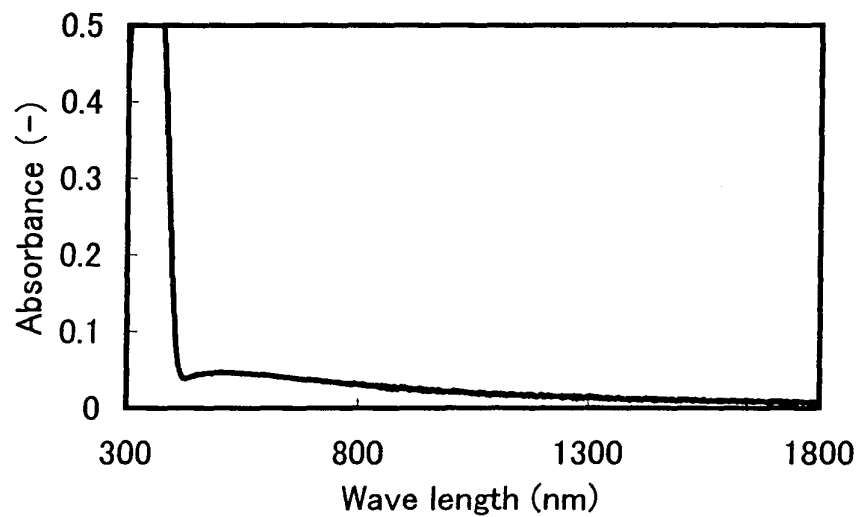


FIG. 22C

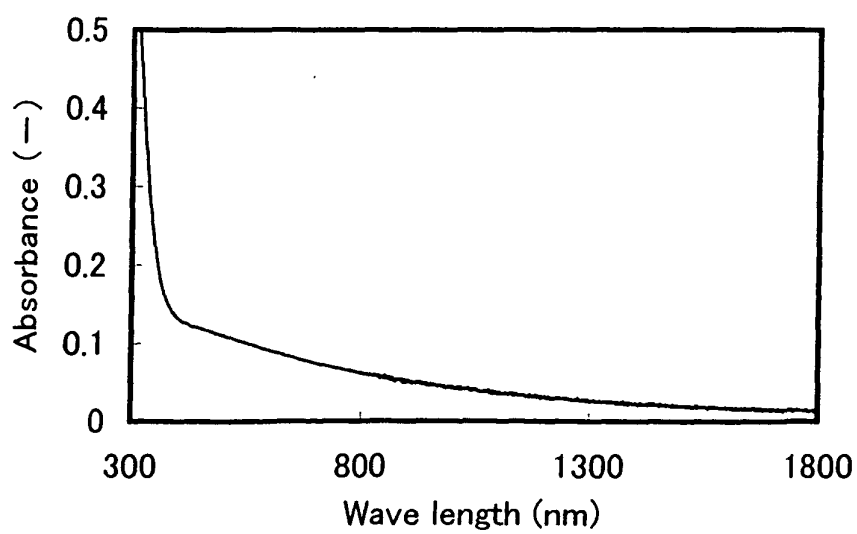


FIG. 23A

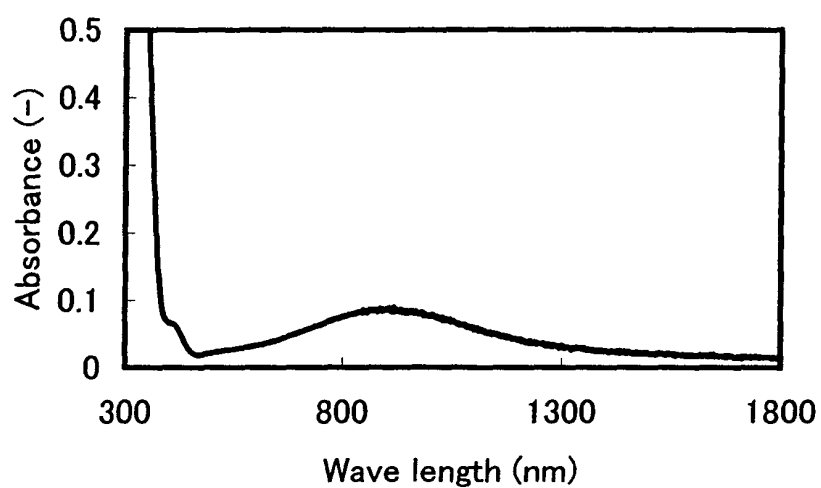


FIG. 23B

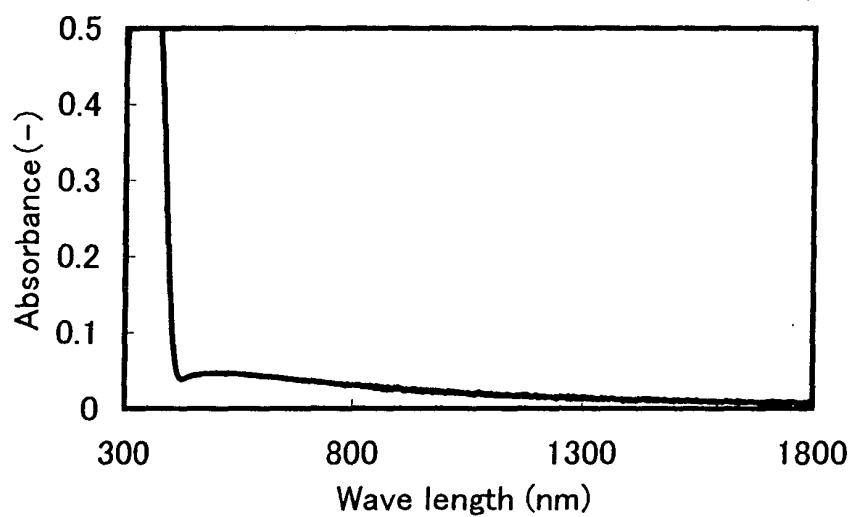


FIG. 23C

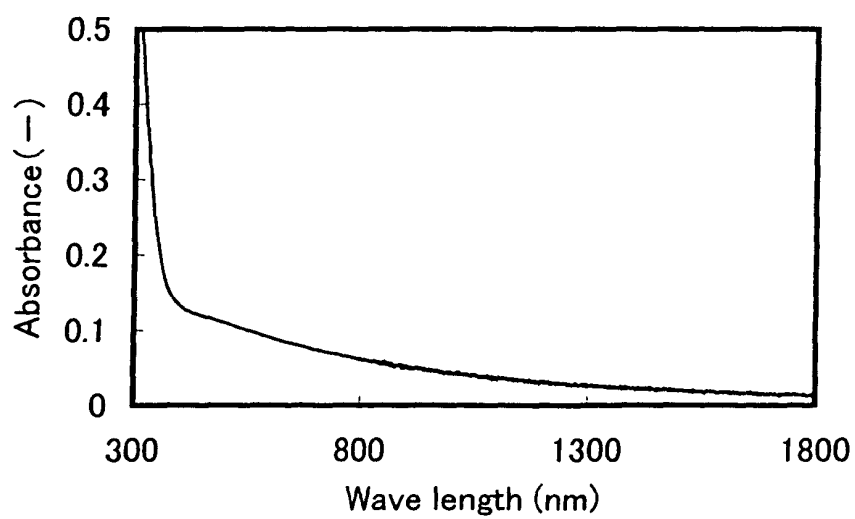


FIG. 24

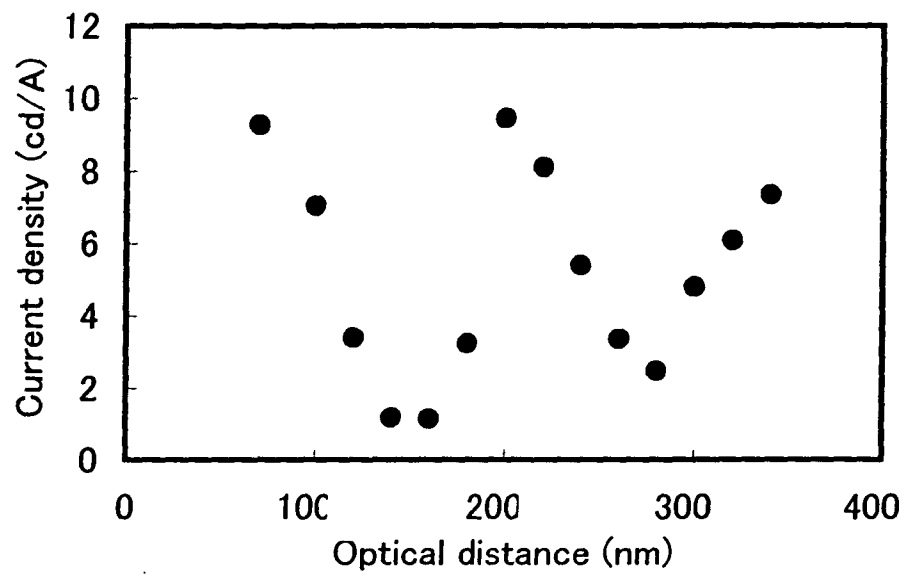
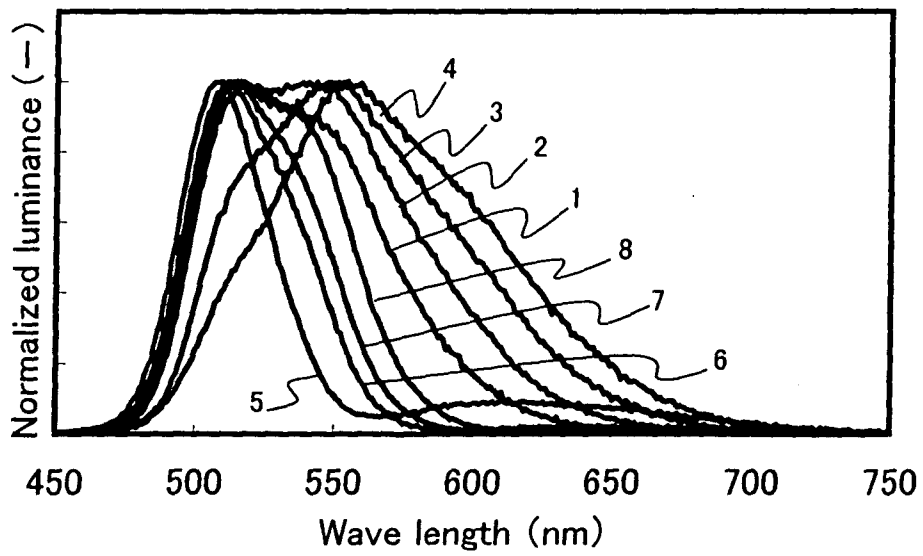


FIG. 25



专利名称(译)	发光元件，显示装置和电子设备		
公开(公告)号	EP1624502A2	公开(公告)日	2006-02-08
申请号	EP2005016696	申请日	2005-08-01
[标]申请(专利权)人(译)	株式会社半导体能源研究所		
申请(专利权)人(译)	半导体能源研究所有限公司.		
当前申请(专利权)人(译)	半导体能源研究所有限公司.		
[标]发明人	KUMAKI DAISUKE SEO SATOSHI C OSEMICON ENERGY LAB CO LTD		
发明人	KUMAKI, DAISUKE SEO, SATOSHI C/OSEMICONDUCTOR ENERGY LAB. CO., LTD		
IPC分类号	H01L51/50 H01L27/32		
CPC分类号	H01L51/5076 H01L27/3244 H01L51/5056 H01L51/506 H01L51/5068 H01L51/5072 H01L2251/558		
优先权	2004227734 2004-08-04 JP		
其他公开文献	EP1624502B1 EP1624502A3		
外部链接	Espacenet		

摘要(译)

本发明提供一种发光元件，其具有驱动电压相对较低的结构，以及驱动电压随时间的增加小的发光元件。此外，本发明提供一种显示装置，其中驱动电压和驱动电压随时间的增加小并且可以抵抗长期使用。与发光元件中的电极接触的层是包含P型半导体的层或诸如包含具有电子接受性质的材料的有机化合物层的空穴产生层。发光层（104）夹在空穴发生层（102,103）之间，电子发生层（105）夹在发光层（104）和阴极侧的空穴发生层之间（103）。

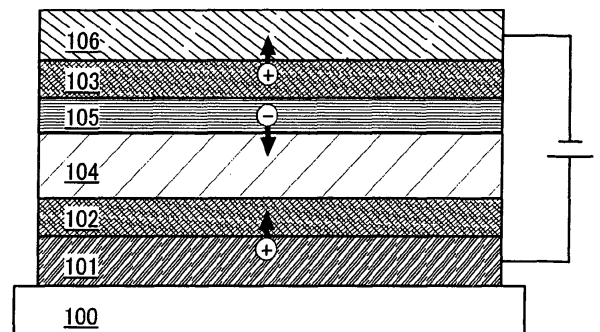


FIG. 1