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(54) **Method of manufacturing cold cathode field emission device and method of manufacturing cold cathode field emission display**

(57) A method of manufacturing a cold cathode field emission device, which comprises the steps of;

- (A) forming a cathode electrode (11) on a support (10),
- (B) forming an insulating layer (12) on the cathode electrode (11) and the support (10),
- (C) forming a gate electrode (13A) on the insulating layer (12),
- (D) forming an opening portion (14) having a bottom portion where the cathode electrode (11) is ex-

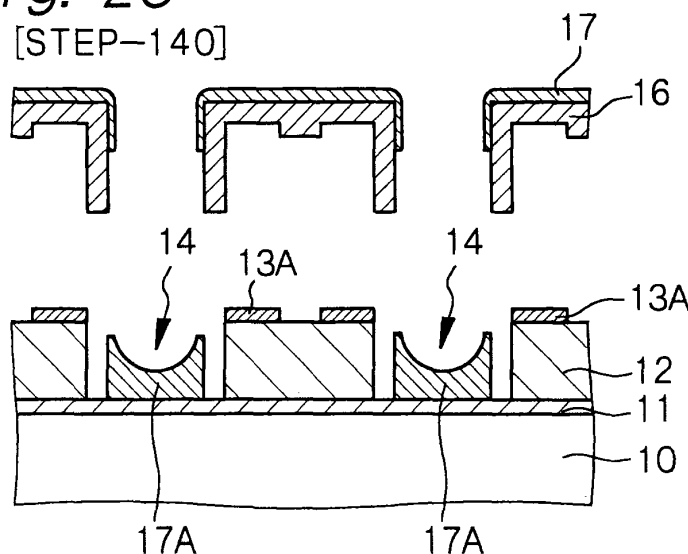
posed, at least in the insulating layer (12),

(E) forming an electron emitting electrode composed of an electric conductive composite (17) containing electric conductive particles and a binder on the cathode electrode (11) exposed in the bottom portion of the opening portion (14), and

(F) removing the binder in a surface layer portion of the electron emitting electrode to expose the electric conductive particles on the surface of the electron emitting electrode (17A).

*Fig. 2C*

[STEP-140]



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## Description

## BACKGROUND OF THE INVENTION AND RELATED ART STATEMENT

5 [0001] The present invention relates to a method of manufacturing a cold cathode field emission device and a method of manufacturing a cold cathode field emission display into which such cold cathode field emission devices are incorporated.

10 [0002] When an electric field having a strength equal to, or greater than, a certain threshold value is applied to a metal or a semiconductor placed in vacuum, electrons pass through a thin energy barrier in the vicinity of the surface of the metal or the semiconductor due to a quantum tunnel effect and are emitted into the vacuum at an ordinary (room) temperature. Electron emission based on the above principle is called "cold cathode electric field electron emission" or "field emission". In recent years, there is proposed a flat type cold cathode field emission display in which the above field emission principle is applied to image displaying, a so-called field emission display (FED), and it is expected to be an image display which can supersede a conventional cathode ray tube (CRT), since it advantageously has a high

15 brightness and attains a low power consumption.  
[0003] A cold cathode field emission display (to be sometimes simply referred to as "display" hereinafter) generally has a structure in which a cathode panel having electron emitting portions corresponding to pixels disposed in the form of a two-dimensional matrix and an anode panel having a fluorescence layer which is excited by collision with electrons emitted from the electron emitting portion to emit light are disposed to be opposed to each other with a high vacuum layer therebetween. In each of the electron emitting portions on the cathode panel, generally, a plurality of electron emitting electrodes are formed, and further, gate electrodes are also formed for extracting electrons from the electron emitting electrodes. A portion having the electron emitting electrode and the gate electrode constitutes a cold cathode field emission device, and will be simply referred to as an electron emitting device.

20 [0004] For obtaining a high electron emission current at a low driving voltage in the above display structure, for example, it is required to sharpen the tip portion of the electron emitting electrode constituting the electron emitting device, it is required to shrink the size of the electron emitting electrode to increase the existing density of electron emitting electrodes in one electron emitting portion corresponding to one pixel, and it is required to decrease the distance from the tip portion of the electron emitting electrode to the edge portion of the gate electrode. For satisfying these requirements, electron emitting devices having various constitutions have been so far proposed.

25 [0005] As one typical example of the above conventional electron emitting devices, there is known a so-called Spindt-type electron emitting device having an electron emitting electrode composed of a conical conductive material. Fig. 10 shows a conceptual view of a display in which the above Spindt-type electron emitting device is incorporated. This display has a cathode electrode 41 formed on a support 40, an insulating layer 42 formed on the cathode electrode 41 and the support 40, a gate electrode 43 formed on the insulating layer 42, an opening portion 44 formed in the gate electrode 43 and the insulating layer 42, and a conical electron emitting electrode 45 formed inside the opening portion 44. A predetermined number of the electron emitting electrode 45 are arranged in the form of a two-dimensional matrix and constitute one pixel. The anode panel has a structure in which a fluorescence layer 52 having a predetermined pattern is formed on a substrate 50 and the fluorescence layer 52 is covered with an anode electrode 51.

30 [0006] When a voltage is applied between the electron emitting electrode 45 and the gate electrode 43, an electric field is generated, and electrons  $e^-$  are extracted from the tip portion of the electron emitting electrode 45 due to the generated field. The electrons  $e^-$  are attracted to the anode electrode 51 of the anode panel and collide with the fluorescence layer 52 which is a light-emitting layer formed between the anode electrode 51 and the substrate 50. As a result, the fluorescence layer 52 is excited to emit light, and a desired image can be obtained. The action of the above electron emitting device is, in principle, controlled by the voltage applied to the gate electrode 43.

35 [0007] The outline of the method of manufacturing the above Spindt-type electron emitting device will be explained with reference Figs. 11A, 11B, 12A and 12B hereinafter. In principle, this method is a method of forming the conical electron emitting electrode 45 by vertical deposition of a metal material. That is, vaporized particles perpendicularly enter the opening portion 44. The amount of the vaporized particles which reach the bottom of the opening portion 44 is gradually decreased by utilizing the shielding effect of an overhanging deposit formed around an opening end portion of the opening portion 44, so that the electron emitting electrode 45 as a conical deposit is formed in a self-aligned manner. This embodiment employs a method of pre-forming a pre-off layer 46 on the gate electrode 43 and the insulating layer 42 for easing the removal of the unnecessary overhanging deposit, and the method will be explained below.

40 [Step-10]

45 [0008] First, the cathode electrode 41 composed of niobium (Nb) is formed on the support 40 made, for example, of glass, and the insulating layer composed of  $\text{SiO}_2$ , the gate electrode 43 composed of a conductive material are consecutively formed thereon. Then, the gate electrode 43 and the insulating layer 42 are patterned to form the opening

portion 44 (see Fig. 11A). This patterning is carried out by forming a resist mask according to a general photolithographic method and carrying out dry-etching through the resist mask.

[Step-20]

[0009] Then, aluminum is obliquely vapor-deposited on the support 40 to form the peel-off layer 46. In this case, the incidence angle of the vaporized particles to a normal of the support 40 is set at a fully large angle, whereby the peel-off layer 46 can be formed on the gate electrode 43 and the insulating layer 42 almost without depositing aluminum in the bottom of the opening portion 44. The peel-off layer 46 extends from the opening end portion of the opening portion 44 so as to form eaves, and the opening portion 44 is therefore substantially decreased in diameter (see Fig. 11B).

[Step-30]

[0010] Then, for example, molybdenum (Mo) is vertically vapor-deposited on the entire surface. In this case, as an electric conductive material layer 45A having an overhanging form grows on the peel-off layer 46, the substantial diameter of the opening portion 44 is decreased, so that the vaporized particles which contributes to deposition on the bottom of the opening portion 44 gradually come to be limited to particles passing the center of the opening portion 44. As a result, a conical deposit is formed on the bottom of the opening portion 44 as shown in Fig. 12A, and the conical deposit constitutes the electron emitting electrode 45.

[Step-40]

[0011] Then, the peel-off layer 46 is peeled off from the surface of the gate electrode 43 and the insulating layer 42 by an electrochemical process and a wet process, and the electric conductive material layer 45A above the gate electrode 43 and the insulating layer 42 is selectively removed (see Fig. 12B).

[0012] The electron emitting characteristic of the electron emitting device structured as shown in Fig. 12B depends greatly upon a distance from an edge portion 43A of the gate electrode 43, i.e., a top end portion of the opening portion 44, to the tip portion of the electron emitting electrode 45. This distance is generally on the order of sub-microns and is greatly dependent upon the forming accuracy and diameter dimensional accuracy of the opening portion 44, the thickness accuracy of the electric conductive material layer 45A formed in [Step-30] and the forming accuracy of the peel-off layer 46 which constitutes a substratum for the electric conductive material layer 45A. However, it is very difficult to form the electric conductive material layer 45A having a uniform thickness on the entire surface of a large-area support by vertical vapor deposition, and it is very difficult to form the peel-off layer 46 having the uniformly-dimensioned form of eaves by oblique vapor deposition. In-plane fluctuation and fluctuation among lots are therefore inevitable to some extent. The above fluctuation causes fluctuation in the image display characteristic of a display, for example, brightness of display images. Further, there are other problems that a large-scale vapor deposition apparatus is required, that a through-put is decreased, and that a residue of the peel-off layer 46 remaining after removal of the peel-off layer 46 formed on a large area contaminates the cathode panel, so that the yield of displays is decreased.

[0013] For obtaining a practical brightness of a display, the existing density of the electron emitting electrodes comes to the order of 10000/mm<sup>2</sup>, and with a decrease in dimensions per electron emitting electrode, the formation thereof tends to use semiconductor processes in many cases. The use of semiconductor processes in many cases inevitably involves the problems of a decrease in throughput and an increase in production cost.

## OBJECT AND SUMMARY OF THE INVENTION

[0014] It is therefore an object of the present invention to provide a method of manufacturing a cold cathode field emission device which method enables uniform and easy formation of an electron emitting electrode having a high electron emitting efficiency and a method of manufacturing a cold cathode field emission display into which the cold cathode field emission devices are incorporated

[0015] According to the present invention, the above object of the present invention is achieved by a method of manufacturing a cold cathode field emission device, which comprises the steps of;

- (A) forming a cathode electrode on a support,
- (B) forming an insulating layer on the cathode electrode and the support,
- (C) forming a gate electrode on the insulating layer,
- (D) forming an opening portion having a bottom portion where the cathode electrode is exposed, at least in the insulating layer,
- (E) forming an electron emitting electrode composed of an electric conductive composite containing electric con-

ductive particles and a binder on the cathode electrode exposed in the bottom portion of the opening portion, and (F) removing the binder in a surface layer portion of the electron emitting electrode to expose the electric conductive particles on the surface of the electron emitting electrode.

**[0016]** According to the present invention, the above object of the present invention is also achieved by a method of manufacturing a cold cathode field emission display into which the cold cathode field emission devices of the present invention are incorporated. That is, the method of manufacturing a cold cathode field emission display comprises arranging a substrate on which an anode electrode and a fluorescence layer are formed and a support on which cold cathode field emission devices are formed such that the fluorescence layer and the cold cathode field emission devices are opposed to each other, and bonding the substrate and the support in their marginal portions, wherein each of the cold cathode field emission devices is manufactured through steps of;

- (A) forming a cathode electrode on the support,
- (B) forming an insulating layer on the cathode electrode and the support,
- (C) forming a gate electrode on the insulating layer,
- (D) forming an opening portion having a bottom portion where the cathode electrode is exposed, at least in the insulating layer,
- (E) forming an electron emitting electrode composed of an electric conductive composite containing electric conductive particles and a binder on the cathode electrode exposed in the bottom portion of the opening portion, and
- (F) removing the binder in a surface layer portion of the electron emitting electrode to expose the electric conductive particles on the surface of the electron emitting electrode.

**[0017]** In the method of manufacturing a cold cathode field emission device and the method of manufacturing a cold cathode field emission display, provided by the present invention, (these methods will be sometimes generally referred to as "the present invention" hereinafter), the electric conductive particles are exposed by removing the binder in the surface layer portion of the electron emitting electrode in the above step (F), so that the surface of the electron emitting electrode comes into a state where protrusions conforming to the particle diameter and form of the electric conductive particles are formed. When a potential difference is applied between the cathode electrode and the gate electrode, the strength of an electric field formed in the opening portion is higher in the vicinity of each protrusion, so that, the most ideally, electrons can be emitted from the exposed portion of each electric conductive particle. That is, unlike the conventional Spindt-type electron emitting device in which electrons are emitted from one place (point) of the tip portion per electron emitting electrode, electrons can be emitted from a plurality of places (points) of the surface per electron emitting electrode in the present invention. Therefore, the electron emission current based on the gate voltage can be easily increased (that is, the electron emitting efficiency can be increased) without extremely finely shrinking each electron emitting electrode or without extremely increasing the existing density of the cold cathode field emission devices (to be abbreviated as "electron emitting device" hereinafter). The whole form of the electron emitting electrode is not specially defined. That is, the electron emitting electrode may have a conical form like a conventional Spindt-type electron emitting device, and it may also have the form of any one of a crown, a pyramid, a cylinder, a prism, a needle, a sphere, a semi-sphere and any other shape.

**[0018]** The "electric conductive composite" constituting the electron emitting electrode in the step (E) may be a type of a material which is not treated or processed in a step to come thereafter and therefore constitutes the electron emitting electrode without undergoing any change in composition or structure. In many types, however, the binder undergoes crosslinking or polymerization or undergoes a change such as partial decomposition, for example, under heat treatment (to be described later) and constitutes the electron emitting electrode. When the electric conductive composite is a composite of type which undergoes some change of the binder by some treatment, the electric conductive composite before the formation of the electron emitting electrode cannot rigorously be identical to the electric conductive composite after the formation of the electron emitting electrode. The "electric conductive composite" referred to in the step (E) includes both the electric conductive composite before the formation of the electron emitting electrode and the electric conductive composite after the formation of the electron emitting electrode. In the present specification, therefore, the electric conductive composite before the formation of the electron emitting electrode will be sometimes referred to as "composite material" for clarification.

**[0019]** The electric conductive particles can be selected from particles of a carbon material such as graphite; particles of a refractory metal such as tungsten (W), niobium (Nb), tantalum (Ta), titanium (Ti), molybdenum (Mo) and chromium (Cr); or particles of a transparent electrically conductive material such as ITO (indium-tin oxide). The binder can be selected from glass or general resins. The glass can be water glass when it is in the composite material. Examples of the general resins include thermoplastic resins such as a vinyl chloride resin, a polyolefin resin, a polyamide resin, a cellulose ester resin and a fluorine resin and thermosetting resins such as an epoxy resin, an acrylic resin and a polyester resin.

**[0020]** In the present invention, the diameter of the electric conductive particle is required to be sufficiently small as compared with the size of the electron emitting electrode, for improving the above electron emitting efficiency as expected. However, the diameter of the electric conductive particle is required to be sufficiently larger than the thickness of the binder to be removed, for preventing the peeling of the electric conductive particles when the binder in the surface layer portion of the electron emitting electrode is removed. The form or shape of the electric conductive particle is not critical and may be spherical, polyhedral, platelike, acicular, cylindrical or amorphous. However, the electric conductive particle preferably has a form or shape such that the exposed portion of the electric conductive particle can constitute sharp protrusions after the binder in the surface layer portion of the electron emitting electrode is removed. The electric conductive particles may be a mixture of electric conductive particles having different dimensions and/or different forms or shapes.

**[0021]** In the present invention, the removal of the binder in the step (F) can be carried out by an etching method. The etching is desirably carried out under a condition where erosion of the electric conductive particles, the gate electrode and the cathode electrode is as small as possible. In the present invention, since the whole form of the electron emitting electrode is not particularly defined, and, as an etching method in which the binder in the surface layer portion of the electron emitting electrode having any form can be removed to a certain level of depth, therefore, it is preferred to employ an isotropic etching method in which etching proceeds in every direction at a nearly equivalent etching rate rather than employing an anisotropic etching method in which etching proceeds in a specific direction at a higher etching rate. The isotropic etching can be carried out by a dry etching method using a radical as main etching species such as chemical dry etching or by a wet etching method using an etchant solution. When glass is used as a binder, the binder can be removed by a dry etching method using a fluorine gas or by a wet etching method using a sodium hydroxide aqueous solution.

**[0022]** In the present invention, the electron emitting electrode composed of the electric conductive composite is formed, and then, the electron emitting electrode can be improved in mechanical strength and stability of electric properties by heat-treating the electron emitting electrode. This heat treatment may be carried out between the steps (E) and (F), or the step (G) of heat-treating the electron emitting electrode may be provided after the step (F).

**[0023]** The temperature for the above heat treatment can be determined depending upon the kind of the binder contained in the composite material. For example, when the binder is an inorganic material such as water glass, the heat treatment can be carried out at a temperature at which the inorganic material can be sintered (calcined). When the binder is a thermosetting resin, the heat treatment can be carried out at a temperature at which the thermosetting resin can be cured. For maintaining the adhesion of the electric conductive particles to one another, preferably, the heat treatment is carried out at a temperature at which the thermosetting resin is not decomposed to excess or lower than a temperature at which the thermosetting resin may be carbonated. Whatever binder may be used, the heat treatment temperature is required to a temperature at which the gate electrode, the cathode electrode and the insulating layer are not at all damaged or caused to have a defect. The heat treatment is preferably carried out in an inert gas atmosphere so that an increase in the electric resistance of the gate electrode and the cathode electrode caused by oxidation is prevented or that the gate electrode and the cathode electrode are not caused to have a defect or damaged. When a thermoplastic resin is used as a binder, the heat treatment is not required in some cases.

**[0024]** In the composite material, the binder may be (1) a dispersing medium for the electric conductive particles, (2) a coating which is coating each of the electric conductive particles, or (3) a binder which is dissolved or dispersed in a proper solvent to form a dispersing medium for the electric conductive particles. A typical example of the above (3) is water glass, and the binder can be selected from those defined under Nos. 1 to 4 of Japanese Industrial Standard JIS K-1408 or products equivalent thereto. The above Nos. 1 to 4 represent four grades based on differences in molar amount (about 2 to 4 mol) of silicon oxide ( $\text{SiO}_2$ ) per mole of sodium oxide ( $\text{Na}_2\text{O}$ ) constituting water glass. The water glasses of these grades greatly differ in viscosity. When water glass is used in a lift-off process to be described later, preferably, a water glass of a suitable grade is selected by taking account of various conditions such as the kind and content of the electric conductive particles to be dispersed in the water glass, the affinity thereof to a peel-off layer to be described later and the aspect ratio of the opening portion, or water glass equivalent to the water glass of such a grade is prepared.

**[0025]** The binder is generally poor in electric conductivity. When the content of the binder in the electric conductive composite is too large relative to the content of the electric conductive particles, therefore, the electric resistance of the electron emitting electrode formed is high, and electrons may not be smoothly emitted. For example, when the composite material is a dispersion of particles of a carbon material as electric conductive particles in water glass, therefore, the content of the particles of a carbon material based on the total weight of the composite material is preferably determined to be in the range of from approximately 30 to 95 % by weight by taking account of properties such as the electric resistance value of the electron emitting electrode, the viscosity of the composite material and the adhesion of the electric conductive particles to one another. When the content of the particles of a carbon material is determined to be in the above range, the electric resistance value of the electron emitting electrode formed is fully low, and the adhesion of the particles of a carbon material to one another can be well maintained. When a mixture of

particles of a carbon material with alumina particles is used as electric conductive particles, the adhesion of the electric conductive particles to one another tends to decrease, so that the content of the particles of a carbon material is preferably high as compared with the content of the alumina particles and particularly preferably at least 60 % by weight based on the weight of the mixture. The composite material may contain a dispersing agent for stabilizing the dispersion state of the electric conductive particles and additives such as a pH adjuster, a desiccant, a curing agent and an antiseptic. There may be also used a composite material prepared by coating the electric conductive particles with a binder to obtain powders and dispersing the powders in a proper solvent.

**[0026]** In the present invention, the step (E) can be carried out by a so-called lift-off process. That is, the step (E) may comprise the steps of

(E-1) forming a peel-off layer on the gate electrode and the insulating layer and also on a side wall of the opening portion,

(E-2) forming an electric conductive composite layer composed of the electric conductive composite on the entire surface, and

(E-3) removing the peel-off layer together with part of the electric conductive composite layer on the peel-off layer, to retain, as the electron emitting electrode, a portion of the electric conductive composite layer on the cathode electrode exposed in the bottom portion of the opening portion. Like the "electric conductive composite" in the step (E), the "electric conductive composite" in the step (E-2) includes the electric conductive composite before the formation of the electron emitting electrode and the electric conductive composite after the formation of the electron emitting electrode.

**[0027]** In the step (E-1), the peel-off layer is formed on the entire surface excluding part of the bottom portion of the opening portion. The thickness of the peel-off layer which is formed on the side wall of the opening portion nearly determines the dimension (size) of the electron emitting electrode. The material for the peel-off layer can be selected from organic polymer materials such as a photoresist material generally used in the field of production of semiconductor devices. The peel-off layer can be formed, for example, by forming a photoresist layer on the entire surface by a spin coating method after completion of the formation of the opening portion in the step (D), and selectively removing part of the photoresist layer on the cathode electrode in the bottom portion of the opening portion.

**[0028]** In the step (E-2), the electric conductive composite layer is formed on the peel-off layer and on the cathode electrode exposed in the bottom surface of the opening portion. The dimension (size) of the electron emitting electrode when the above lift-off process is applied is a dimension (size) obtained by deducting the thickness of the peel-off layer from the dimension (size) of the opening portion. When the composite material is a liquid having a proper viscosity, the electric conductive composite layer can be formed, for example, by a spin coating method in the step (E-2). In this case, the electric conductive composite layer having a top surface dented toward the central portion of the opening portion is formed in the opening portion depending upon the viscosity and surface tension of the composite material, whereby the electron emitting electrode having a top surface dented toward the central portion of the opening portion can be formed in the step (E-3). For example, when the opening portion has the form of a circle when viewed as a plan view, the electron emitting electrode has the form of a crown as a whole. Since the electron emitting electrode having the form of a crown has a sharp steep marginal portion, many electric conductive particles are exposed on the marginal portion as the binder in the surface layer portion is removed, so that efficient electron emission can be expected. When the electric conductive particles having a form uniformity to some extent tend to be aligned in a specific direction in the electric conductive composite layer, the form and protrusion direction of the portion of the electric conductive particle exposed due to the removal of the binder in the surface layer portion can be put in order to some extent.

**[0029]** For example, when the electron emitting electrode having the form of a crown has a diameter of approximately 1 to 20  $\mu\text{m}$ , and when particles of a carbon material are used as electric conductive particles, the diameter of the particles of a carbon material is preferably in the range of from approximately 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ . When the particles of a carbon material have a diameter in the above range, the electron emitting electrode having the form of a crown has a sufficiently high mechanical strength in its marginal portion, and the electron emitting electrode has excellent adhesion to the cathode electrode.

**[0030]** When the lift-off process is used, there may be employed the step (E-4) of heat-treating the electron emitting electrode after the step (E-3), or there may be employed the step (G) of heat-treating the electron emitting electrode after the step (F).

**[0031]** The present invention may include the step of forming a second insulating layer on the gate electrode and the insulating layer after the step (C), forming a focus electrode on the second insulating layer, and further, forming a second opening portion at least in the second insulating layer, and the step (D) in the present invention may include the step of forming the opening portion communicating to the second opening portion, at least in the insulating layer. The focus electrode refers to an electrode provided for preventing the divergence of paths of electrons emitted from the electron emitting electrode in a so-called high voltage type cold cathode field emission display in which the anode

electrode and the cathode electrode have a potential difference by the order of several kilovolts and the distance between these two electrodes is relatively large. When the convergence of the paths of emitted electrons is improved, an optical crosstalk between pixels can be decreased, and therefore, a higher fineness of a display screen can be attained even if the pixel is further finely shrunk. It is not necessarily required to provide each electron emitting device with one focus electrode, and for example, the focus electrodes may be provided such that one focus electrode in the form of a stripe is formed per column or row of the electron emitting devices arranged in a two-dimensional matrix. When the focus electrodes are provided such that one focus electrode in the form of a stripe is formed per column or row, it is sufficient to form the second opening portion in the second insulating layer alone. When the focus electrodes are provided such that one focus electrode is formed per electron emitting device, the second opening portion is formed so as to penetrate through both the focus electrode and the second insulating layer.

**[0032]** In the electron emitting device or in the cold cathode field emission display (to be sometimes simply referred to as "display" hereinafter) according to the present invention, the cathode electrode can be composed of a refractory metal such as tungsten (W), niobium (Nb), tantalum (Ta), titanium (Ti), molybdenum (Mo) or chromium (Cr), a carbon material or a transparent electrically conductive material such as ITO (indium-tin oxide). In the electron emitting device or the display according to the present invention, the gate electrode and the focus electrode can be composed of a metal layer of tungsten (W), niobium (Nb), tantalum (Ta), titanium (Ti), molybdenum (Mo), chromium (Cr), aluminum (Al), copper (Cu) or silver (Ag), an alloy layer containing any one of these metals, a semiconductor layer of a silicon containing an impurity, a carbon material or a transparent electrically conductive material such as ITO (indium-tin oxide). In the display according to the present invention, further, the material for the anode electrode can be selected depending upon the constitution of the display. That is, when the display is a transmission type and has a structure in which the anode electrode and the fluorescence layer are formed in this order on the substrate, not only the substrate on which the anode electrode is formed but also the anode electrode itself is required to be transparent, and a transparent electrically conductive material such as ITO (indium-tin oxide) is used. When the display is a reflection type, or when it is a transmission type but has a structure in which the fluorescence layer and the anode electrode are formed in this order on the substrate, not only ITO can be selected, but also the material for the anode electrode can be selected from the above materials described with regard to the cathode electrode and the gate electrode as required.

**[0033]** The cathode electrode, the gate electrode or the anode electrode can be formed by a known method such as a CVD method, a vapor deposition method, a coating method, a sputtering method or a printing method such as a screen-printing method, depending upon their materials. In a CVD method, a vapor deposition method and a sputtering method, a material layer for constituting the cathode electrode or the gate electrode is formed on the entire surface, and the cathode electrode or the gate electrode may be patterned by a lift-off process or by a photolithographical method and an etching method. In a printing method such as a screen printing method, a final pattern of the cathode electrode or the gate electrode can be obtained by a single step, and concerning the gate electrode in particular, the gate electrode having the opening portion from the beginning can be formed if its dimensional accuracy is within a tolerance. In the step (D), the formation of the opening portion is expressed as forming the opening portion "at least" in the insulating layer. That is because the formation of the opening portion in the gate electrode is not necessarily required in the step (D) since the opening portion can be formed concurrently by the above printing method.

**[0034]** The insulating layer or the second insulating layer can be formed of SiO<sub>2</sub>, SiN, SiON or glass-paste cured product alone or by stacking them as required. The material constituting the insulating layer and the material constituting the second insulating layer may be the same or different. The insulating layer can be formed by a known method such as a CVD method, a coating method, a sputtering method or a printing method such as a screen-printing method, depending upon a material used for forming it.

**[0035]** The substrate includes a glass substrate, a glass substrate having a surface formed of an insulating layer, a quartz substrate and a quartz substrate having a surface formed of an insulating layer. The support may be any support so long as at least its surface is formed of an insulating member, and the support includes a glass substrate, a glass substrate having a surface formed of an insulating layer, a quartz substrate, a quartz substrate having a surface formed of an insulating layer and a semiconductor substrate having a surface formed of an insulating layer.

**[0036]** When the substrate in which the anode electrode and the fluorescence layer are formed and the support in which the electron emitting devices are formed are bonded in their marginal portions to form the display, the marginal portions may be bonded to each other with a frit glass or a metal material having a low melting point, or may be bonded through a frame. The bonded substrate and support have a space therebetween, and the space is maintained to have a vacuum degree of the order of 10<sup>-2</sup> Pa or higher (i.e., lower pressure). When the frame is used, the frame and the substrate can be bonded to each other, and the frame and the support can be bonded to each other, with a frit glass or a metal material having a low melting point. The "lower melting point" in the above metal material having a lower melting point refers to a temperature equal to, or less than, approximately 400 °C, and the metal material having a low melting point can be selected from indium, an indium-containing alloy, a tin-containing solder, a lead-containing solder or a zinc-containing solder as required. These metal materials having low melting points do not much cause degassing as compared with a frit glass, so that they are advantageous for maintaining the vacuum degree of the space surrounded

by the support and the substrate for a long period of time and therefore attaining a longer lifetime of the display.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0037] The present invention will be explained on the basis of Examples with reference to drawings. In an explanation to follow, a total of a support and structure(s) formed thereon at any step will be sometimes referred to as "substratum" hereinafter.

[0038] Figs. 1A, 1B and 1C are process drawings for showing the method of manufacturing an electron emitting device in Example 1.

[0039] Figs. 2A, 2B and 2C following Fig. 1B are process drawings for showing the method of manufacturing the electron emitting device in Example 1.

[0040] Figs. 3A and 3B are schematic views of a substratum at a step where lift-off is completed.

[0041] Figs. 4A, 4B, 4C, 4D, 4E and 4F are schematic views for showing the process of forming the electron emitting electrode by sintering and etching.

[0042] Figs. 5A and 5B are schematic views for showing a state where the electron emitting device is completed.

[0043] Fig. 6 is a graph showing electron emitting characteristics of electron emitting devices obtained by experiments using different etching conditions.

[0044] Fig. 7 is a schematic view of an constitution example of the display manufactured in Example 1.

[0045] Figs. 8A, 8B and 8C are process drawings for showing the method of manufacturing an electron emitting device in Example 2.

[0046] Figs. 9A and 9B following Fig. 8C are process drawings for showing the method of manufacturing the electron emitting device in Example 2.

[0047] Fig. 10 is schematic view of a constitution example of a general display having Spindt-type electron emitting devices incorporated.

[0048] Figs. 11A and 11B are process drawings for showing the method of manufacturing a conventional Spindt-type electron emitting device.

[0049] Figs. 12A and 12B following Fig. 11B are process drawings for showing the method of manufacturing the conventional Spindt-type electron emitting device.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

### Example 1

[0050] Example 1 is concerned with the method of manufacturing an electron emitting device and a display of the present invention. Figs. 1A, 1B, 1C, 2A, 2B, 2C, 3A, 3B, 4A, 4B, 4C, 4D, 4E, 4F, 5A and 5B show the process drawings of the method of manufacturing the electron emitting device, and Fig. 6 shows the electron emitting characteristic of the electron emitting devices. Further, Fig. 7 shows a conceptual view of the display having such electron emitting devices incorporated.

[Step-100]

[0051] First, a cathode electrode 11 having the form of a stripe is formed on a support 10 made, for example, of a glass substrate. The cathode electrode 11 can be formed, for example, by forming an approximately 0.2  $\mu\text{m}$  thick ITO film on the entire surface of the support 10 by a sputtering method and then patterning the ITO film. The cathode electrode 11 may be a layer of a single material, or it may be constituted of a stack of a plurality of material layers. For example, the cathode electrode 11 may have a surface layer constituted of a material having a higher electric resistance than its remaining portion, for reducing the fluctuation in electron emitting characteristics of the electron emitting electrodes (numeral 17B in Figs. 5A and 5B) to be formed in a step to come later. Then, an insulating layer 12 is formed on the cathode electrode 11 and the support 10. Specifically, a glass paste having a thickness of approximately 3  $\mu\text{m}$  is screen-printed on the entire surface. Then, for removing water and a solvent contained in the insulating layer 12 and for flattening the insulating layer 12, sintering is carried out, for example, at two stages at which temporary sintering is carried out at 100  $^{\circ}\text{C}$  for 10 minutes and main sintering is carried out at 500  $^{\circ}\text{C}$  for 20 minutes. The above screen-printing with the glass paste may be substituted, for example, by formation of an  $\text{SiO}_2$  layer by a plasma CVD method.

[0052] Then, a gate electrode 13 having the form of a stripe is formed on the insulating layer 12. The gate electrode 13 can be formed, for example, by consecutively forming an approximately 20 nm thick chromium (Cr) layer and a 0.2  $\mu\text{m}$  thick gold (Au) layer on the insulating layer 12 in this order by an electron beam deposition method and then patterning the stacked layers. The above chromium layer is formed for compensating for the deficient adhesion of the gold layer to the insulating layer 12. The extending direction of a projection image of the gate electrode 13 having the

form of a stripe is in the direction at right angles with the extending direction of a projection image of the cathode electrode 11 having the form of a stripe. Fig. 1A shows the gate electrode 13 obtained by carrying out only the patterning in the form of a stripe, and Fig. 1B shows a gate electrode 13A obtained by simultaneously carrying out the patterning in the form of a stripe and the formation of an opening portion in a region which overlaps the cathode electrode 11.

[Step-110]

**[0053]** Then, etching is carried out through an etching mask 15 composed, for example, of a photoresist material. When [Step-100] ends in a state shown in Fig. 1A, both of the gate electrode 13 and the insulating layer 12 are etched. When [Step-100] ends in a state shown in Fig. 1B, the insulating layer 12 alone is etched. In any case, by the above etching, there can be formed an opening portion 14 having the form of, for example, a circle having a diameter of approximately 2 to 50  $\mu\text{m}$  and having a bottom portion where the cathode electrode 11 is exposed (see Fig. 1C). For example, the opening portion 14 having a vertical wall can be formed by an anisotropic dry etching method using a fluorine gas.

[Step-120]

**[0054]** Then, the etching mask 15 is removed, and as shown in Fig. 2A, a peel-off layer 16 is formed on the gate electrode 13A and the insulating layer 12 and on a side wall of the opening portion 14. The peel-off layer 16 can be formed, for example, by applying a photoresist material onto the entire surface with a spin coating method, and patterning the photoresist material such that the photoresist material is removed only from the central portion of the bottom portion of the opening portion 14. At this moment, the diameter of the opening portion 14 is substantially decreased to approximately 1 to 20  $\mu\text{m}$ .

[Step-130]

**[0055]** Then, as shown in Fig. 2B, an electric conductive composite layer 17 composed of a composite material is formed on the entire surface. The composite material used above contains, for example, 60 % by weight of graphite particles having an average particle diameter of approximately 0.1  $\mu\text{m}$  as electric conductive particles and 40 % by weight of a No. 4 grade water glass as a binder. The composite material is spin-coated on the entire surface of the substratum under a condition of 1400 rpm and 10 seconds. The top surface of the electric conductive composite layer 17 in the opening portion 14 is lifted up along the side wall of the opening portion 14 and dented toward the central portion of the opening portion 14 due to the surface tension of the composite material. Then, temporary sintering is carried out, for example, in atmosphere at 400 °C for 30 minutes for removing water contained in the electric conductive composite layer 17.

[Step-140]

**[0056]** Then, as shown in Fig. 2C, the peel-off layer 16 is removed. The peel-off layer is removed by immersing the substratum in a sodium hydroxide aqueous solution of 2 % by weight for 30 seconds. In this case, the peeling may be carried out with applying ultrasonic vibration. In this manner, the peel-off layer 16 and a portion of the electric conductive composite layer 17 on the peel-off layer 16 are removed together, and only a portion of the electric conductive composite layer 17 on the cathode electrode 11 exposed in the bottom portion of the opening portion 14 is retained. This remaining portion constitutes an electron emitting electrode 17A. The electron emitting electrode 17A has the form of a crown, since the top surface thereof is dented toward the central portion of the opening portion 14. Figs. 3A and 3B show a state of the substratum obtained when [Step-140] is completed. Fig. 3B shows a schematic perspective view of part of the electron emitting devices, and Fig. 3A is a cross-sectional view taken along A-A line in Fig. 3B. In Fig. 3B, part of the insulating layer 12 and part of the gate electrode 13A are exploded so that the whole of the electron emitting electrode 17A can be viewed. For simplification, further, Figs. 3A and 3B show a state where one electron emitting electrode 17A is formed in each overlapping region where the cathode electrode 11 and the gate electrode 13A overlap. In an actually structured electron emitting device, a plurality of sets of the opening portions 14 and the electron emitting electrodes 17A are formed in each overlapping region, and the set of a plurality of the electron emitting electrodes 17A constitutes an electron emitting portion corresponding to one pixel in many cases. However, the present invention requires no integration of the electron emitting electrodes on the order of tens to thousands for the electron emitting portion corresponding to one pixel unlike the conventional Spindt-type electron emitting device, and it is sufficient to provide approximately 5 to 100 electron emitting electrode per electron emitting portion.

[Step-150]

**[0057]** Then, as shown in Figs. 4A, 4B, 4C, 4D, 4E and 4F, a binder 172 in a surface layer portion of the electron emitting electrode 17A is etched to finally form an electron emitting electrode 17B having electric conductive particles 171 exposed on the surface. [Step-150] can be carried out by any one of different two methods depending upon the order of the etching and the sintering (corresponding to heat treatment) of the electron emitting electrode 17A or 17B. That is, one method is a method in which the electron emitting electrode 17A after the lift-off is first sintered and then the binder 172 is etched as shown in Fig. 4A → Fig. 4B → Fig. 4C. The other method is a method in which the binder in the surface layer portion of the electron emitting electrode 17A after the lift-off is first etched and then the electron emitting electrode 17A is sintered as shown in Fig. 4D → Fig. 4E → Fig. 4F. The above sintering was carried out in dry atmosphere at 400 °C for 30 minutes. The etching was carried out in the presence of a sodium hydroxide (NaOH) aqueous solution under conditions shown in Tables 1 and 2. Table 1 shows four runs (Run 1 to Run 4) according to the order of "sintering → etching". Table 2 shows three runs (Run 5 to Run 7) according to the order to "etching → sintering". The sodium hydroxide aqueous solution was renewed every run. In Tables 1 and 2, "Solution temperature" refers to a temperature obtained by heat generation which occurred when sodium hydroxide was dissolved in water, and the solution temperature was maintained during the etching time period. After the etching and the sintering were completed, the obtained electron emitting electrodes 17B were observed for their forms through a scanning electron microscope.

Table 1

Run	Concentration of NaOH aqueous solution (wt%)	Solution temperature (°C)	Etching time period (minute)
1	2	21	1
2	10	37	10
3	10	34	20
4	10	37	30

Table 2

Run	Concentration of NAOH aqueous solution (wt%)	Solution temperature (°C)	Etching time period (minutes)
5	2	19	1
6	10	33	10
7	10	34	20

**[0058]** In Run 1, no change was observed in the electron emitting electrode 17A due to an insufficient concentration of the sodium hydroxide aqueous solution and an insufficient etching time period. In Runs 2 and 3, there were observed states where the electric conductive particles 171 (graphite particles in this Example) were exposed on the surface of the electron emitting electrode 17B, and the marginal portion of the electron emitting electrode 17B having the form of a crown was more sharpened. In Run 4, the exposure of the electric conductive particles 171 on the surface of the electron emitting electrode 17B was clearly observed, however, the etching time period was long, and the binder 172 in the bottom portion of the electron emitting electrode 17B was etched, so that peeling was partly observed between the electron emitting electrode 17B and the cathode electrode 11.

**[0059]** In Run 5, the height of the electron emitting electrode 17B having the form of a crown decreased, and the exposure of the electric conductive particles 171 was observed in part of its marginal portion. In a most part of the surface of the electron emitting electrode 17B, however, the electric conductive particles 171 were covered with the binder 172. In Run 6, there was observed a state where the height of the electron emitting electrode 17B was smaller than that in Run 5, the electric conductive particles 171 were more clearly exposed on the surface of the electron emitting electrode 17B, and the marginal portion of the electron emitting electrode 17B having the form of a crown was more sharpened. In Run 7, the etching time period was long and the binder 172 was etched deep into the electron emitting electrode 17B, so that there was observed a state where the electric conductive particles 171 overlapped one another and the crown-shaped whole form was destroyed.

**[0060]** Figs. 5A and 5B schematically show a state of the crown-shaped electron emitting electrode 17B having the electric conductive particles 171 exposed and having a sharpened marginal portion of a crown form. Reference nu-

merals in Figs. 5A and 5B are the same as those in Figs. 3A and 3B, and detailed explanations thereof are omitted. The sodium hydroxide aqueous solution used for etching the binder composed of glass may etch the exposed portion of the insulating layer 12 to some extent. That is, that portion of the insulating layer 12 which constitutes the side wall of the opening portion 14 may be withdrawn to some extent, or the insulating layer 12 may be etched between neighboring gate electrodes 13A to some extent. However, these phenomena cause no problem in the function of the electron emitting device. The withdrawing of the side wall of the opening portion 14 is rather preferred since it results in the projection of the opening end portion of the gate electrode 13A from the side wall of the opening portion 14.

**[0061]** The electron emitting characteristics of the electron emitting devices obtained in Runs 2, 3 and 6 were compared. As Reference Run, electron emitting devices were manufactured by carrying out only sintering after the lift-off without carrying out etching, and their electron emitting characteristic was compared. Fig. 6 shows the results. Fig. 6 shows a graph prepared by plotting changes of electron emission currents (unit: ampere) relative to gate voltages (unit: volt). The electron emitting devices obtained in Reference Run showed a highest threshold voltage, and the threshold voltage decreased in the order of Run 2, Run 3 and Run 6. The degree of a decrease in the threshold voltage increases with an increase in the degree of exposure of graphite particles as electric conductive particles, so that it has been found that the present invention has an effect on improvement in the electron emitting efficiency. The binder is cured by sintering, and the etching rate thereof greatly decreases as compared with that before the sintering. In Run 6, the binder was etched in a soft state before the sintering, so that the binder was removed for a short period of time as compared with Runs 2 and 3.

**[0062]** For manufacturing the display, the support 10 in which the above electron emitting devices are formed and a substrate 30 in which an anode electrode 32 and fluorescence layer 31 (see Fig. 7 for these reference numerals and others to be described hereinafter) are formed are arranged such that the fluorescence layer 31 and the electron emitting devices are opposed to each other, and the substrate 30 and the support 10 are bonded in their marginal portions. The support 10 in which the electron emitting devices are formed will be referred to as a cathode panel CP, and the substrate in which the anode electrode and the fluorescence layer are formed will be referred to as an anode panel AP. Specifically, an approximately 1 mm high frame (not shown) made of a ceramic or glass is provided, and the frame, the anode panel AP and the cathode panel CP are temporarily bonded with a frit glass, followed by sintering around 450 °C for 10 to 30 minutes. Then, gas inside the display is exhausted until a vacuum degree of approximately  $10^{-4}$  Pa is achieved, and the display is sealed by an appropriate method. Otherwise, the frame, the anode panel AP and the cathode panel CP may be bonded with a frit glass in a vacuum chamber. In this case, the inside space of the display is a vacuum space concurrently with the bonding, so that the post-step of gas exhaustion is no longer necessary.

**[0063]** The above-obtained display is constituted of a plurality of pixels as shown in Fig. 7. Each pixel comprises a plurality of the above electron emitting devices, and the anode electrode 32 and the fluorescence layer 31 formed on the substrate 30 so as to be opposed thereto. The anode electrode 32 is composed, for example, of aluminum, and is formed so as to cover the fluorescence layer 31, in a predetermined pattern, formed on the substrate 30 made of glass. The order of stacking the fluorescence layer 31 and the anode electrode 32 on the substrate 30 may be reversed. When the display is a transmission type, the anode electrode 32 is positioned in front of the fluorescence layer 31 from a viewer side, so that it is required to form the anode electrode 32 from a transparent electrically conductive material such as ITO (indium-tin oxide).

**[0064]** A relatively negative voltage is applied to the cathode electrode 11 from a scanning circuit 33, a relatively positive voltage is applied to the gate electrode 13A from a control circuit 34, and a positive voltage higher than the voltage applied to the gate electrode 13A is applied to the anode electrode 32 from an acceleration power source 35. For displaying with the display, video signals are inputted to the control circuit 34, and scanning signals are inputted to the scanning circuit 33. Due to an electric field generated when the voltages are applied to the cathode electrode 11 and the gate electrode 13A, electrons  $e^-$  are extracted from the surface of the electron emitting electrode 17B. When these electrons  $e^-$  are attracted to the anode electrode 32 and collide with the fluorescence layer 31, the fluorescence layer 31 emits light to give a desired image. In the display according to the present invention, electrons are emitted from a plurality of portions on the surface of the electron emitting electrode 17B, so that a high electron emission current can be obtained at a low threshold voltage without much increasing the integration density of the electron emitting electrodes 17B. Since it is not required to increase the integration density of the electron emitting electrodes 17B much, it is no longer necessary to finely shrink each electron emitting electrode to a high degree, and the electron emitting electrodes can be easily formed without using many semiconductor processes. The displays which can attain a high brightness and a high image quality at a low power consumption can be produced at a low cost with a high throughput and a high yield.

## Example 2

**[0065]** Example 2 is a variant of Example 1, and Example 2 is concerned with an electron emitting device provided further with a focus electrode. The method of manufacturing an electron emitting device in Example 2 will be explained

with reference to Figs. 8A, 8B, 8C, 9A and 9B. Those portions which are the same as those in Figs. 1A to 5B are indicated by the same reference numerals, and detailed explanations thereof will be omitted.

[Step-200]

**[0066]** Procedures up to the step of forming the gate electrode 13 or the gate electrode 13A on the insulating layer are carried out in the same manner as in [Step-100] in Example 1 (see Fig. 1A or Fig. 1B). Then, as shown in Fig. 8A, a second insulating layer 18 is formed on the entire surface, that is, on the gate electrode 13 and the insulating layer 12, and further, a focus electrode 19 is formed on the second insulating layer 18. Fig. 8A shows the gate electrode 13, while the gate electrode 13A may be formed. The second insulating layer 18 can be formed in the same manner as in the formation of the insulating layer 12, and the focus electrode 19 can be formed in the same manner as in the formation of the gate electrode 13 or 13A. The focus electrode 19 is formed, for example, in a pattern having the form of a stripe extending in the same direction as that of the gate electrode 13.

[Step-210]

**[0067]** Then, the second insulating layer 18, the gate electrode 13 and the insulating layer 12 are consecutively etched through an etching mask (not shown), to form an opening portion 20 having a bottom portion where the cathode electrode 11 is exposed. The gate electrode 13 becomes the gate electrode 13A at this point of time (see Fig. 8B).

[Step-220]

**[0068]** Then, a peel-off layer 21 is formed on the focus electrode 19 and the second insulating layer 18 and on the side wall of the opening portion 20. Further, an electric conductive composite layer 22 composed of a composite material is formed on the entire surface (see Fig. 8C). The peel-off layer 21 and the electric conductive composite layer 22 can be formed in the same manner as in Example 1. Then, the electric conductive composite layer 22 is temporarily sintered.

[Step-230]

**[0069]** Then, the peel-off layer 21 is removed. Part of the electric conductive composite layer 22 on the peel-off layer 21 is also removed together with the peel-off layer 21, and remaining is only a portion of the electric conductive composite layer 22 on the cathode electrode 11 exposed in the bottom portion of the opening portion 20. The remaining portion constitutes an electron emitting electrode 22A (see Fig. 9A).

[Step-240]

**[0070]** Further, a step similar to [Step-150] in Example 1 is carried out in the order of sintering (corresponding to heat treatment) → etching or etching → sintering (corresponding to heat treatment), whereby there can be manufactured an electron emitting device having the electron emitting electrode 22B having electric conductive particles (graphite particles in this Example) exposed on its surface, as shown in Fig. 9B. Further, the electron emitting devices manufactured in Example 2 can be used to manufacture the display in the same manner as in Example 1.

**[0071]** The present invention is explained with reference to preferred embodiments hereinabove, while the present invention shall not be limited thereto. The structure and details of the electron emitting device, the processing conditions of manufacturing the electron emitting device, details of materials used and details of the structure of the display to which the electron emitting devices are applied are given for an explanation purpose, and can be altered, selected and combined as required.

**[0072]** As is clear from the above explanations, the electron emitting electrode having a high electron emitting efficiency can be very easily manufactured by the method of manufacturing a cold cathode field emission device, provided by the present invention. Since it is not required to increase the integration density of electron emitting electrodes much and to finely shrink each of the electron emitting electrodes excessively, the cold cathode field emission devices can be produced by relatively easy processes without using many semiconductor processes. According to the method of manufacturing a cold cathode field emission display, provided by the present invention, there can be manufactured displays which can attain a high brightness and a high image quality at a low power consumption at a low cost with a high throughput and a high yield. Therefore, when displays having a larger display screen are produced, an investment in production facilities can be decreased, the process time period can be decreased, and the production cost can be decreased.

## Claims

1. A method of manufacturing a cold cathode field emission device, which comprises the steps of;

- (A) forming a cathode electrode on a support,
- (B) forming an insulating layer on the cathode electrode and the support,
- (C) forming a gate electrode on the insulating layer,
- (D) forming an opening portion having a bottom portion where the cathode electrode is exposed, at least in the insulating layer,
- (E) forming an electron emitting electrode composed of an electric conductive composite containing electric conductive particles and a binder on the cathode electrode exposed in the bottom portion of the opening portion, and
- (F) removing the binder in a surface layer portion of the electron emitting electrode to expose the electric conductive particles on the surface of the electron emitting electrode.

2. The method of manufacturing a cold cathode field emission device according to claim 1, in which the removal of the binder in the step (F) is carried out by an etching method.

3. The method of manufacturing a cold cathode field emission device according to claim 1, in which a heat treatment of the electron emitting electrode is carried out between the steps (E) and (F).

4. The method of manufacturing a cold cathode field emission device according to claim 1, further including;  
(G) heat-treating the electron emitting electrode after the step (F).

5. The method of manufacturing a cold cathode field emission device according to claim 1, in which the step (E) comprises the steps of;

- (E-1) forming a peel-off layer on the gate electrode and the insulating layer and also on a side wall of the opening portion,
- (E-2) forming an electric conductive composite layer composed of the electric conductive composite on the entire surface, and
- (E-3) removing the peel-off layer together with part of the electric conductive composite layer on the peel-off layer, to retain, as the electron emitting electrode, a portion of the electric conductive composite layer on the cathode electrode exposed in the bottom portion of the opening portion.

6. The method of manufacturing a cold cathode field emission device according to claim 5, in which the electric conductive composite layer having a top surface dented toward the central portion of the opening portion is formed in the opening portion in the step (E-2), and the electron emitting electrode having a top surface dented toward the central portion of the opening portion is formed in the step (E-3).

7. The method of manufacturing a cold cathode field emission device according to claim 5, in which the step (E) further includes the step of;  
(E-4) heat-treating the electron emitting electrode after the step (E-3).

8. The method of manufacturing a cold cathode field emission device according to claim 5, further including;  
(G) heat-treating the electron emitting electrode after the step (F).

9. The method of manufacturing a cold cathode field emission device according to claim 1, further including the step of;

- forming a second insulating layer on the gate electrode and the insulating layer after the step (C),
- forming a focus electrode on the second insulating layer, and further,
- forming a second opening portion at least in the second insulating layer,
- and in which
- the step (D) includes the step of forming the opening portion communicating to the second opening portion, at least in the insulating layer.

10. A method of manufacturing a cold cathode field emission display comprises arranging a substrate on which an anode electrode and a fluorescence layer are formed and a support on which cold cathode field emission devices

are formed such that the fluorescence layer and the cold cathode field emission devices are opposed to each other, and bonding the substrate and the support in their marginal portions,  
wherein each of the cold cathode field emission devices is manufactured through steps of;

- 5 (A) forming a cathode electrode on the support,
- (B) forming an insulating layer on the cathode electrode and the support,
- (C) forming a gate electrode on the insulating layer,
- (D) forming an opening portion having a bottom portion where the cathode electrode is exposed, at least in the insulating layer,
- 10 (E) forming an electron emitting electrode composed of an electric conductive composite containing electric conductive particles and a binder on the cathode electrode exposed in the bottom portion of the opening portion, and
- (F) removing the binder in a surface layer portion of the electron emitting electrode to expose the electric conductive particles on the surface of the electron emitting electrode.
- 15

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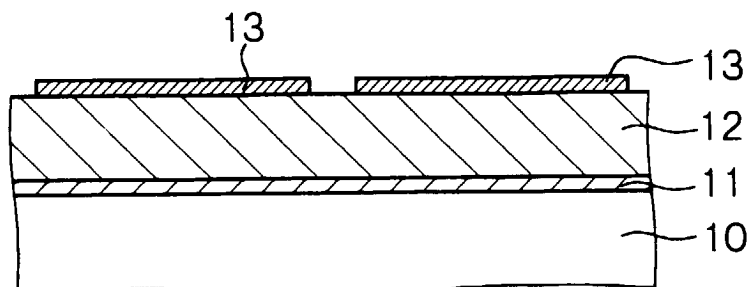
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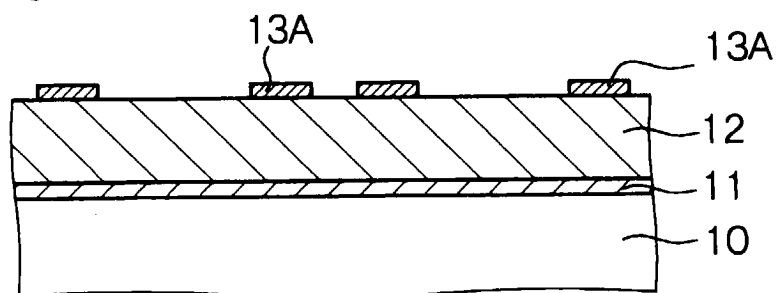
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*Fig. 1A*

[STEP-100]

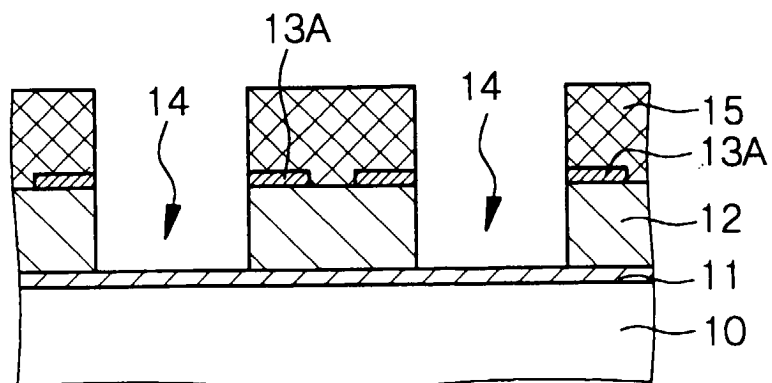


*Fig. 1B*



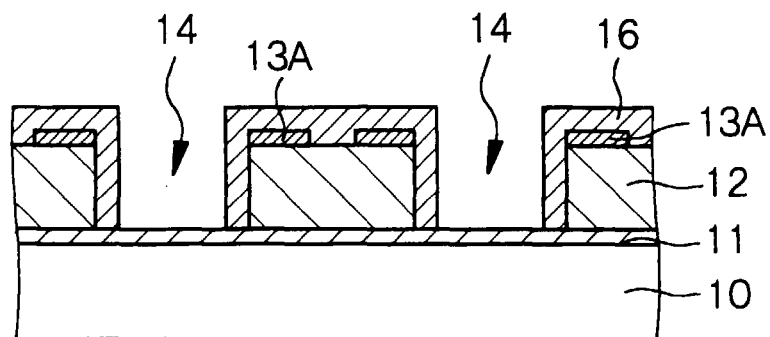
*Fig. 1C*

[STEP-110]



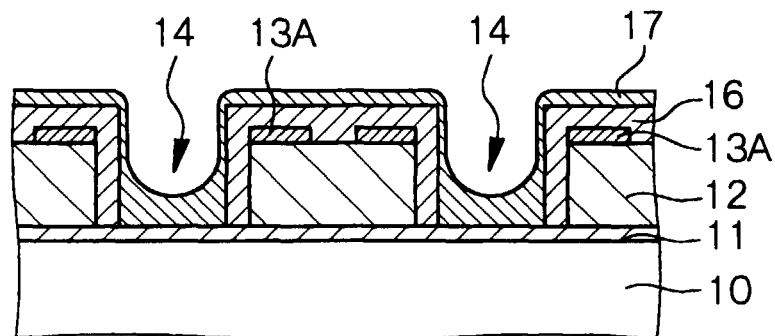
*Fig. 2A*

[STEP-120]



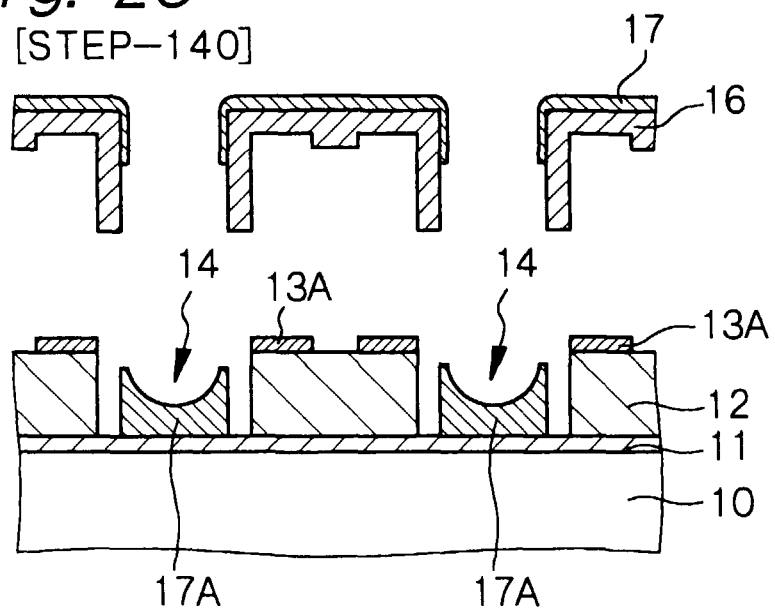
*Fig. 2B*

[STEP-130]

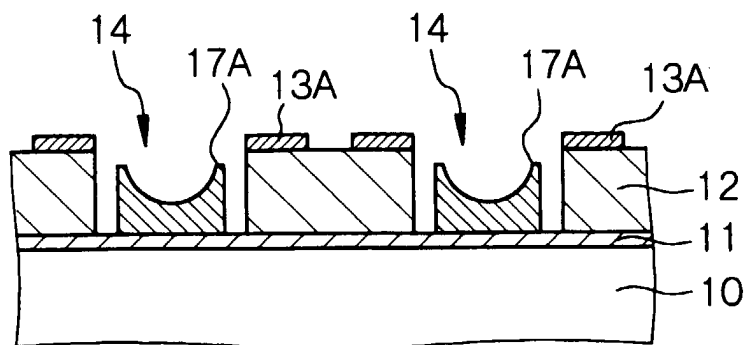


*Fig. 2C*

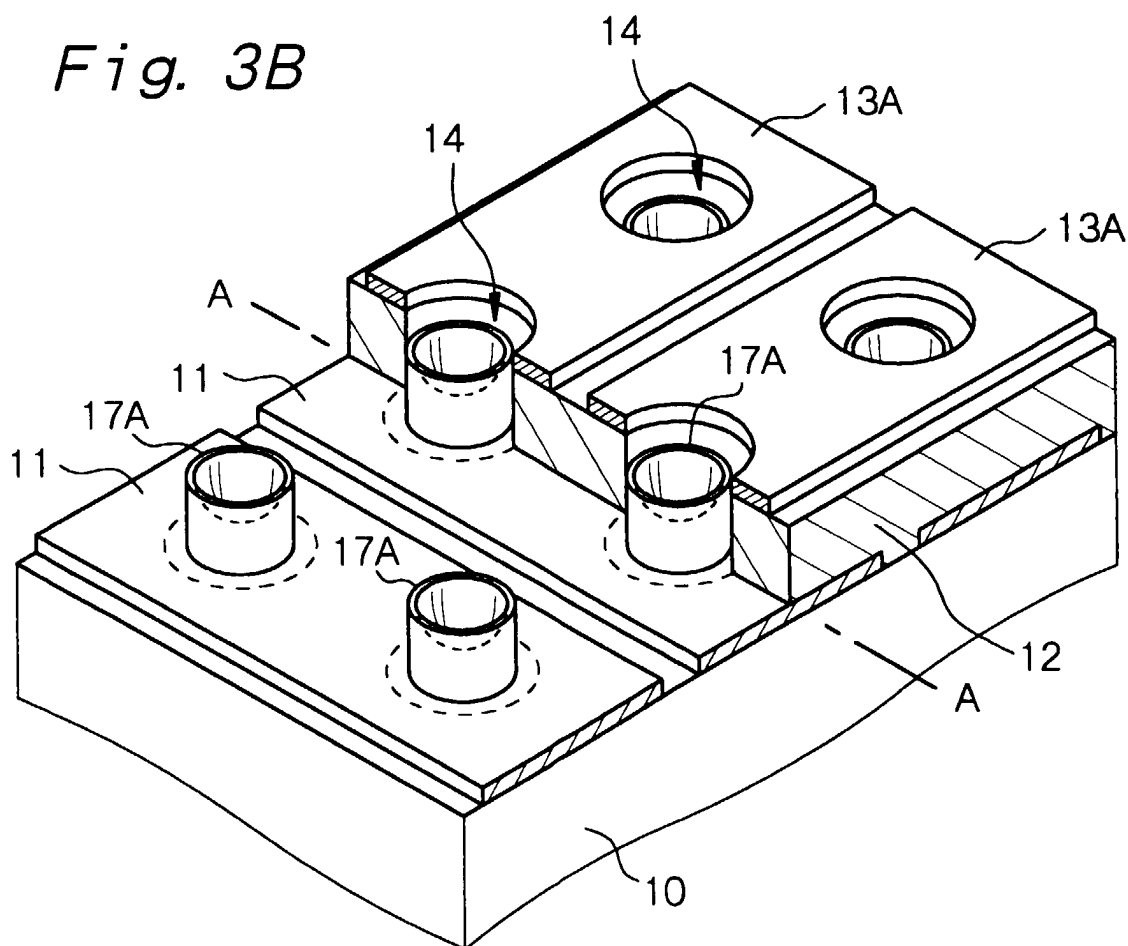
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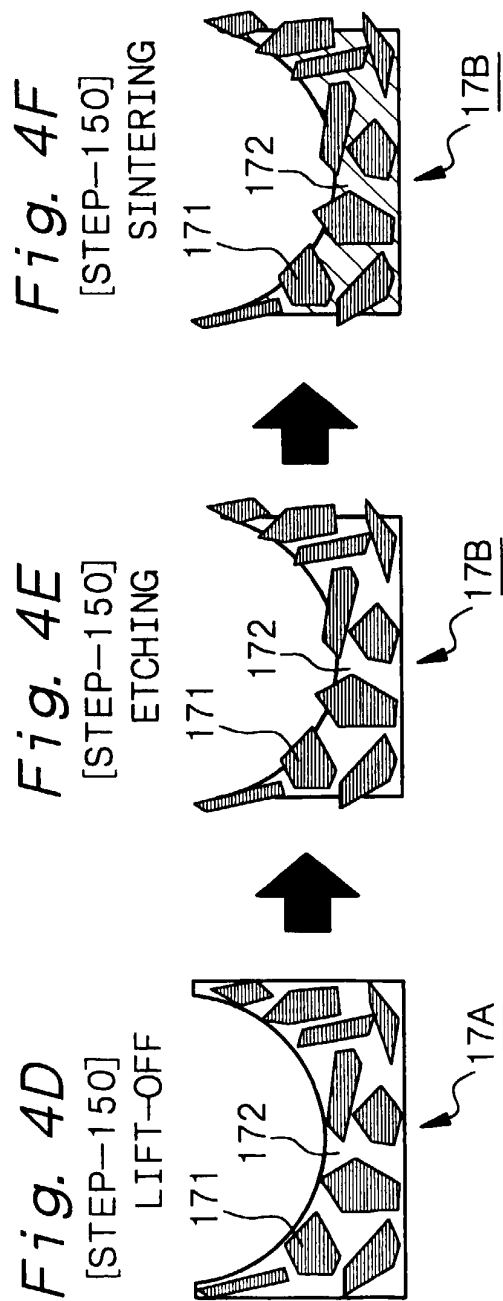
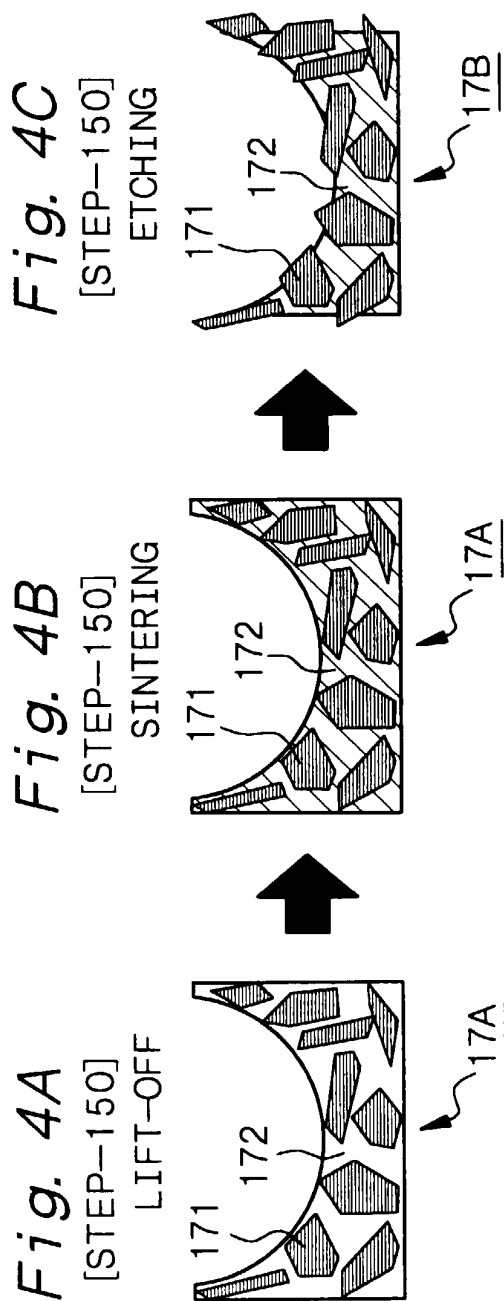


*Fig. 3A*

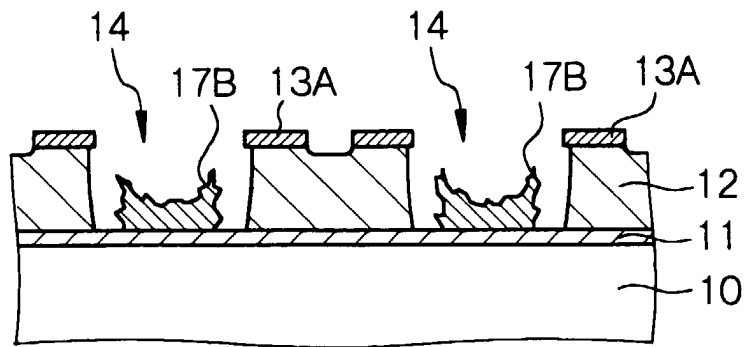


*Fig. 3B*

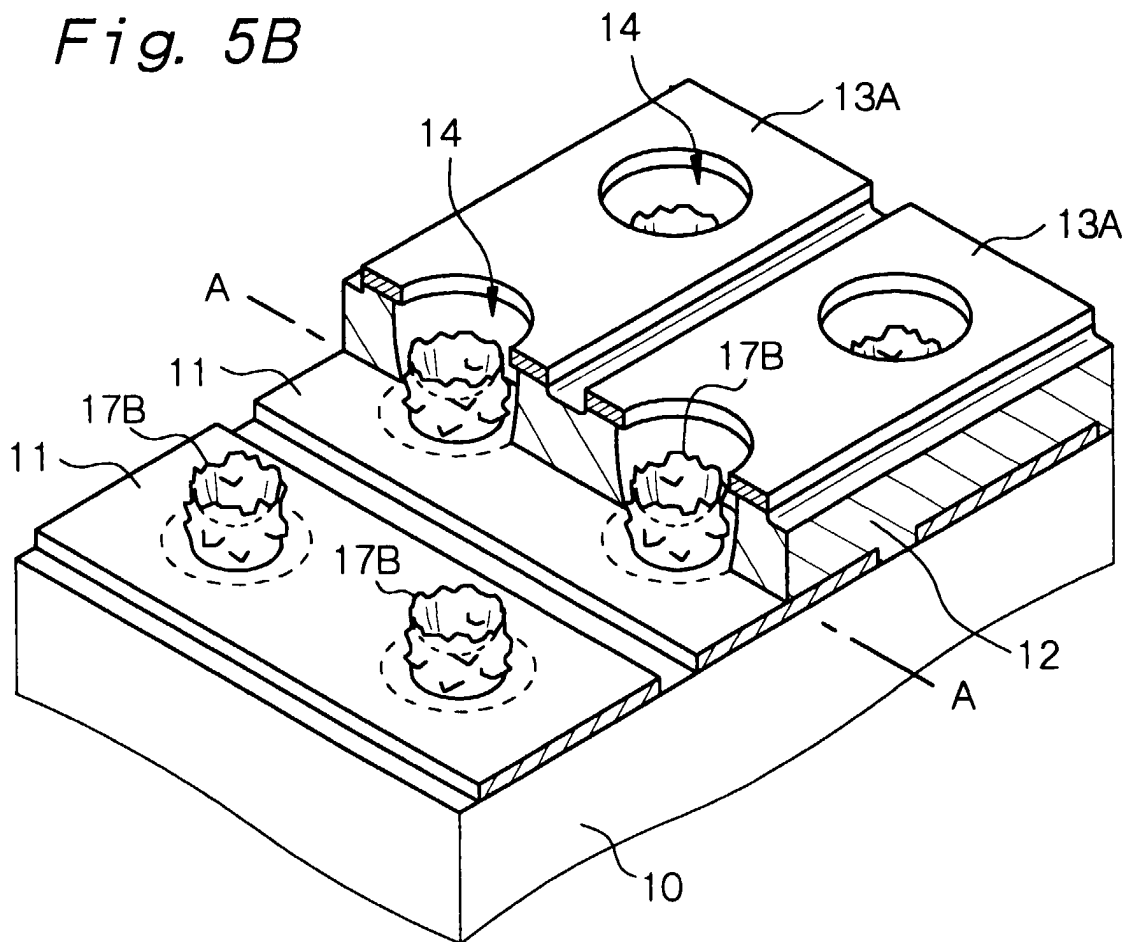




*Fig. 5A*



*Fig. 5B*



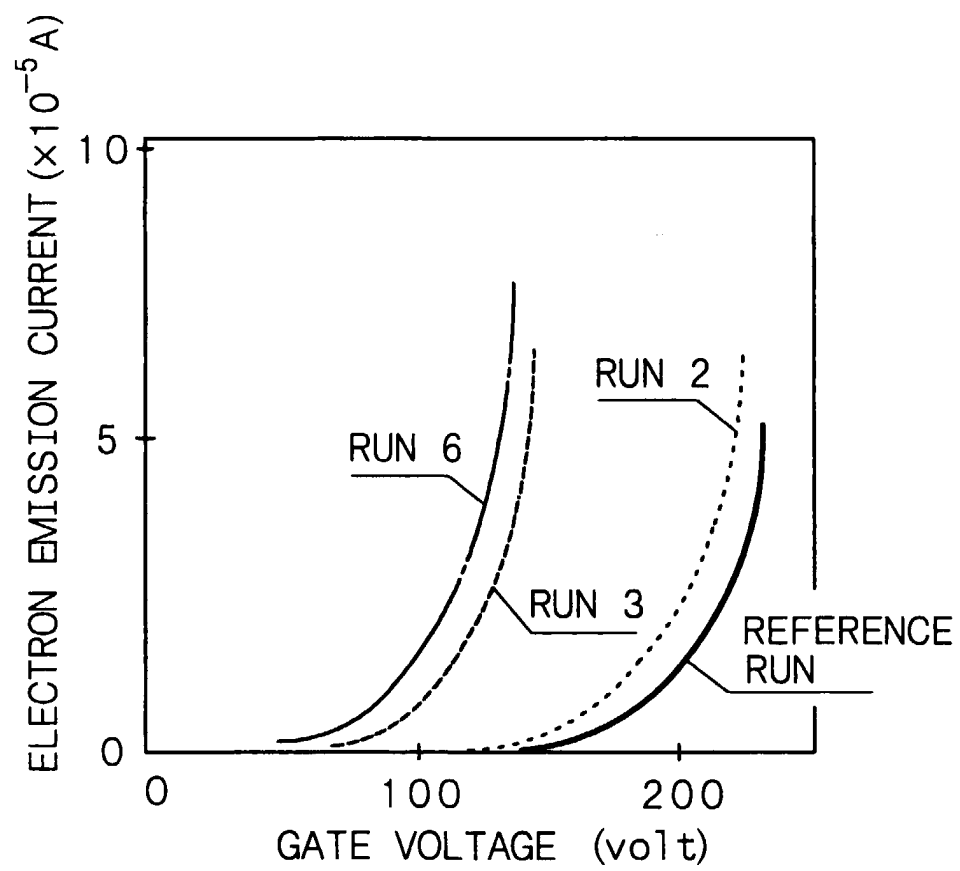
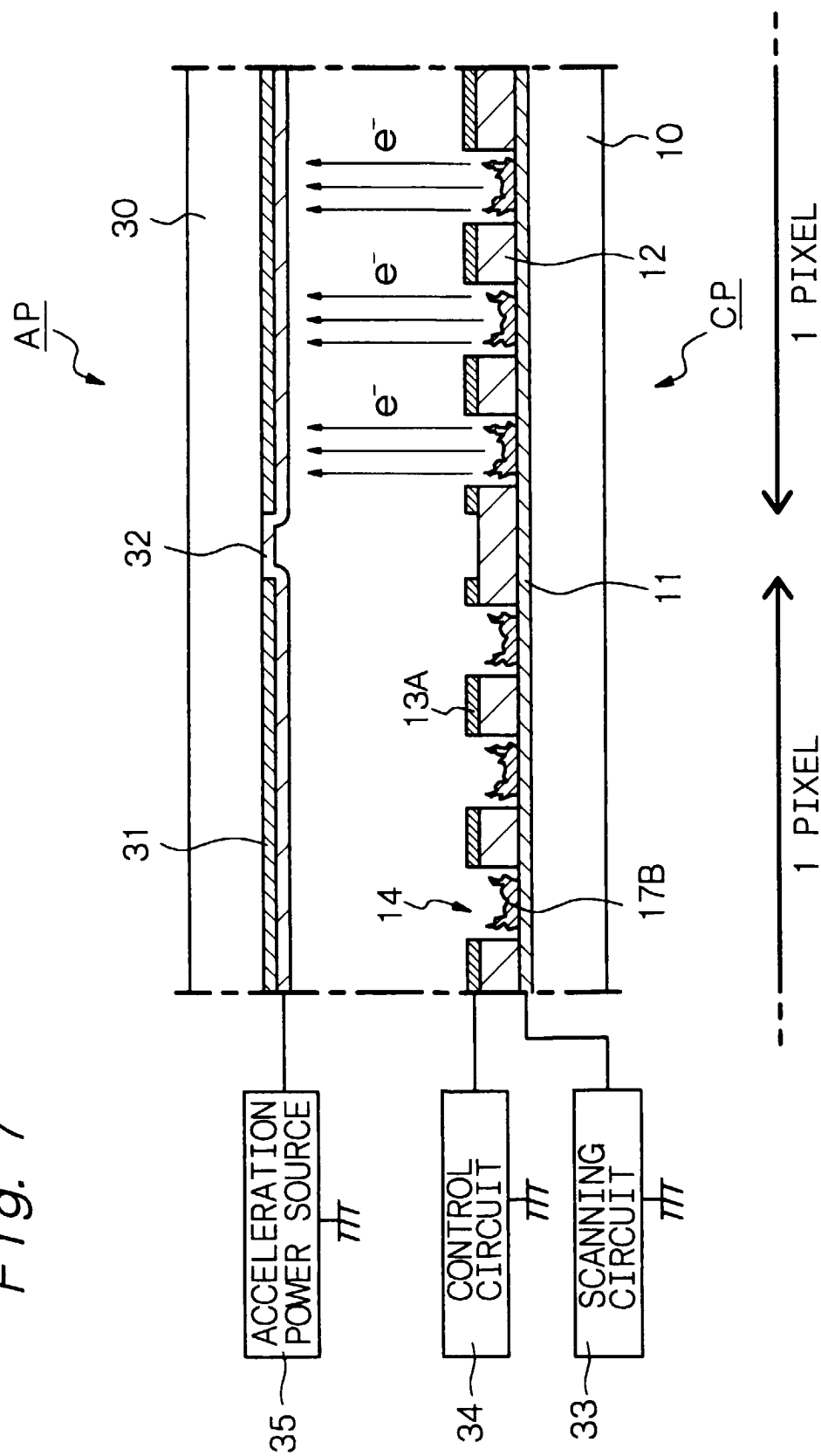
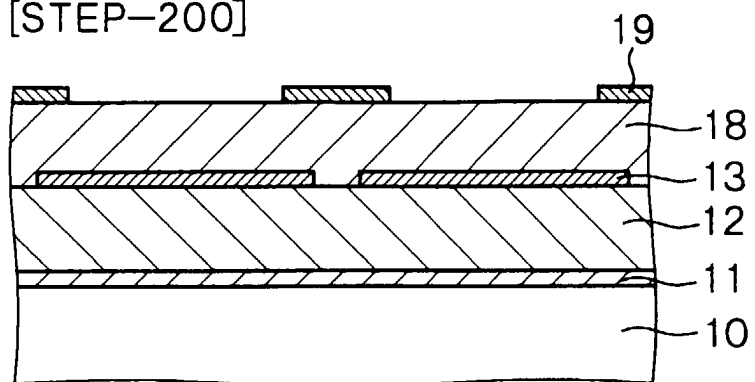
*Fig. 6*

Fig. 7



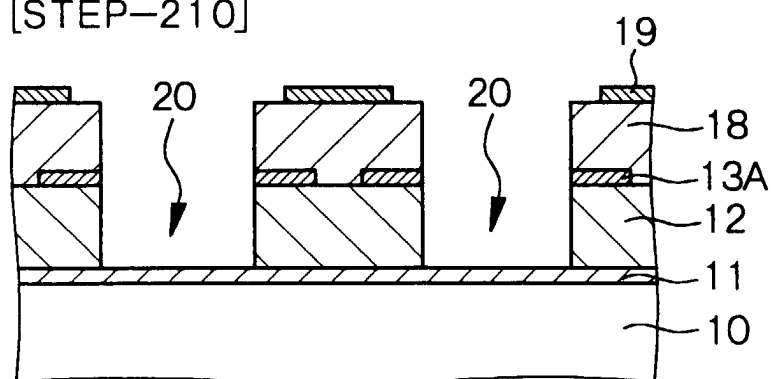
*Fig. 8A*

[STEP-200]



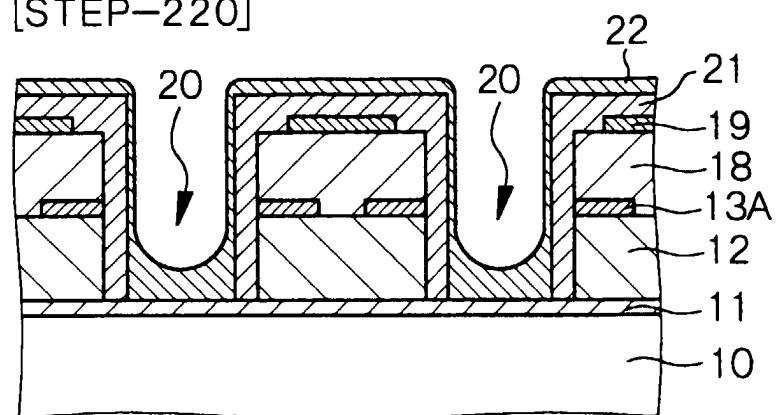
*Fig. 8B*

[STEP-210]



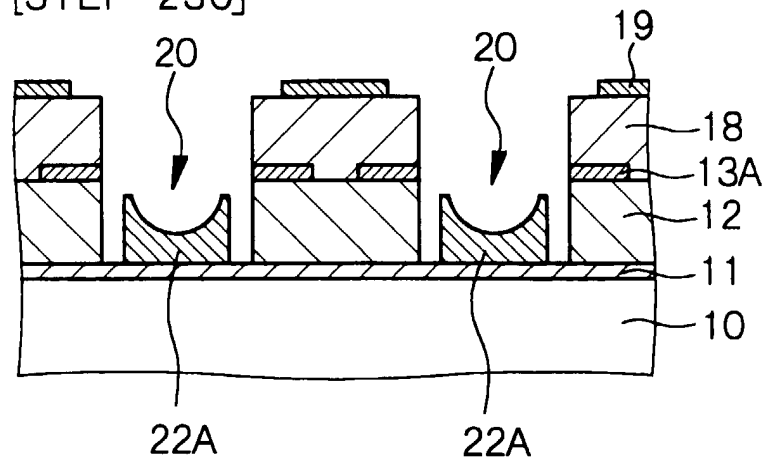
*Fig. 8C*

[STEP-220]



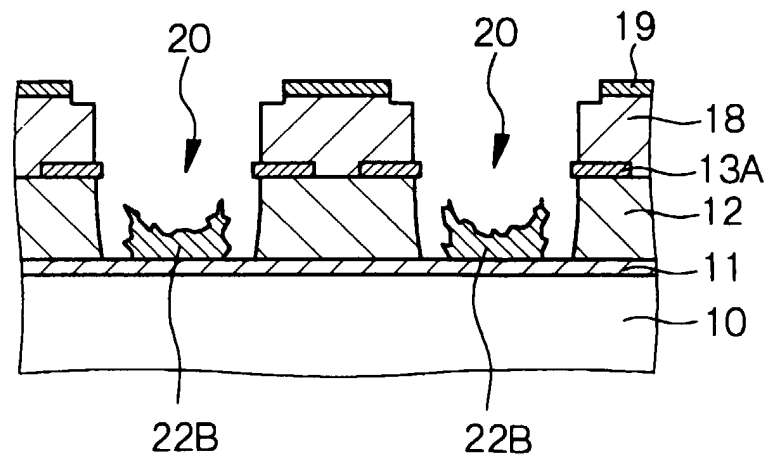
*Fig. 9A*

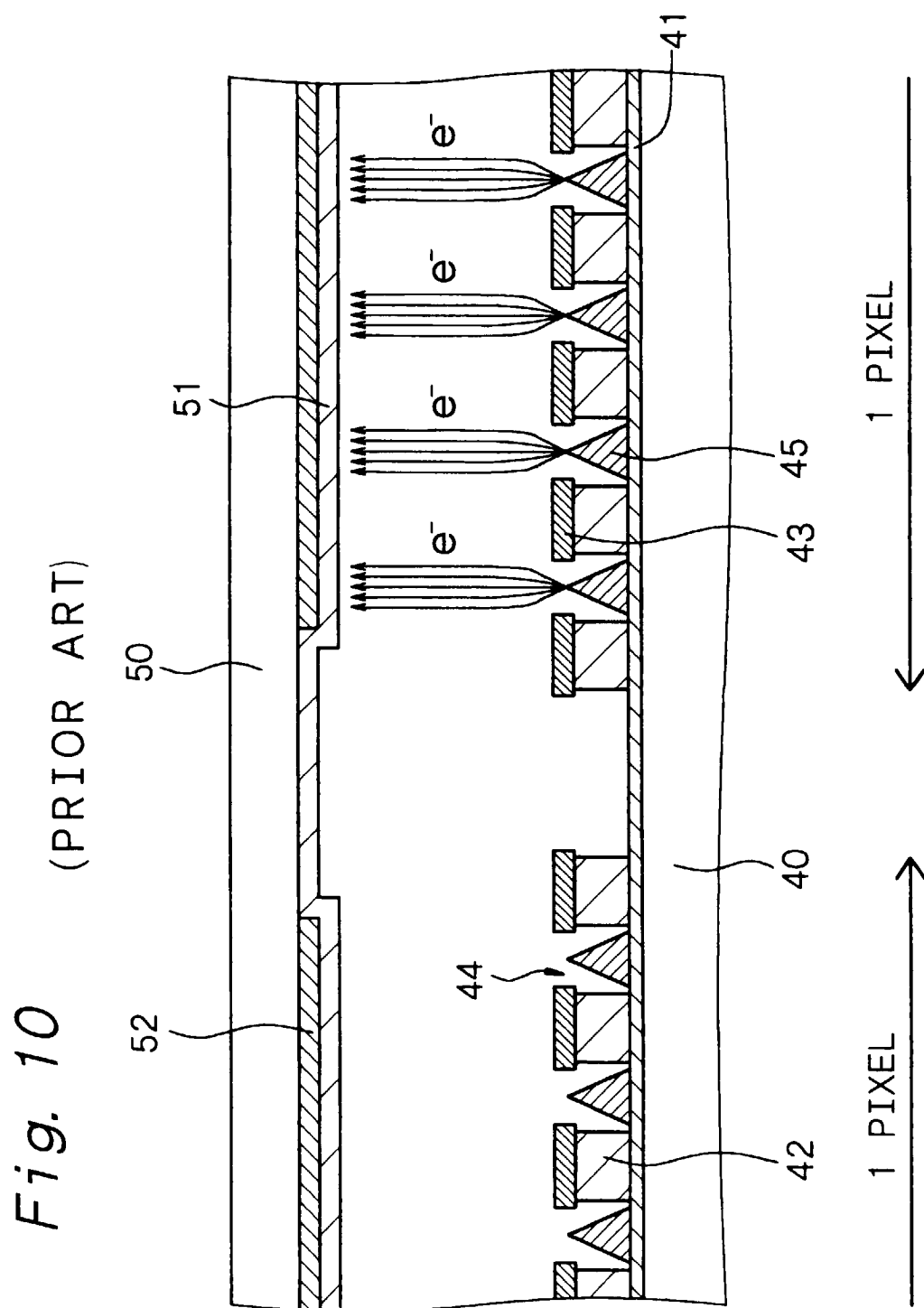
[STEP-230]



*Fig. 9B*

[STEP-240]

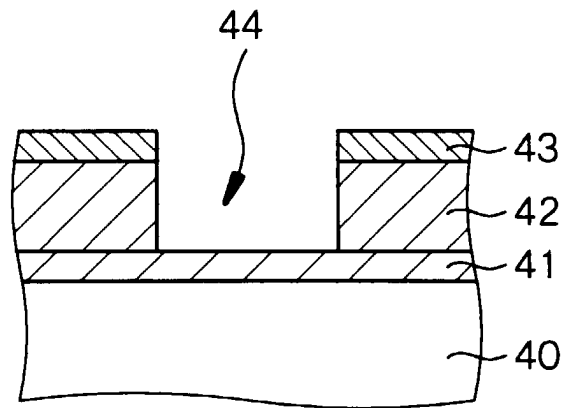




(PRIOR ART)

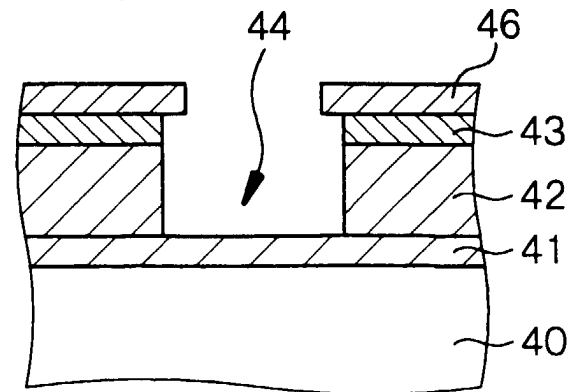
*Fig. 11A*

[STEP-10]



*Fig. 11B*

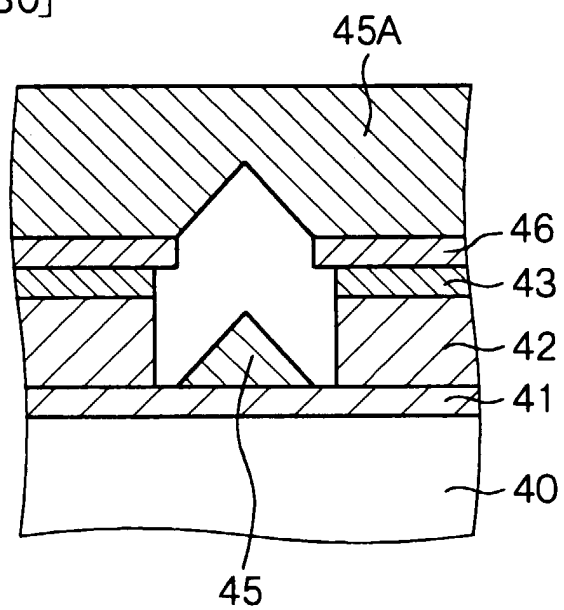
[STEP-20]



(PRIOR ART)

*Fig. 12A*

[STEP-30]



*Fig. 12B*

[STEP-40]

