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(54) **ELECTROPHORETIC DEPOSITION METHOD FOR A FIELD EMISSION DEVICE**

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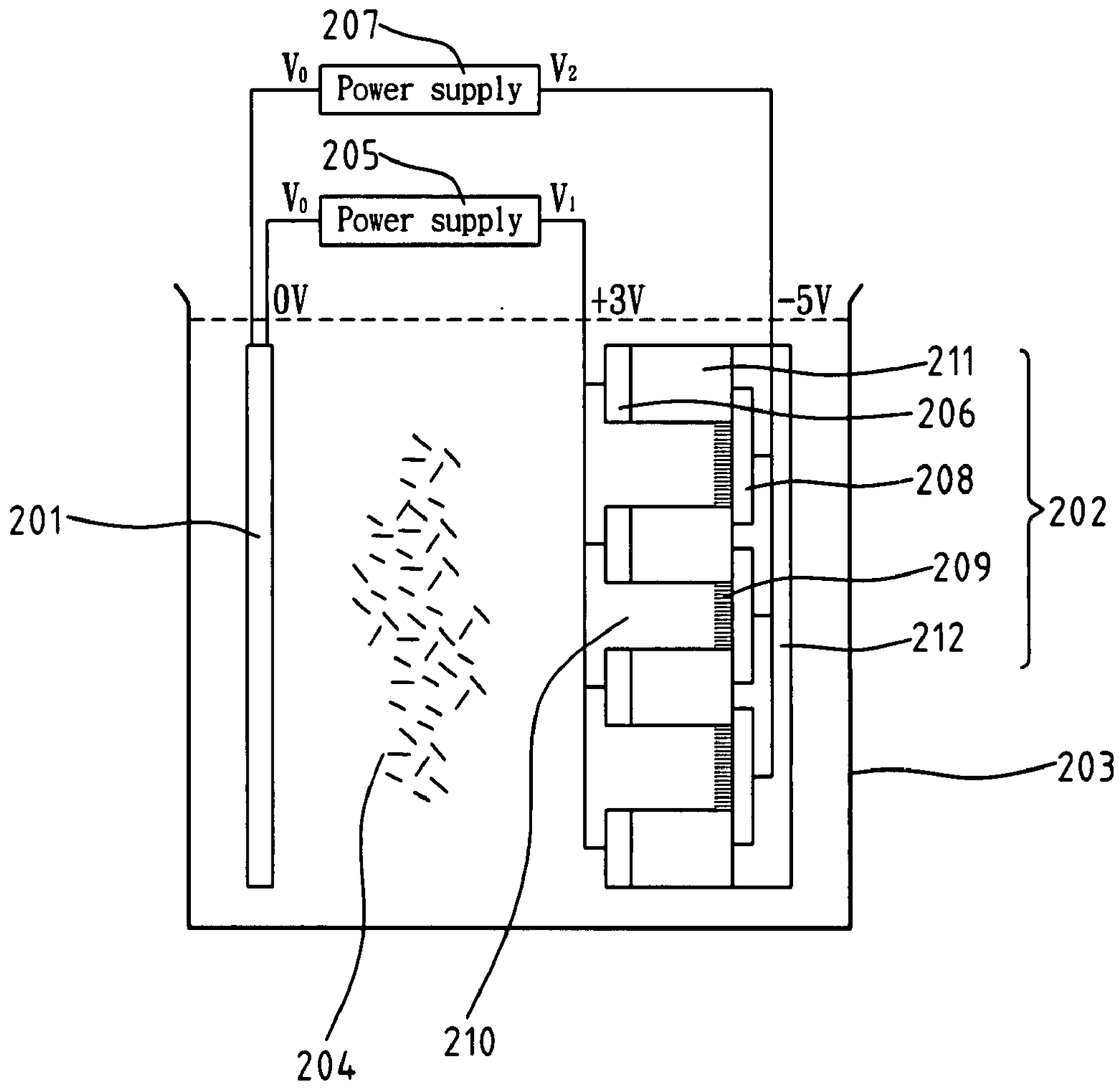
(57) **ABSTRACT**

The invention provides an electrophoretic deposition method of CNTs for a field emission device. It uses a triode structure having gates and a proper arrangement of applied voltages to improve the selectivity of the conventional EPD method. The electric field around the gates repels the charged or polarized nanostructure suspension in the electrophoresis bath and prevents the charged or polarized nanostructure materials from depositing in the neighborhood of the gates. Therefore, the nanostructure materials are selectively deposited on the cathode. An electrical short circuit between the gates and the cathodes can be avoided. It does not require a masked sacrificial layer, and therefore keeps the manufacturing process simple and the cost down.



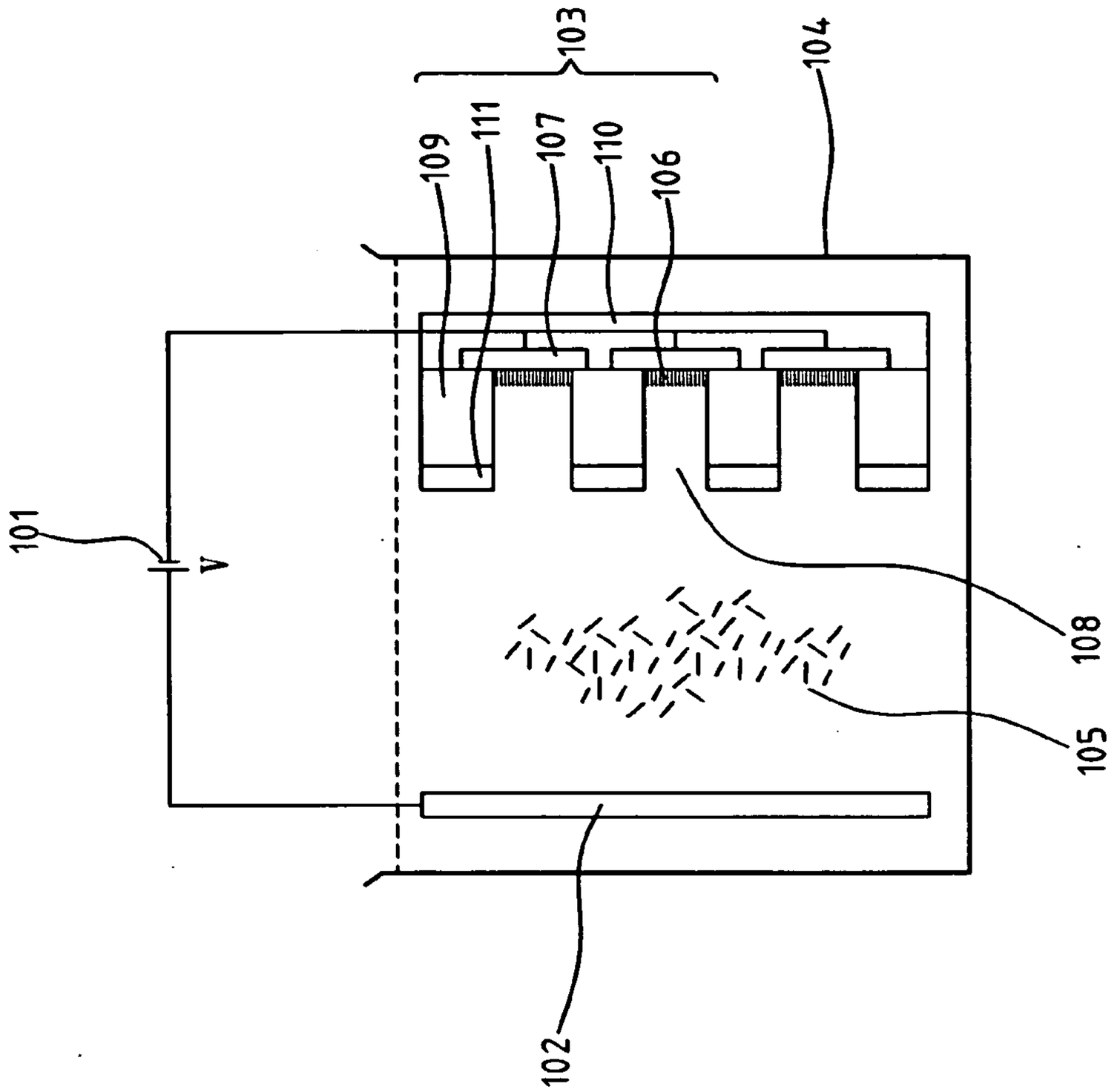


FIG. 1(Prior Art)

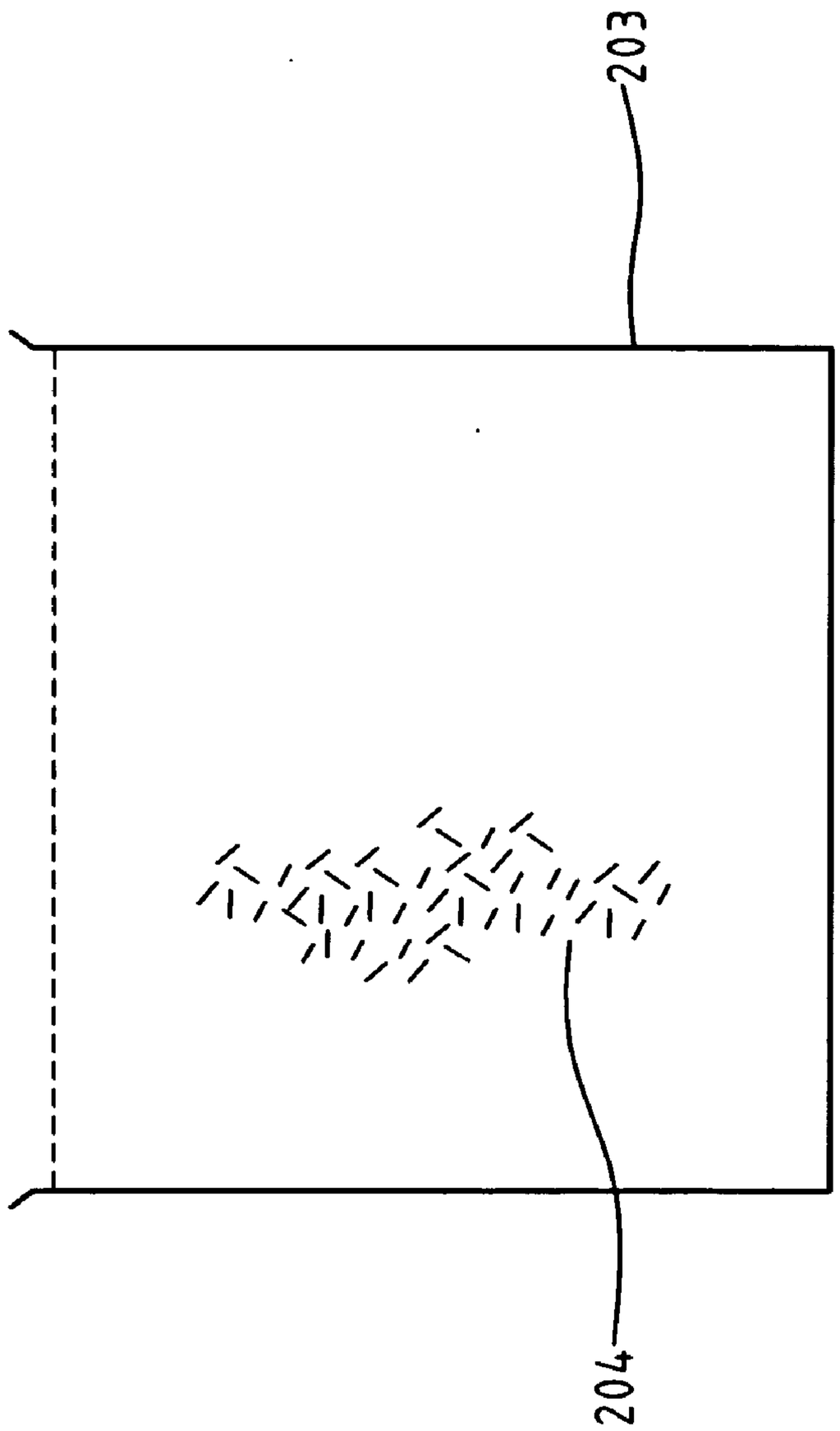


FIG. 2a

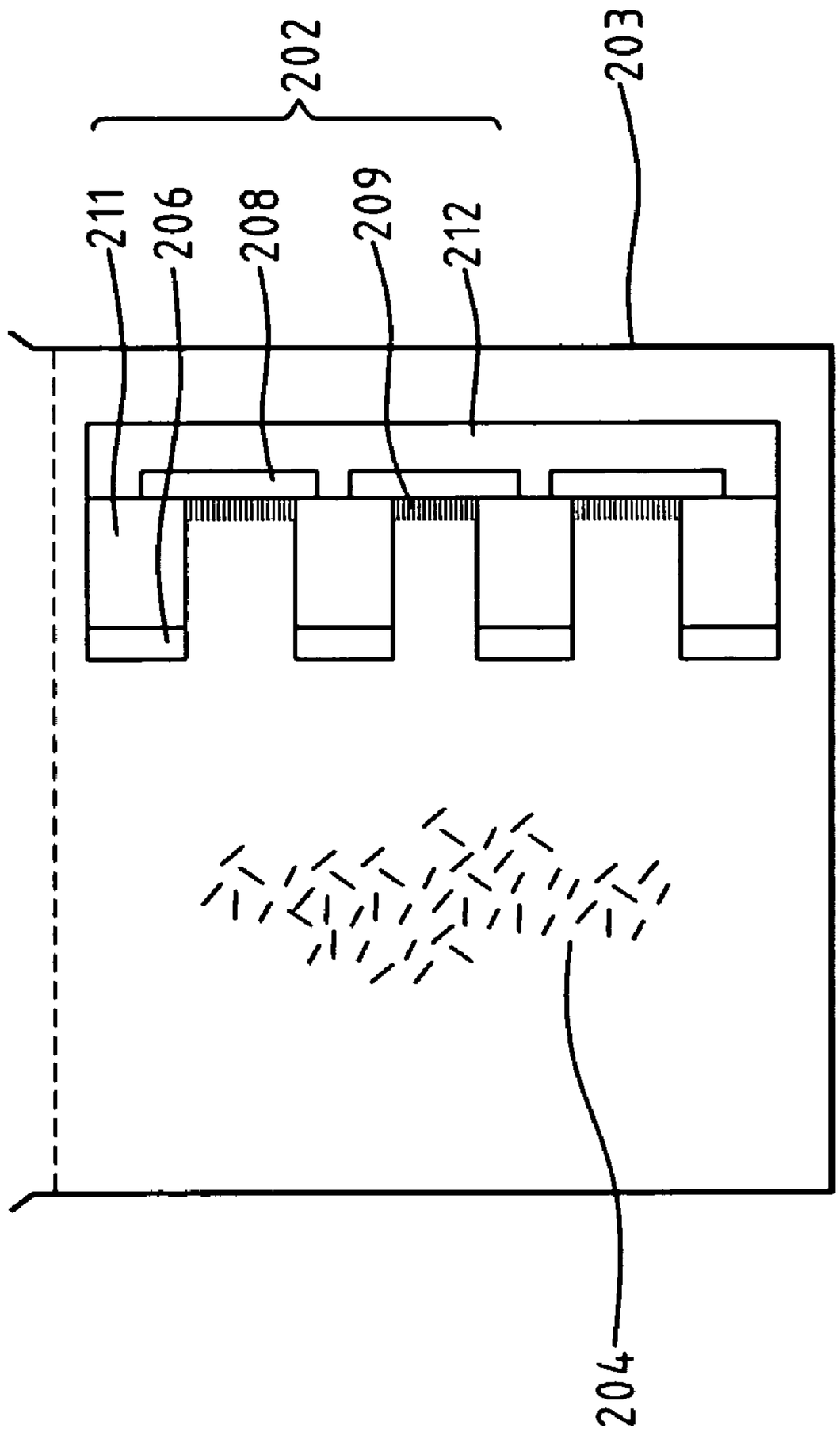


FIG. 2b

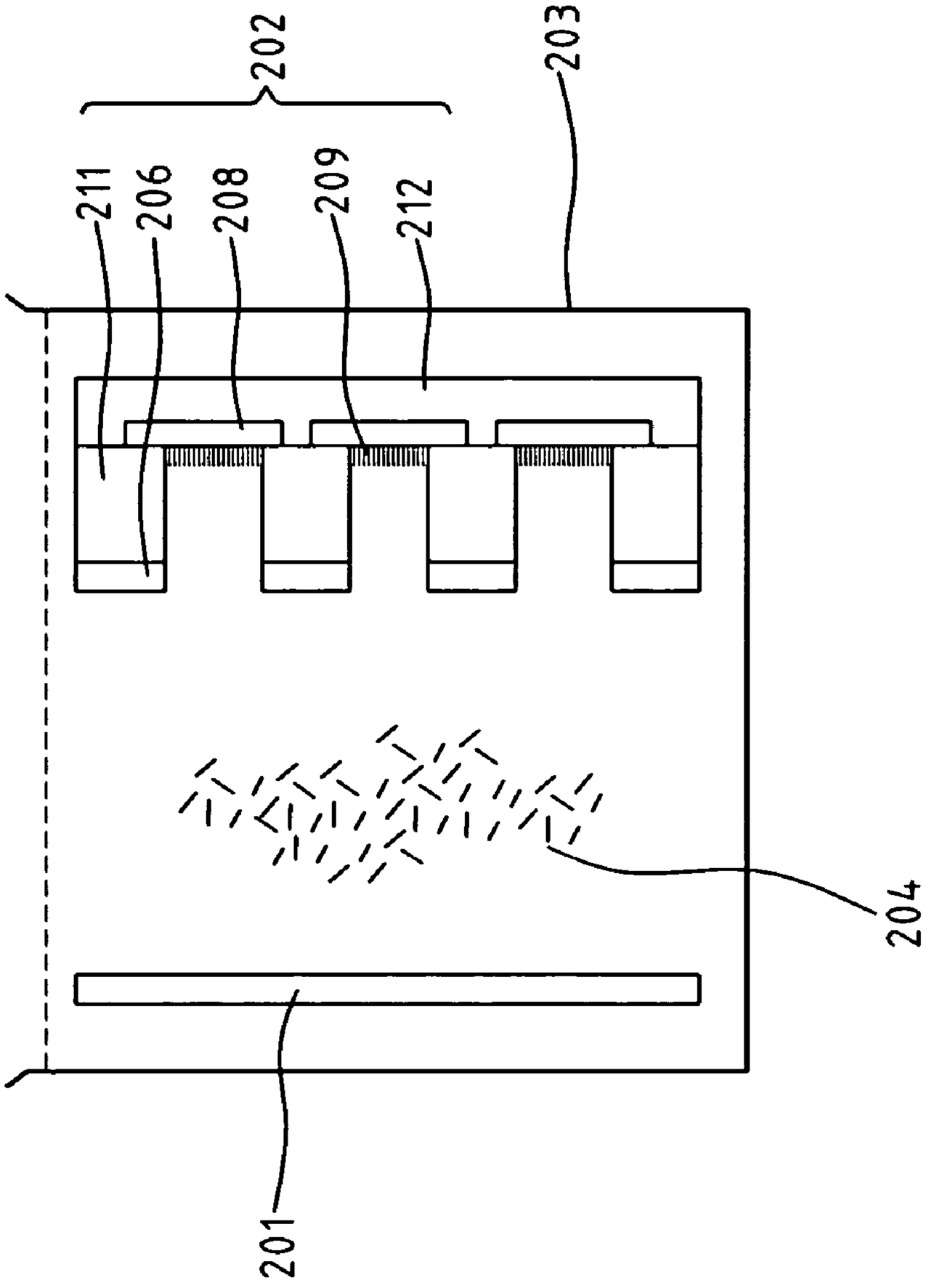


FIG. 2c

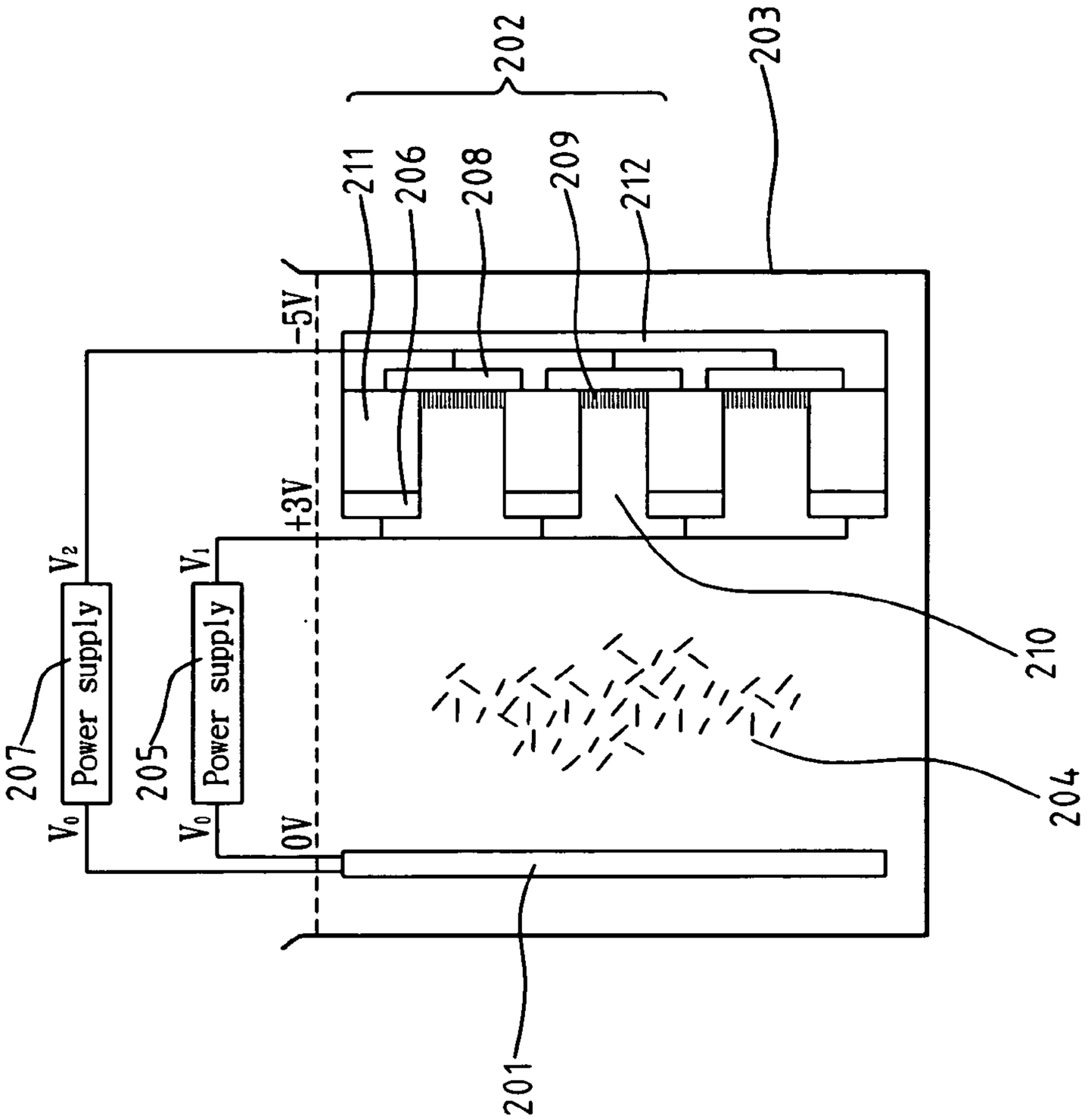

202
203
211
206
208
209
212
-5V
+3V
0V
V_2
V_1
V_0
V_0
Power supply
Power supply
207
205
210
204
201

FIG. 2d

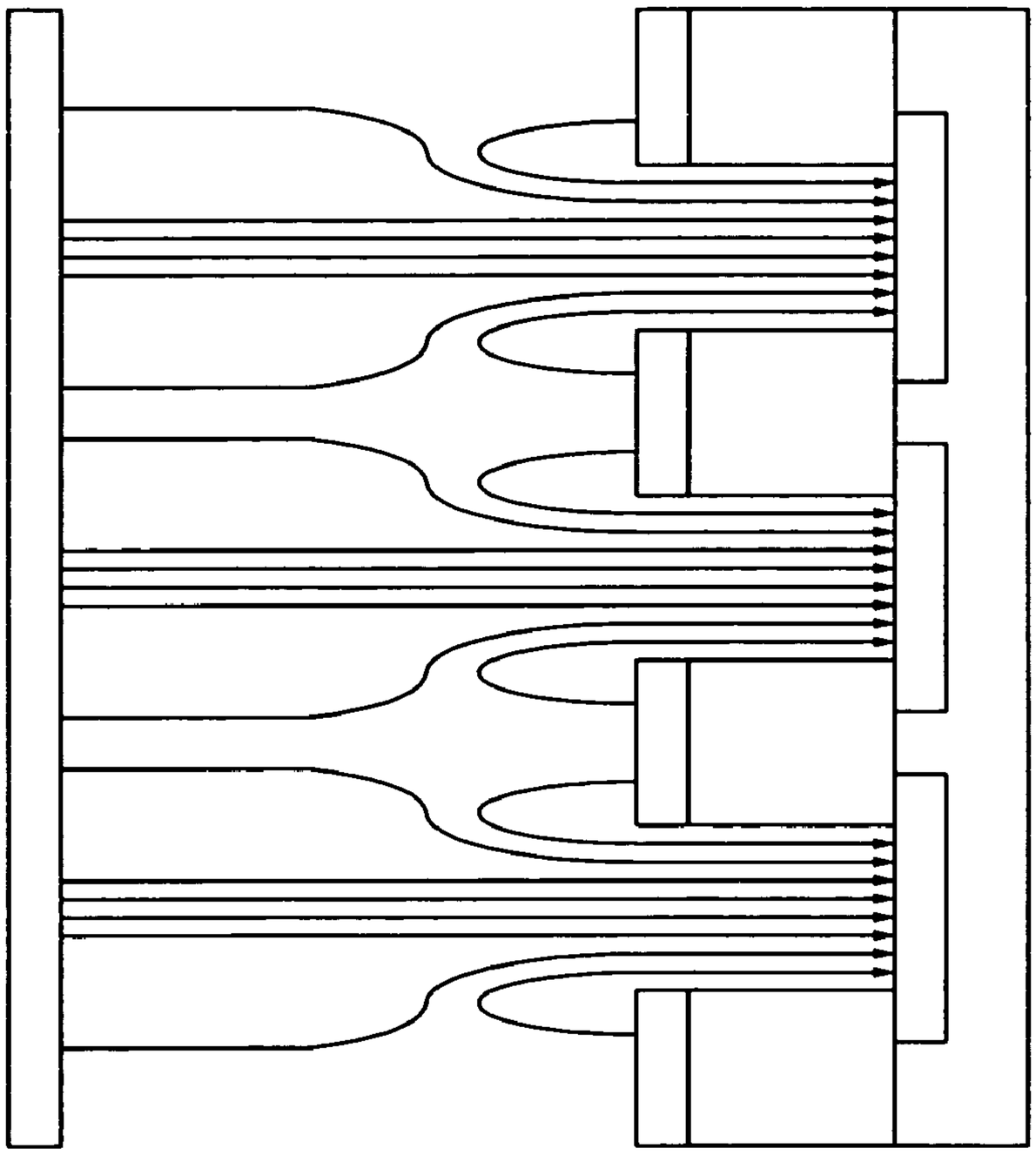


FIG. 3

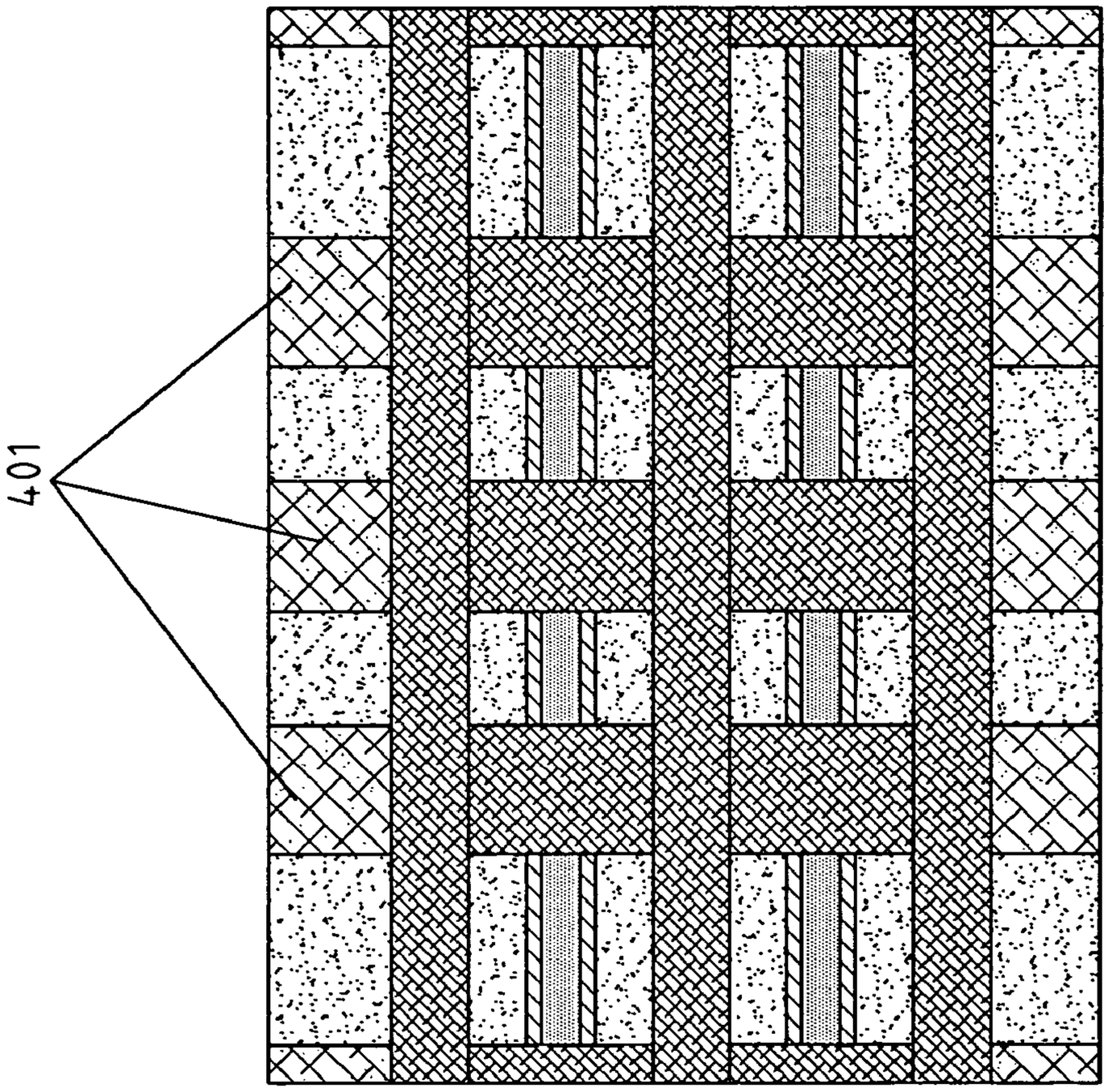


FIG. 4a

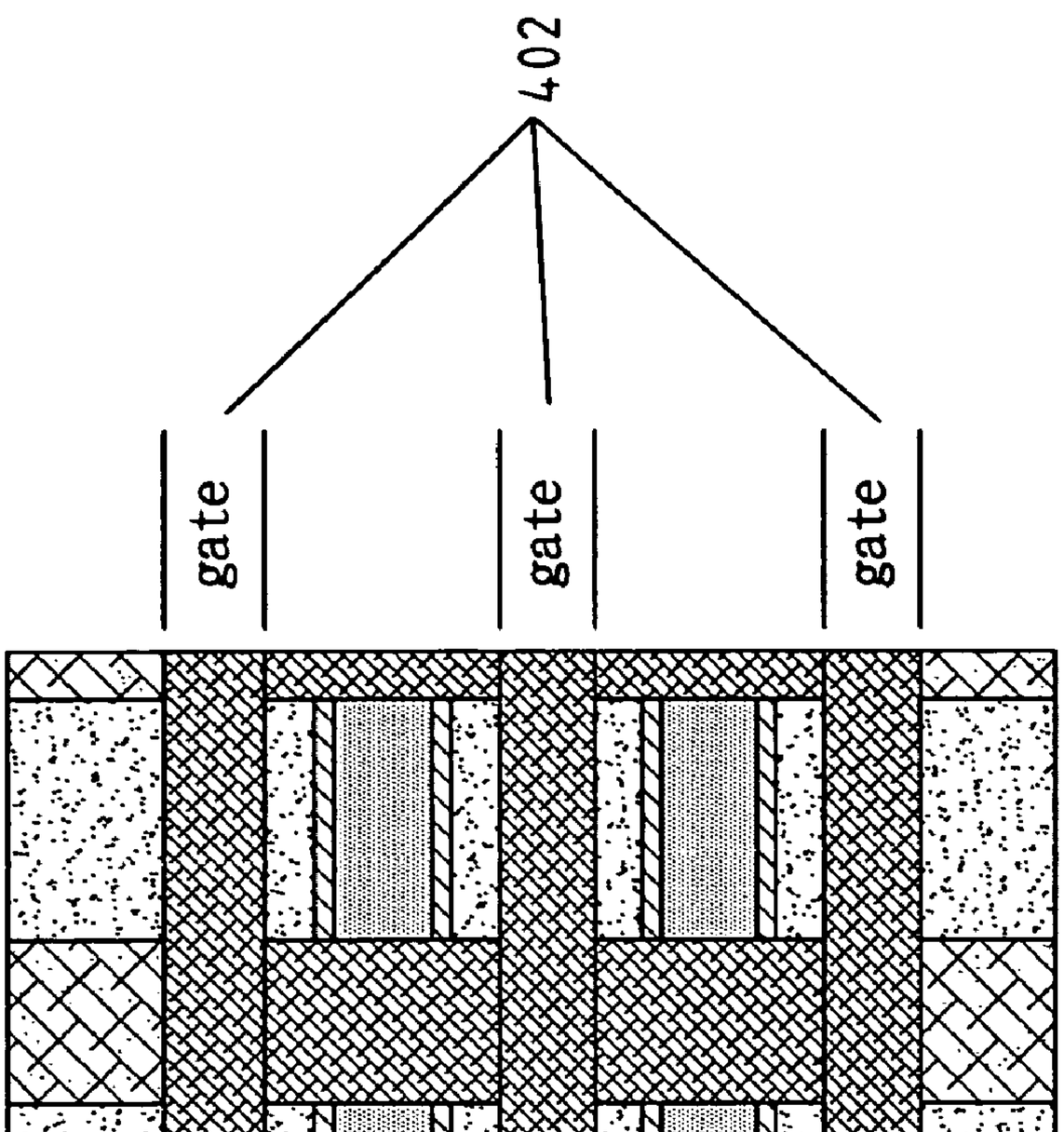


FIG. 4b

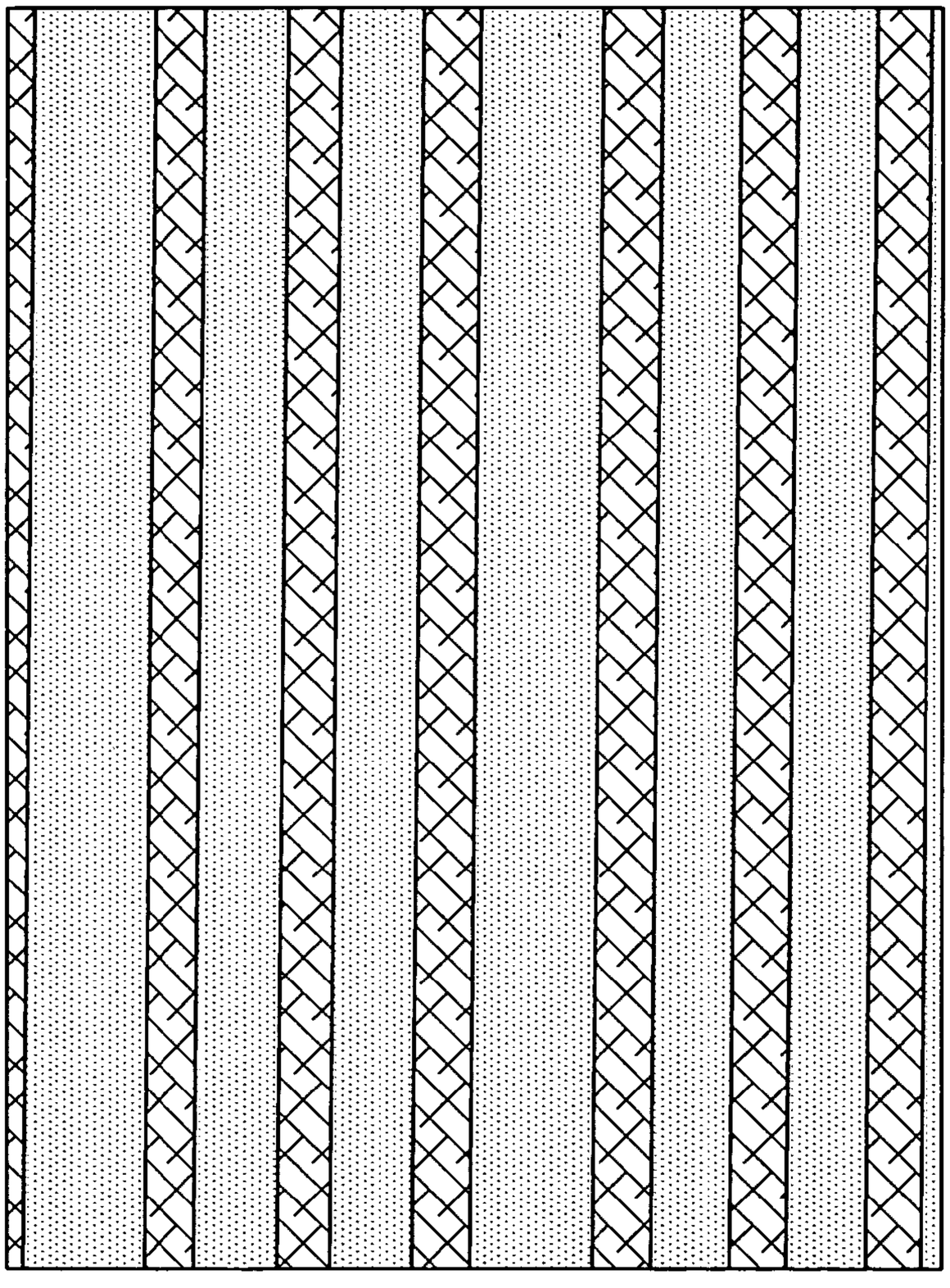


FIG. 4c

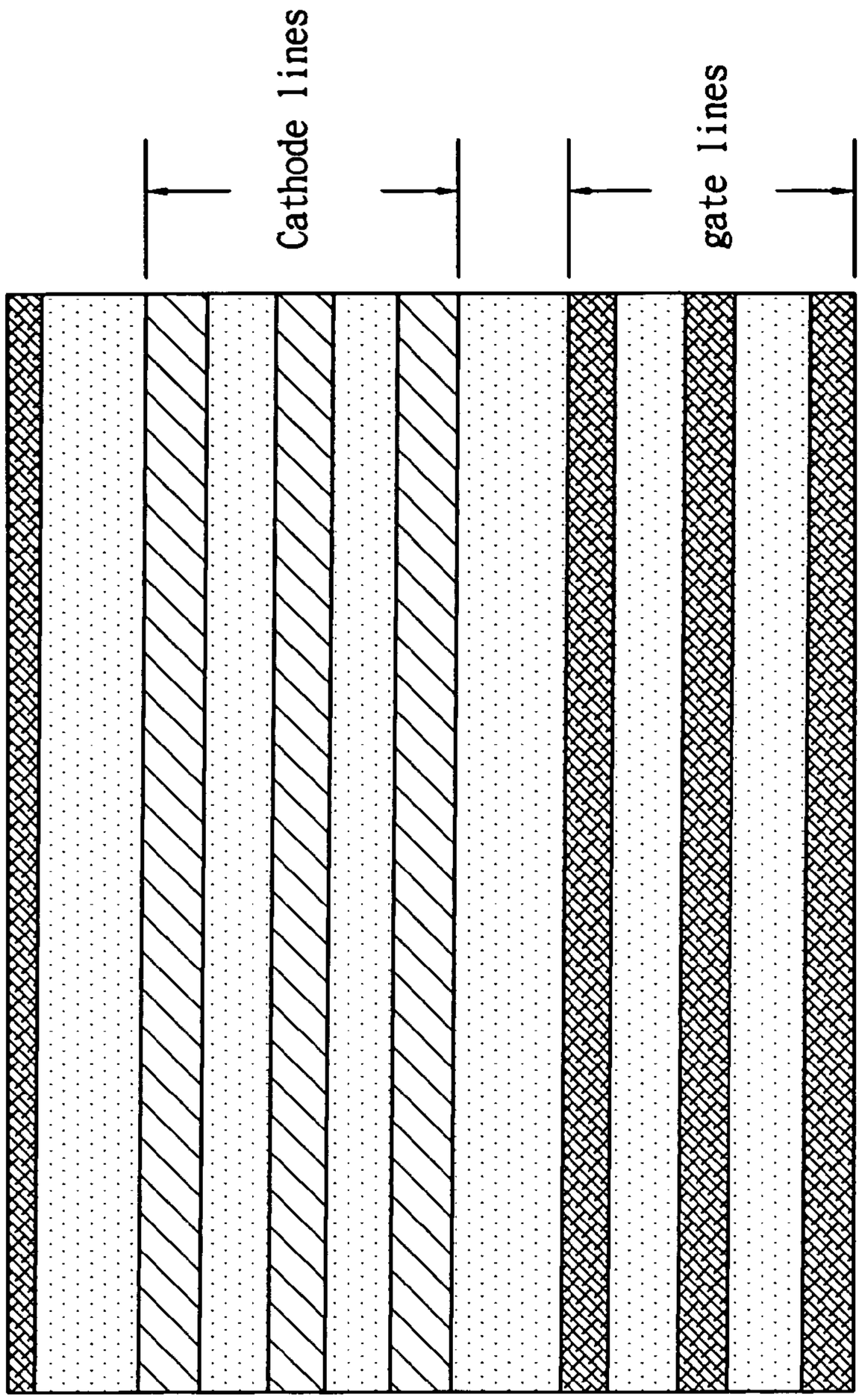


FIG. 4d

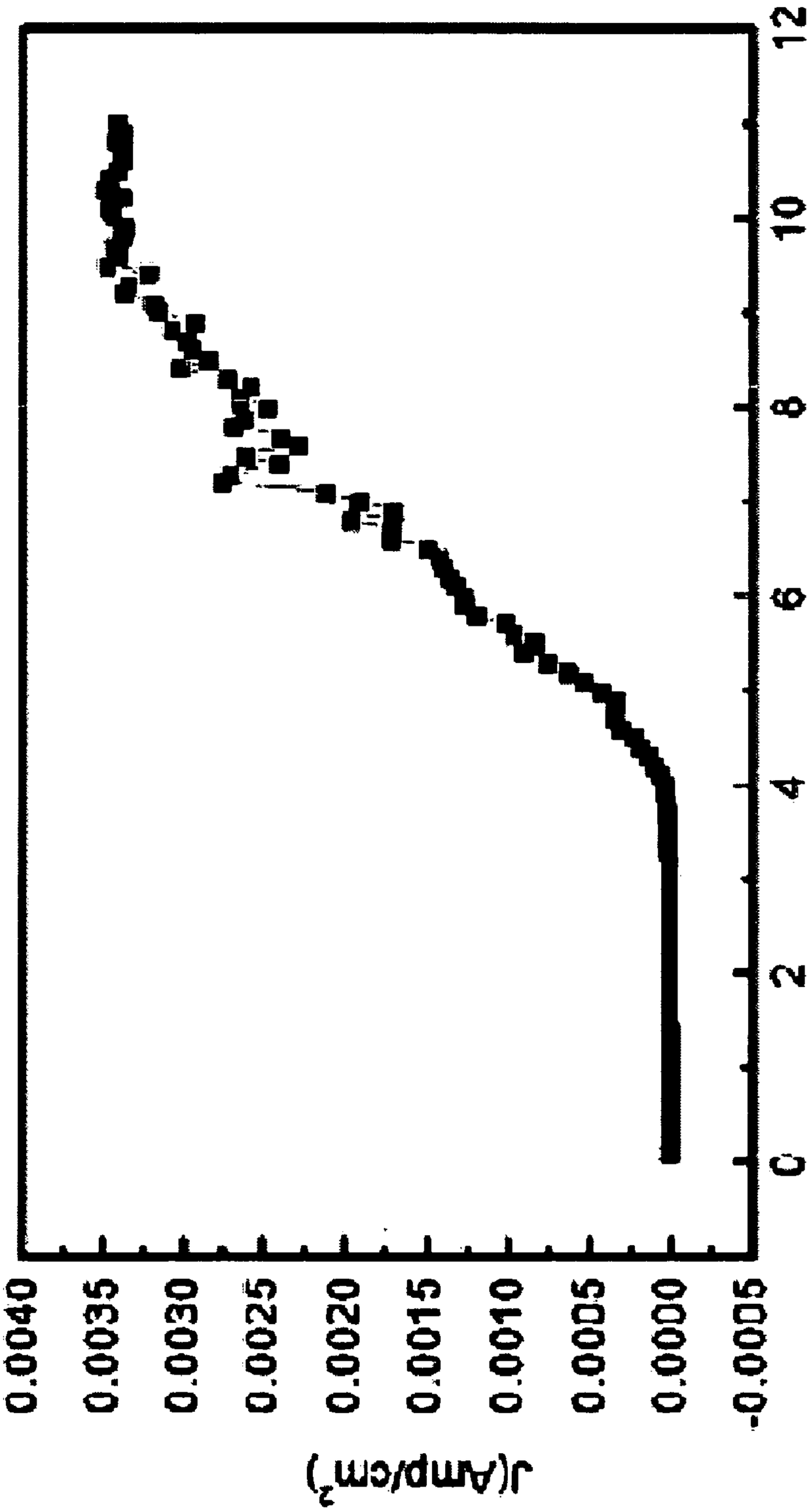

J(Amp/cm²)
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
E (volt/μm)
0
2
4
6
8
10
12

FIG.5

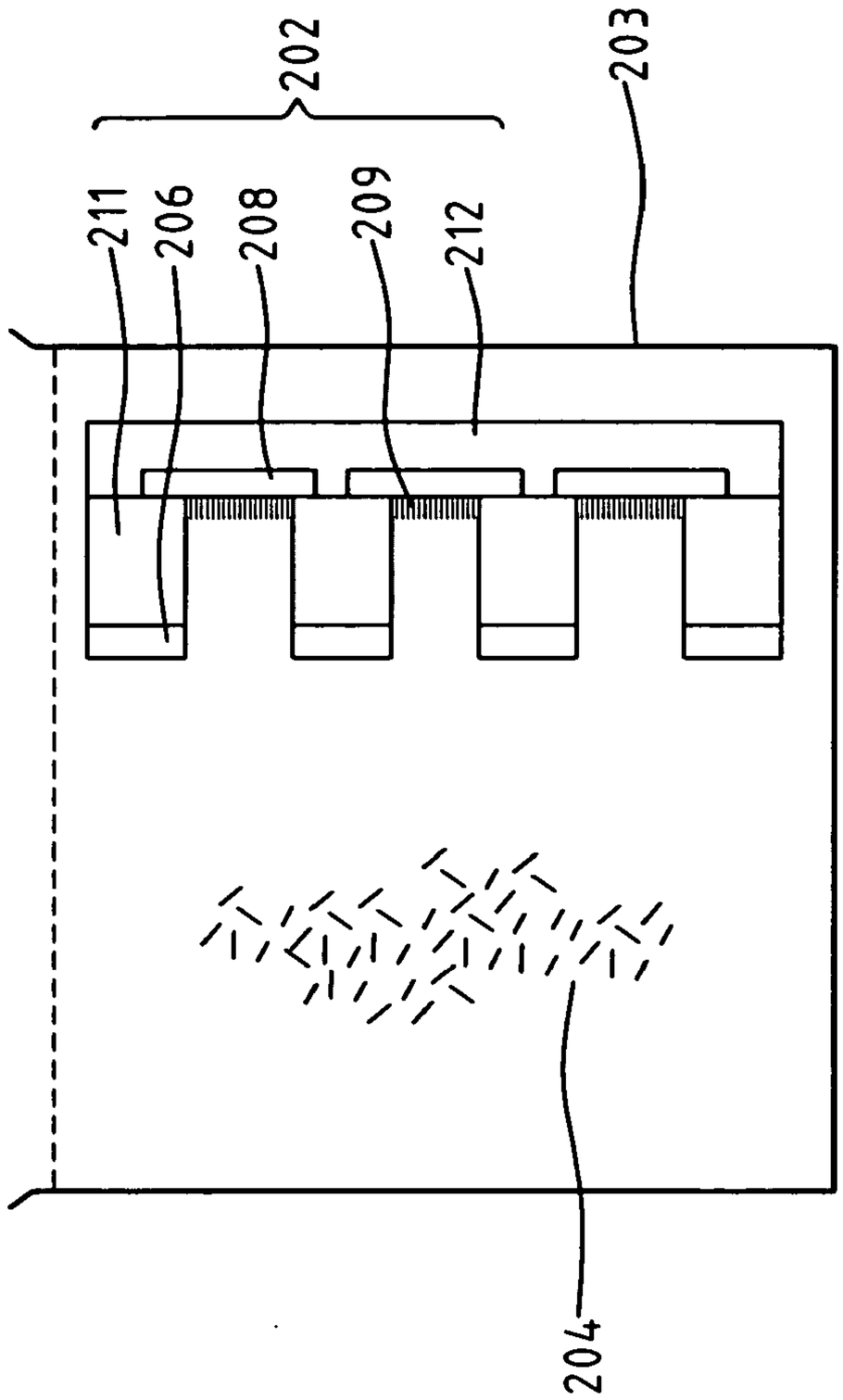


FIG. 6a

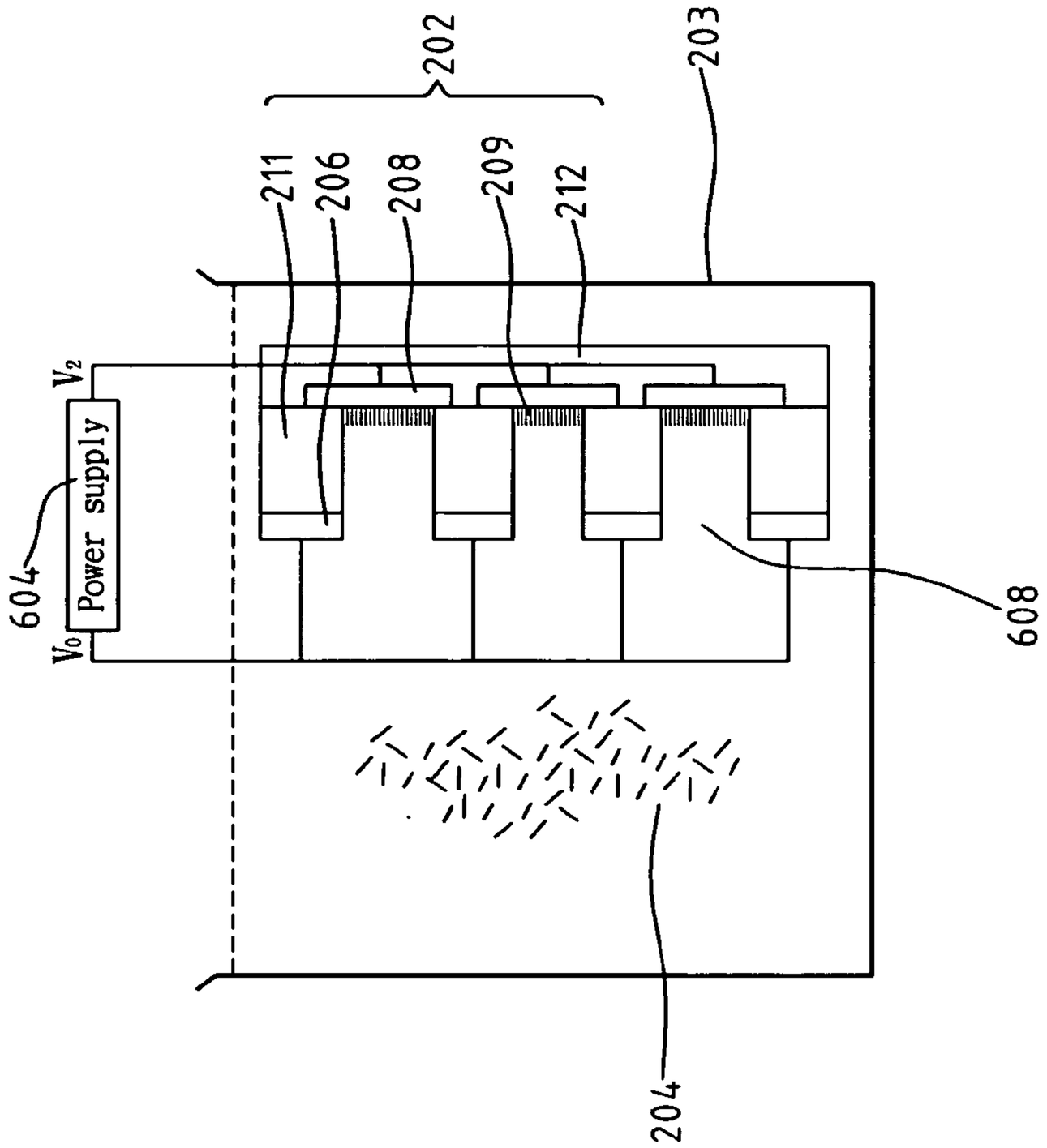


FIG. 6b

ELECTROPHORETIC DEPOSITION METHOD FOR A FIELD EMISSION DEVICE

FIELD OF THE INVENTION

[0001] The present invention generally relates to electrophoretic deposition (EPD) of carbon nanotube (CNT), and more specifically to an electrophoretic deposition method for a field emission device.

BACKGROUND OF THE INVENTION

[0002] Nowadays, liquid crystal display (LCD) has almost become the most popular display devices. However, many researches on different kinds of display technologies are still being pursued. The use of field emitters as electron emitters for field emission displays (FEDs) is expected to increase dramatically in future generation flat displays. Unlike conventional cathode ray tubes (CRTs) that use a hot cathode electron gun, cold cathode emitter tips are used as the electron source in FEDs. When an FED device is placed in an electric field, cold cathode emitter tips aim at the phosphor-coated anode substrate and emit a bundle of electrons. The emitted electrons are accelerated by the positive voltage applied to the anode substrate, and then hit the coated phosphor on the anode to produce luminescence.

[0003] Some conventional cathode plates of field emission displays are fabricated by a screen printing method. The drawbacks of the method are poor resolution because of the limitation of the size of the screen mesh and non-uniform film thickness due to non-uniform tension of the screen. The non-uniform film thickness may lead to alignment problem at subsequent processes. Other conventional field emitters are formed with conic tips produced by a spindt technique. The above method usually results in a high turn on voltage and/or a short lifetime of the emitter tips.

[0004] In order to solve the aforementioned problems, CNT field emitters have been proposed. The CNT field emitters have far superior electron field emission characteristics, such as lower turn on voltage and larger emission current density, to any conventional field emission devices. However, formation of CNTs field emitters has been hindered by difficulties encountered in the processing of such materials. The CNTs are usually fabricated by laser ablation or arc discharge or electrochemical deposition. A post-formation method, such as screen printing and spraying, must be utilized to deposit pre-formed CNTs on a field emission substrate. Both screen printing and spraying suffer poor resolution and poor uniformity problems, and are not practical for large-scale fabrication. Though the CNTs can be grown directly on the field emission substrate by use of chemical vapor deposition (CVD) techniques, such techniques require relatively high temperatures and reactive environments in order to effectively grow the CNTs. The harsh environmental conditions severely limit the substrate materials which can be utilized during the CVD, and thus make the technique non-practical.

[0005] Therefore, CNT field emitters manufactured by photosensitive paste or EPD have been disclosed to solve the above-described problems. The method described by Hua-Chi Cheng et al in U.S. Pat. No. 6,811,457 uses a photosensitive paste and etchable dielectric material to fabricate the cathode plate of a CNT FED. The EPD method offers many advantages, such as simple process, low cost, low temperature, and feasibility of large panel production. A conventional EPD of CNT particles to form CNT field emitters was proposed by Won-bong Choi et al in U.S. Pat. No. 6,616,497 and by Otto Z. Zhou et al in US Publication 2003/0102222. In the conventional method shown in **FIG. 1**, a bias voltage from a power supply **101** was applied between two separate electrodes (anode plate **102** and cathode plate **103**) immersed in an electrophoresis bath **104** containing CNT suspension **105** to selectively deposit CNT particles **106** on the surface of the cathodes **107** exposed through the gate holes **108** of the dielectric film **109**. The cathode plate **103** comprises a substrate **110**, a dielectric film **109**, a plurality of cathodes **107**, a plurality of gates **111**, and CNT particles **106**. Under an applied electric field in the bath **104**, one dimensional nanostructure materials (such as nanotubes, nanorods and linear polymers) are easily polarized along their longitudinal axis forming polarized dipoles, and these polarized dipoles can drift along the direction of the dielectrophorectic force.

[0006] Additives can be added to the electrophoresis bath to charge the nanostructure materials (e.g., CNT particles) and to facilitate electrophoretic deposition. The nanostructure materials charged by positive ions in the nanostructure suspension drift along the direction of the electrical force created by the voltage difference between the electrodes. The drawback of the method is that the selectivity of the deposition may not good enough to prevent the top area or sidewall of the gate **111** from CNT particle deposition. This sidewall deposition will result in an electrical short circuit between gate **111** and cathode **107**. One way to solve the above problem is to use a masked sacrificial layer (e.g., photoresist) protecting or covering the gate **111** during the deposition process. The sacrificial layer and the CNT particles on the top and sidewall of the gate **111** are removed after EPD. This method requires an additional photolithographic process and thus complicates the manufacturing process and increases the manufacturing cost.

SUMMARY OF THE INVENTION

[0007] The electrophoretic deposition method of the present invention uses a triode structure having gates and a proper arrangement of applied voltages to improve the selectivity of the conventional EPD method.

[0008] In a preferred embodiment of the present invention, two different bias voltages are applied to the gate and the cathode with respect to the anode. In general, the electrophoretic deposition method for a field field emission device according to the preferred embodiment of the present invention comprises the following steps: (a) preparing an electrophoresis bath containing nanostructure suspension, (b) preparing a field emitter plate with a triode structure having gates, wherein the field emitter plate acts as a cathode plate and comprises a substrate, plural cathodes on the substrate, a dielectric film on the substrate and the cathodes, and plural gates on the dielectric film and the substrate, (c) immersing an anode plate and the field emitter plate in the electrophoresis bath, and (d) applying two different bias voltages for a certain period of time to said gates and said cathodes, respectively, to selectively deposit nanostructure materials on the surfaces of said cathodes exposed through the gate holes of the dielectric film.

[0009] In the first embodiment, during a selective electrophoretic deposition, a positive voltage is applied to the gates

and a negative voltage is applied to the cathodes while the anode plate is kept at a common voltage.

[0010] In another embodiment of the present invention, a bias voltage is applied between the gates and the cathodes during a selective electrophoretic deposition. In the embodiment, the electrophoretic deposition method for a field emission device comprises the same steps of (a) and (b), and two following different steps. Instead of the mentioned-above steps (c) and (d), this second embodiment immerses the field emitter plate in the electrophoresis bath, then applies a bias voltage between the gates and the cathodes for a certain period of time to selectively deposit nanostructure materials on the surfaces of said cathodes exposed through the gate holes of the dielectric film.

[0011] The electrophoretic deposition method for a field emission device of the present invention not only has the advantages offered by the conventional EPD method but also provides a better selectivity of deposition than the conventional EPD method. It is performed at low temperature and does not require a masked sacrificial layer, and therefore keeps the manufacturing process simple and the cost down.

[0012] The foregoing and other objects, features, aspects and advantages of the present invention will become better understood from a careful reading of a detailed description provided herein below with appropriate reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] **FIG. 1** is a schematic view illustrating a CNT field emitter formed by a conventional electrophoretic deposition.

[0014] **FIGS. 2*a*-2*d*** illustrate the steps of an electrophoretic deposition method for a field emission device according to a first embodiment of the present invention.

[0015] **FIG. 3** is a schematic drawing of electrical field distribution in the electrophoresis bath shown in **FIG. 2**.

[0016] **FIG. 4*a*** shows a magnified schematic top view of the cross-type cathode plate of a field emitter before a selective EPD according to the present invention.

[0017] **FIG. 4*b*** shows a magnified schematic top view of the cross-type cathode plate of a field emitter after a selective EPD according to the present invention.

[0018] **FIG. 4*c*** shows a magnified schematic top view of the parallel-type cathode plate of a field emitter before a selective EPD according to the present invention.

[0019] **FIG. 4*d*** shows a magnified schematic top view of the parallel-type cathode plate of a field emitter after a selective EPD according to the present invention.

[0020] **FIG. 5** is a plot of the measured electron field emission current versus the applied voltage from a CNT field emitter according to the present invention.

[0021] **FIGS. 6*a*-6*b*** illustrate the steps of an electrophoretic deposition method for a field emission device according to another embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] The present invention combines thick-film printing technique and photolithographic technology to construct a triode structure having gates for electrophoretic deposition. Then, the arrangement of applied voltages during the electrophoretic deposition and the solution in the electrophoresis bath are properly chosen to deposit nanostructure materials on the selective area of a substrate. The substrate can be a field emission substrate used as a field emitter in an FED device.

[0023] Filtration or purification of the nanostructure materials prior to EPD is recommended in order to enhance the performance of the filed emitter. The solution in the electrophoresis bath contains a solution base and additives. Deionized (DI) water or acetone or isopropyl alcohol (IPA) can be used as the solution base. Various additives have been proposed in the literature. These additives include Benzalkonium Chloride, $Mg(NO_3)_26H_2O$, AOT (bis(1-ethylhexyl) sodium sulfosuccinate), Tritron X-100, Na_2CO_3 and nitrate with $Mg(OH)_2$ or $Al(OH)_3$ or $La(OH)_3$. Either direct current (DC) or alternating current (AC) power supplies can be utilized. According to the present invention, the cathode plate was immersed in the Tritron solution for about 10 minutes before EPD to enhance the adhesion of nanostructure materials (e.g., CNT particles) on the surface of the cathode. Moreover, 1 ppm Na_2CO_3 was chosen as the additive to a DI water solution with 50 ppm of CNTs to improve the electrophoretic efficiency. The conductivity of the solution increased from 0.444 ms/m to 0.702 ms/m. EPD temperature was maintained at about 50 Celsius degrees.

[0024] **FIGS. 2*a*-2*d*** illustrate the steps of an electrophoretic deposition method for a field emission device according to a first embodiment of the present invention. In the embodiment, an electrophoresis bath **203** containing nanostructure suspension **204** is first prepared, as shown in **FIG. 2a**. Next, a field emitter plate **202** with a triode structure having gates **206** is provided. The field emitter plate **202** acts as a cathode plate and includes a substrate **212**, plural cathodes **208** on the substrate **212**, a dielectric film **211** on the substrate **212** and the cathodes **208**, and plural gates **206** on the dielectric film **211** and the substrate **212**, as illustrated in **FIG. 2b**. Then, an anode plate **201** and the field emitter plate **202** are immersed in the electrophoresis bath **203**, as shown in **FIG. 2*c***. Finally, as shown in **FIG. 2*d***, the electrophoretic deposition method according to the first embodiment applies a bias voltage V_1 from a power supply **205** to the gates **206** and a bias voltage V_2 from a power supply **207** to the cathodes **208** for a certain period of time to selectively deposit nanostructure materials **209** on the surfaces of the cathodes **208** exposed through the gate holes **210** of the dielectric film **211**.

[0025] Referring to **FIG. 2*d***, the anode plate **201** is electrically connected to the other two terminals of the power supplies **205** and **207**, and is kept at a common voltage V_0.

[0026] According to the present invention, the nanostructure materials may include nanotubes, nanowires, nanoparticles, carbon nanotubes, carbon nanowires, and carbon nanoparticles. The dimension of the gate holes **210** used in the embodiment was around 80 μm and the thickness of the dielectric film **211** was about 25 μm. The anode plate **201** was made of a mesh structure in order to homogenize the electrical field distribution.

[0027] **FIG. 3** is a schematic drawing of electrical field distribution in the electrophoresis bath shown in **FIGS.**

2*a*-**2***d*. The charged or polarized nanostructure materials drift along the electrical lines and then deposit on the cathode plates. The electrical field near the anode plates repels the charged or polarized nanostructure materials and thus prevents them from adhering to the anodes.

[**0028**] The bias voltage V_1 is usually, but not limited to, a positive voltage with respect to the common voltage V_0. The bias voltage V_2 is usually, but not limited to, a negative voltage with respect to the common voltage V_0. During a selective electrophoretic deposition, the charged or polarized nanostructure suspension **204** is pulled through the gate holes **210** by the electrical force from the negative cathode voltage V_2, and drifts toward the cathodes **208** and then deposits onto the surfaces of the cathodes **208**. The positive gate voltage VI repels the charged or polarized nanostructure suspension **204** and prevents the nanostructure materials from depositing in the neighborhood of the gates **206**. Therefore, the nanostructure materials **209** are selectively deposited on the cathodes **208**. Therefore, an electrical short circuit between the gates **206** and the cathodes **208** can be avoided.

[**0029**] **FIGS. 4***a* and **4***b* show a magnified schematic top view of the cross-type cathode plate of a field emitter before and after the electrophoretic deposition method according to the present invention, respectively. Vertical electrode lines are cathode lines **401**, while horizontal electrode lines are gate lines **402**. The substance between gate lines and cathode lines is a dielectric layer. A scanning electron microscope (SEM) image (not shown) of the deposited CNT particles in a gate hole on a cathode shown in **FIG. 4***b* was observed.

[**0030**] A great amount of CNTs were coated on the cathode lines. Because CNT powder was not purified in the pre-treatment, there still existed some carbon particles coated on the cathode lines. It is suggested that removal of these particles can both enhance the field emission properties and improve the vacuum situation during the panel package process.

[**0031**] **FIGS. 4***c* and **4***d* show a magnified schematic top view of the parallel-type cathode plate of a field emitter before and after the electrophoretic deposition method according to the present invention, respectively.

[**0032**] **FIG. 5** is a plot of the measured electron field emission current versus the applied voltage from a CNT field emitter according to the present invention. Referring to **FIG. 5**, the turn-on electric field intensity was as low as 4.5 volt/micron, while current density reached 3.5 mA/Vcm^2 at 9.5 volt/volt/micron. **FIGS. 4***a*, **4***b*, and **5** confirm that a good selectivity of electrophoretic deposition and a good field emission property of CNT field emitter have been achieved by the electrophoretic deposition method for a field emission device according to the present invention.

[**0033**] In another embodiment of the present invention, a bias voltage is applied between the gates and the cathodes during a selective electrophoretic deposition. The electrophoretic deposition method for a field emission device according to the second embodiment comprises the same steps illustrated in **FIG. 2a** and **FIG. 2b**, and two following different steps. **FIG. 6***a* and **FIG. 6***b* illustrate the two different steps, respectively. After having performed the steps illustrated in **FIG. 2***a* and **FIG. 2***b*, the electrophoretic deposition method for a field emission device according to the second embodiment immerses the field emitter plate **202** in the electrophoresis bath **203**, as shown in **FIG. 6***a*. It then applies a bias voltage V_2 from a power supply **604** for a certain period of time between the gates **206** and the cathodes **208** to selectively deposit nanostructure materials **209** on the surfaces of the cathodes **208** exposed through the gate holes **608** of the dielectric film **211**. The other terminal of the power supply **604**, which is held at a voltate of V_0, is electrically connected to the gates **206**. This is illustrated as **FIG. 6***b*.

[**0034**] The bias voltage V_2 is usually, but not limited to, a negative voltage with respect to the common voltage V_0. During a selective electrophoretic deposition, the charged or polarized nanostructure suspension **204** is pulled through the gate holes **608** by the electric field formed by the potential difference between the gates **206** and the cathodes **208**, and drifts toward the cathodes **208** and then deposits onto the surfaces of the cathodes **208**. The electric field around the gates **206** repels the charged or polarized nanostructure suspension **204** and prevents the charged or polarized nanostructure materials **204** from depositing in the neighborhood of the gates **206**. Therefore, the nanostructure materials **209** are selectively deposited on the cathodes **208**. An electrical short circuit between the gates **206** and the cathodes **208** can be avoided.

[**0035**] In summary, the present invention provides an electrophoretic deposition method for a field emission device through the use of selective electrophoretic deposition on the cathodes of a triode having gates. It resolves the problem of electrical short circuit between the gates and the cathodes through improvement of the EPD selectivity. In addition, it is performed at low temperature and does not require a masked sacrificial layer, and therefore keeps the manufacturing process simple and the cost down.

[**0036**] Although the present invention has been described with reference to the preferred embodiments, it will be understood that the invention is not limited to the details described thereof. Various substitutions and modifications have been suggested in the foregoing description, and others will occur to those of ordinary skill in the art. Therefore, all such substitutions and modifications are intended to be embraced within the scope of the invention as defined in the appended claims.

What is claimed is:

1. An electrophoretic deposition method for a field emission device, comprising the steps of:

(a) preparing an electrophoresis bath containing nanostructure suspension;

(b) preparing a field emitter plate with a triode structure having gates, wherein said field emitter plate acts as a cathode plate and comprises a substrate, plural cathodes on said substrate, a dielectric film on said substrate and said cathodes, and plural gates on said dielectric film and said substrate;

(c) immersing an anode plate and said field emitter plate in said electrophoresis bath; and

(d) applying two different bias voltages from one or more power supplies for a period of time to said gates and said cathodes, respectively, to selectively deposit nanostructure materials on the surfaces of said cathodes

exposed through gate holes of said dielectric film, wherein said anode plate is electrically connected to a common terminal of said power supplies.

2. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein said power supplies are direct current power supplies.

3. The electrophoretic deposition method for a field emission device as claimed in claim 1; wherein said power supplies are alternating current power supplies.

4. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein a positive voltage is applied to said gates and a negative voltage is applied to said cathodes while said anode plate is kept at a common voltage.

5. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein said nanostructure materials include nanotubes, nanowires, nanoparticles, carbon nanotubes, carbon nanowires, and carbon nanoparticles.

6. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein said field emission device is used as an electron emitter for field emission displays.

7. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein said anode plate is made of a mesh structure in order to homogenize the electrical field distribution.

8. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein said cathode plate is a cross-type cathode plate.

9. The electrophoretic deposition method for a field emission device as claimed in claim 1, wherein said cathode plate is a parallel-type cathode plate.

10. An electrophoretic deposition method for a field emission device, comprising the steps of:

(a) preparing an electrophoresis bath containing nanostructure suspension;

(b) preparing a field emitter plate with a triode structure having gates, wherein said field emitter plate acts as a cathode plate and comprises a substrate, plural cathodes on said substrate, a dielectric film on said substrate and said cathodes, and plural gates on said dielectric film and said substrate;

(c) immersing said field emitter plate in said electrophoresis bath; and

(d) applying a bias voltage from a power supply between said gates and said cathodes for a period of time to selectively deposit nanostructure materials on the surfaces of said cathodes exposed through gate holes of said dielectric film.

11. The electrophoretic deposition method for a field emission device as claimed in claim 10, wherein said power supplies are direct current power supplies.

12. The electrophoretic deposition method for a field emission device as claimed in claim 10, wherein said power supplies are alternating current power supplies.

13. The electrophoretic deposition method for a field emission device as claimed in claim 10, wherein a negative voltage is applied to said cathodes with respect to said gates.

14. The electrophoretic deposition method for a field emission device as claimed in claim 10, wherein said nanostructure materials comprise nanotubes, nanowires, nanoparticles, carbon nanotubes, carbon nanowires, and carbon nanoparticles.

15. The electrophoretic deposition method for a field emission device as claimed in claim 10, wherein said field emission device is used as an electron emitter for field emission displays.

16. The electrophoretic deposition for a field emission device as claimed in claim 10, wherein said cathode plate is a cross-type cathode plate.

17. The electrophoretic deposition method for a field emission device as claimed in claim 10, wherein said cathode plate is a cross-type cathode plate.

* * * * *