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Cathey

(54) ELECTRONIC EMITTERS WITH DOPANT GRADIENT

(76) Inventor: **David A. Cathey**, Boise, ID (US)

Correspondence Address:
TRASK BRITT
P.O. BOX 2550
SALT LAKE CITY, UT 84110 (US)

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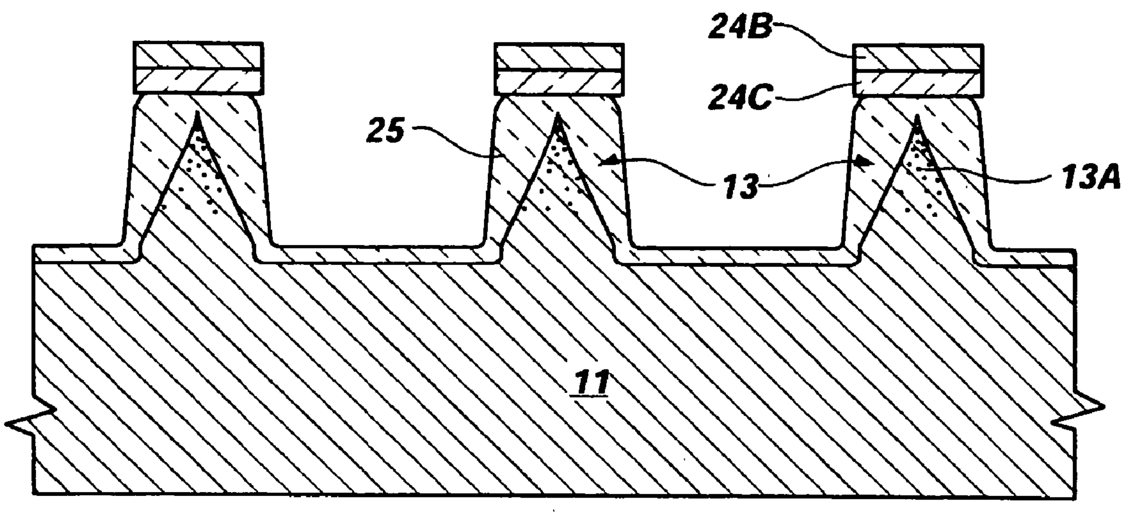
(57) **ABSTRACT**

Electron emitters and a method of fabricating emitters are disclosed, having a concentration gradient of impurities, such that the highest concentration of impurities is at the apex of the emitters and decreases toward the base of the emitters. The method comprises the steps of doping, patterning, etching, and oxidizing the substrate, thereby forming the emitters having impurity gradients.



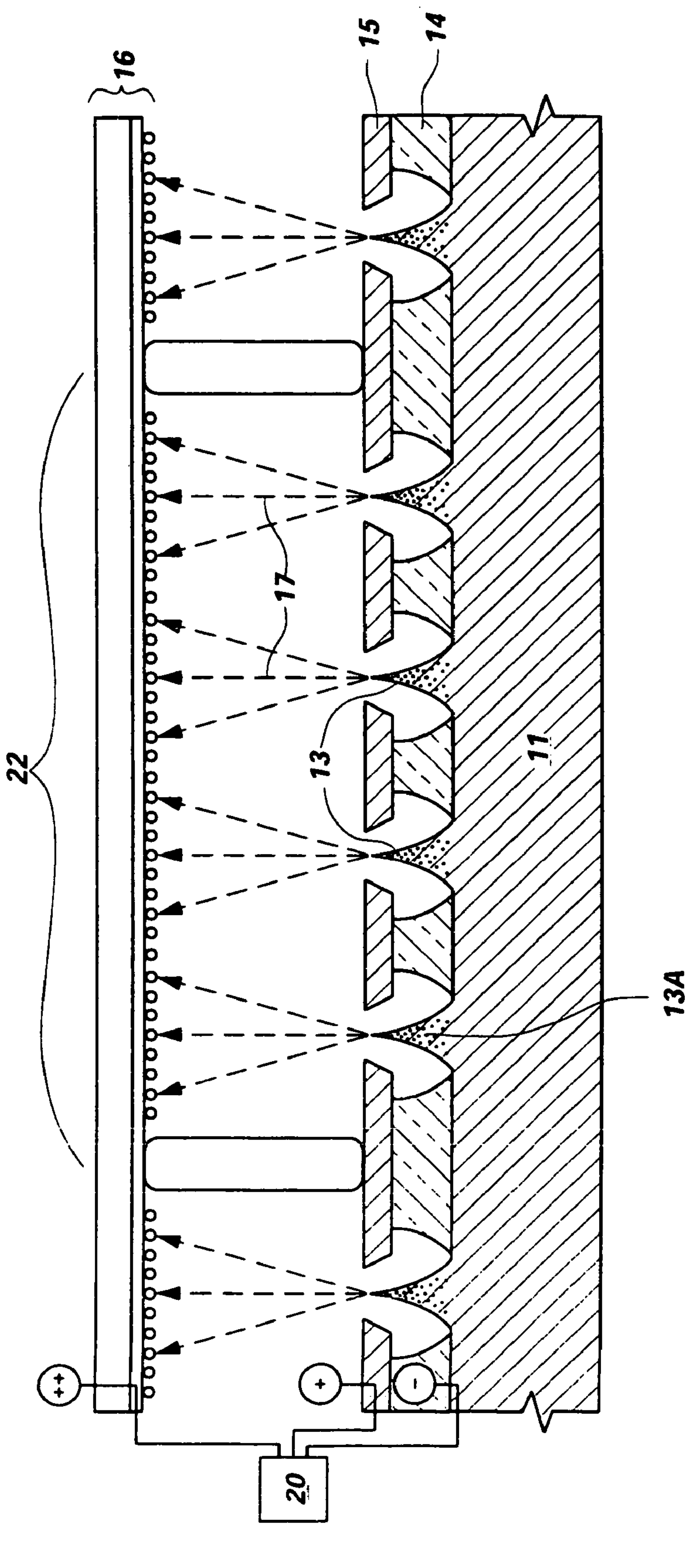


Fig. 1

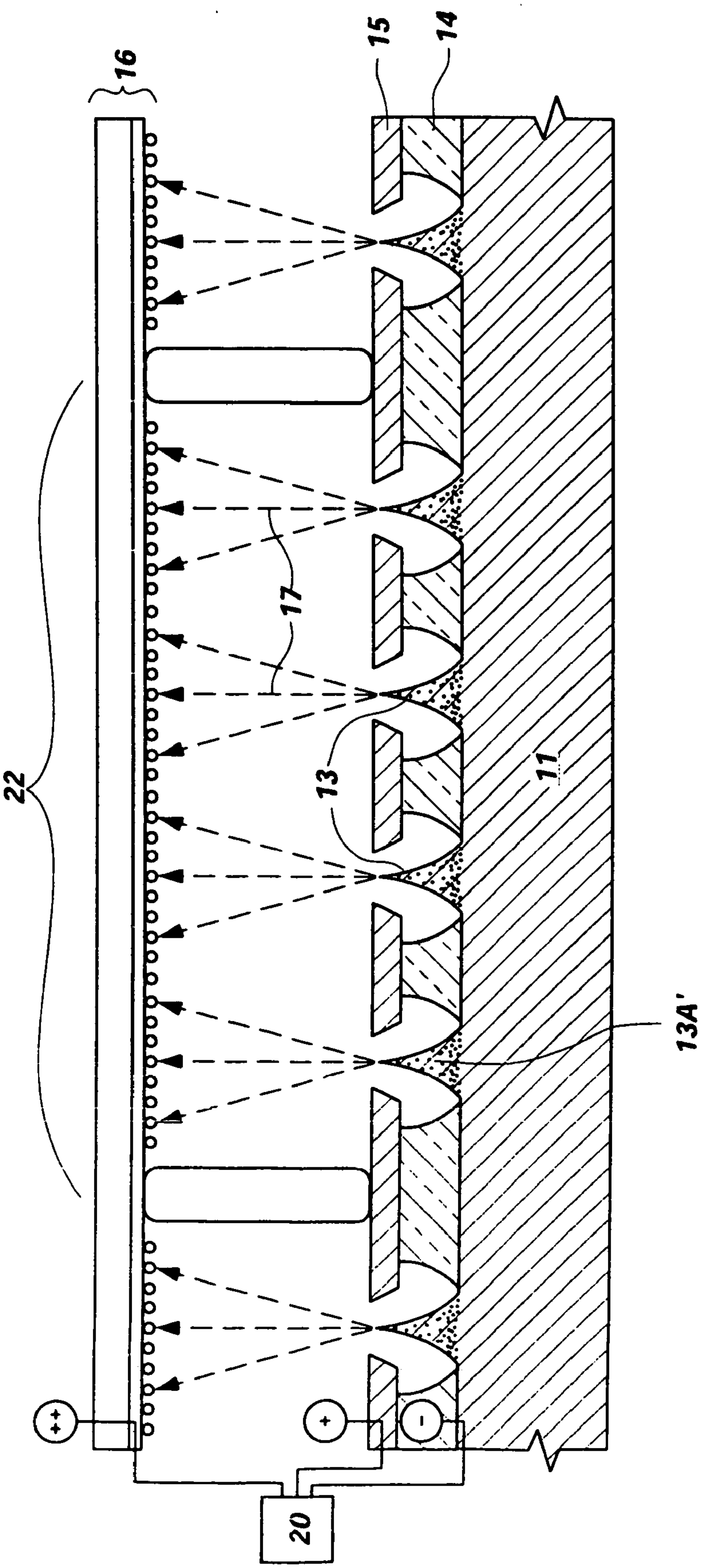


Fig. 1A

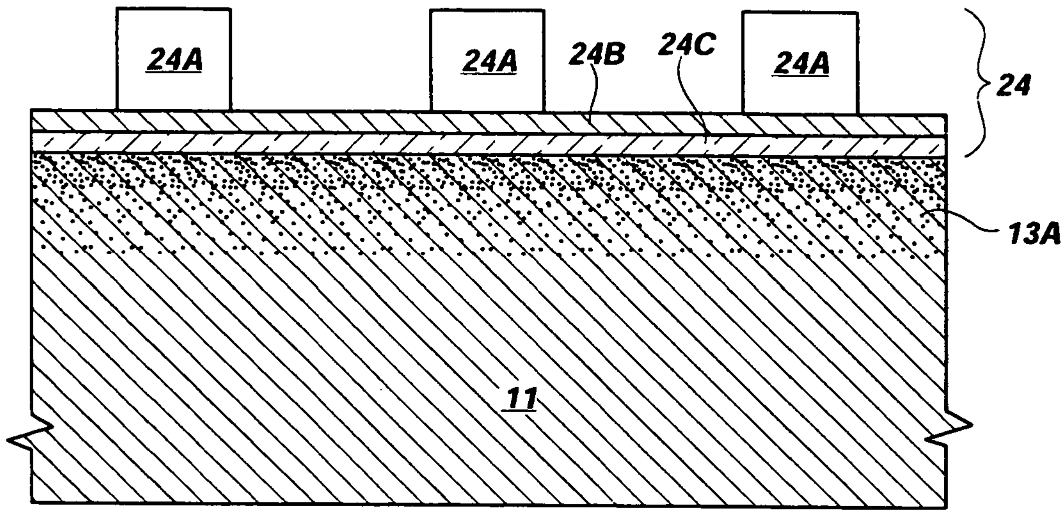


Fig. 2

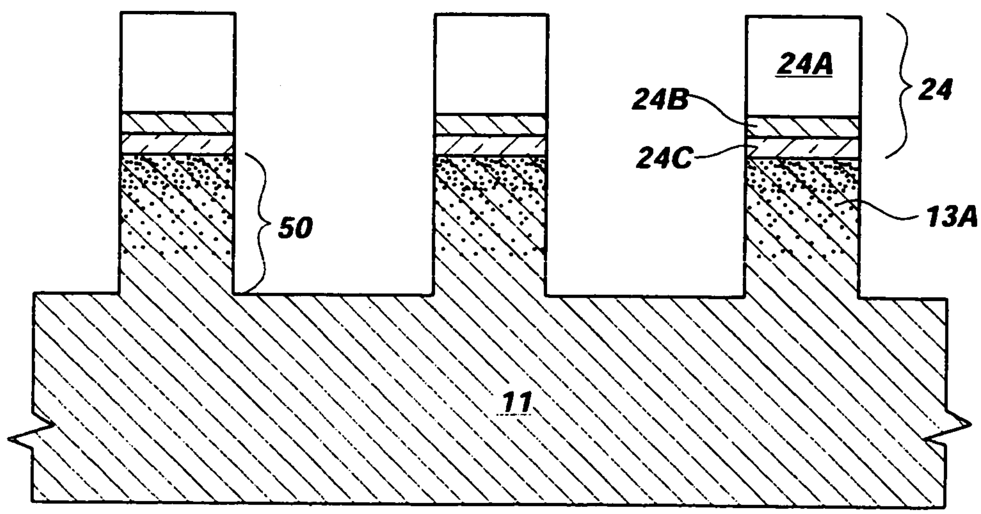


Fig. 3

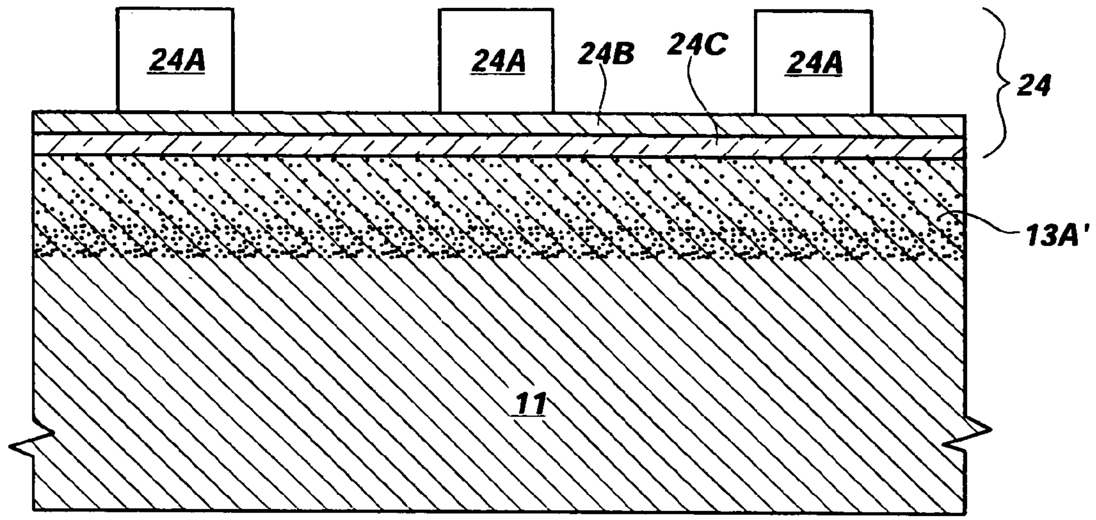


Fig. 2A

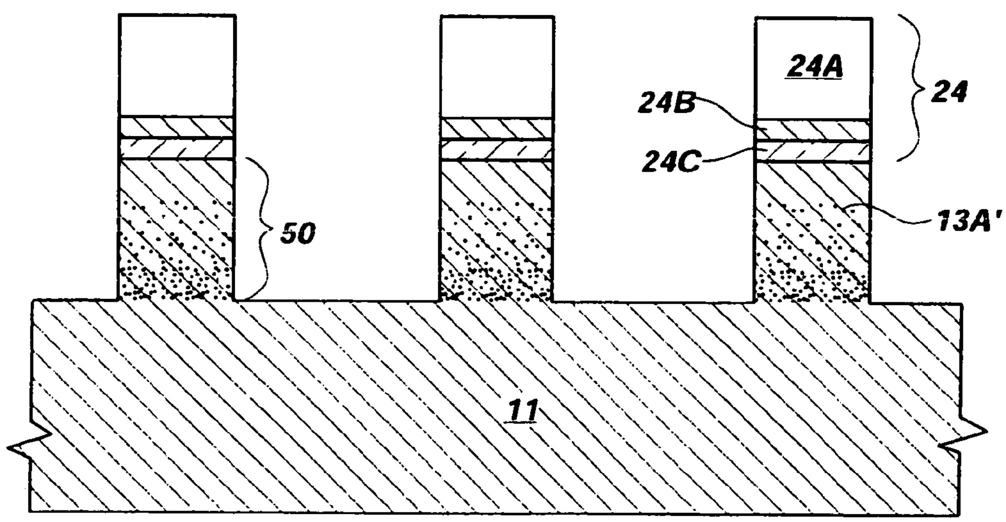


Fig. 3A

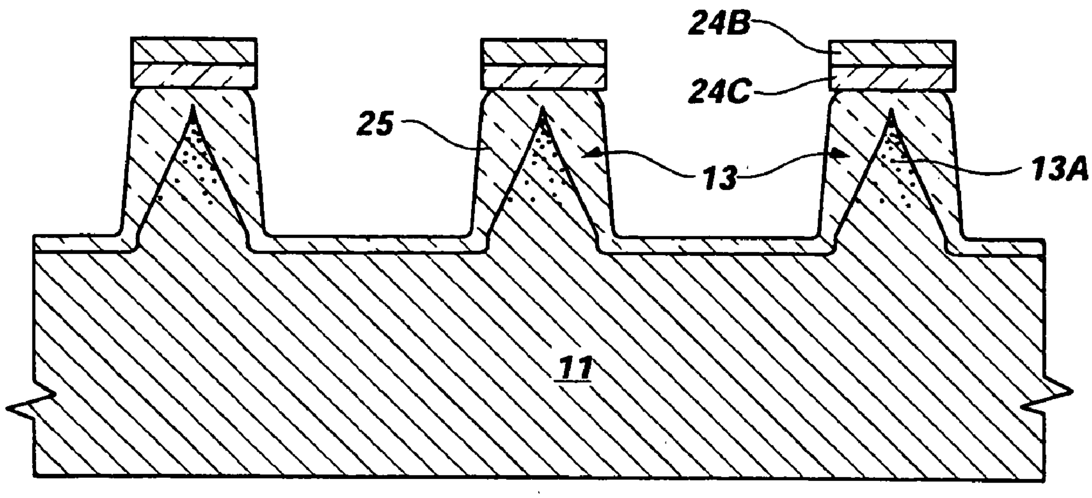


Fig. 4

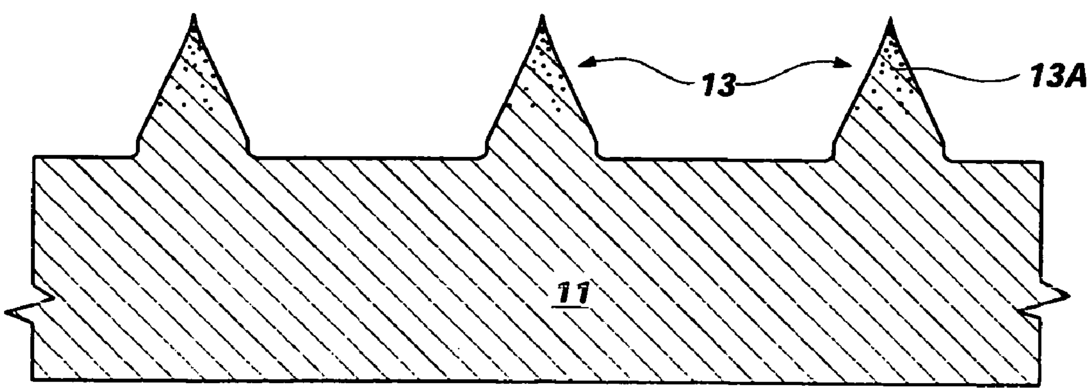


Fig. 5

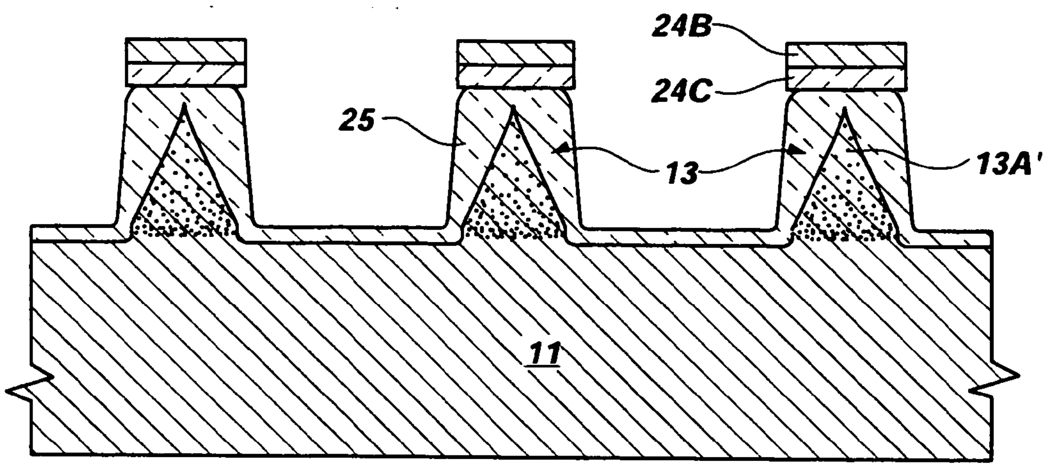


Fig. 4A

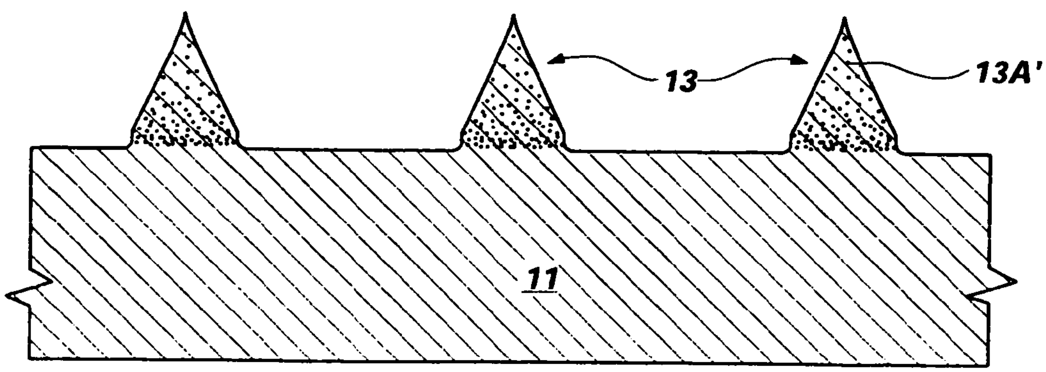


Fig. 5A

ELECTRONIC EMITTERS WITH DOPANT GRADIENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a divisional of application Ser. No. 09/759,746 filed Jan. 12, 2001, pending, which is a continuation of application Ser. No. 08/609,354, filed Mar. 1, 1996, now U.S. Pat. No. 6,825,596, issued Nov. 30, 2004, which is a divisional of application Ser. No. 08/089,166, filed Jul. 7, 1993, now U.S. Pat. No. 5,532,177, issued Jul. 2, 1996. There is a continuation application having Ser. No. 08/555,908, filed on Nov. 13, 1995, now abandoned. That application is a continuation of application Ser. No. 08/089,166, filed on Jul. 7, 1993 and issued as U.S. Pat. No. 5,532,177 on Jul. 2, 1996. Also, there is a divisional of application Ser. No. 08/609,354, which was filed on Sep. 25, 1998 as application Ser. No. 09/161,338, now U.S. Pat. No. 6,049,089 issued Apr. 11, 2000.

FIELD OF THE INVENTION

[0002] This invention relates to field emitter technology and, more particularly, to electron emitters and a method for forming them.

BACKGROUND OF THE INVENTION

[0003] Cathode ray tube (CRT) displays, such as those commonly used in desktop computer screens, function as a result of a scanning electron beam from an electron gun impinging on phosphors on a relatively distant screen. The electrons increase the energy level of the phosphors. The phosphors release energy imparted to them from the bombarding electrons, thereby emitting photons, which photons are transmitted through the glass screen of the display to the viewer.

[0004] Flat panel displays have become increasingly important in appliances requiring lightweight portable screens. Currently, such screens use electroluminescent, liquid crystal, or plasma technology. A promising technology is the use of a matrix-addressable array of cold cathode emission devices to excite phosphor on a screen.

[0005] In U.S. Pat. No. 3,875,442, entitled "Display Panel," Wasa et al., disclose a display panel comprising a transparent gas-tight envelope, two main planar electrodes that are arranged within the gas-tight envelope parallel with each other, and a cathode luminescent panel. One of the two main electrodes is a cold cathode, and the other is a low potential anode, gate, or grid. The cathode luminescent panel may consist of a transparent glass plate, a transparent electrode formed on the transparent glass plate, and a phosphor layer coated on the transparent electrode. The phosphor layer is made of, for example, zinc oxide which can be excited with low-energy electrons.

[0006] Spindt et al., discuss field emission cathode structures in U.S. Pat. Nos. 3,665,241; 3,755,704; 3,812,559; and 4,874,981. To produce the desired field emission, a potential source is provided with its positive terminal connected to the gate, or grid, and its negative terminal connected to the emitter electrode (cathode conductor substrate). The potential source may be made variable for the purpose of controlling the electron emission current. Upon application of a potential between the electrodes, an electric field is established between the emitter tips and the grid, thus causing electrons to be emitted from the cathode tips through the holes in the grid electrode.

[0007] An array of points in registry with holes in grids is adaptable to the production of gate emission sources subdivided into areas containing one or more tips from which areas of emission can be drawn separately by the application of the appropriate potentials thereto.

[0008] There are several methods by which to form the electron emission tips. Examples of such methods are presented in U.S. Pat. No. 3,970,887 entitled, "Micro-structure Field Emission Electron Source."

BRIEF SUMMARY OF THE INVENTION

[0009] The performance of a field emission display is a function of a number of factors, including emitter tip or edge sharpness.

[0010] In the process of the present invention, a dopant material that affects the oxidation rate or the etch rate of silicon is diffused into a silicon substrate or film. "Stalks" or "pillars" are then etched, and the dopant differential is used to produce a sharpened tip. Alternatively, "fins" or "hedges" may be etched, and the dopant differential used to produce a sharpened edge.

[0011] One of the advantages of the present invention is the manufacturing control and available process window for fabricating emitters, particularly if a high-aspect ratio is desired. Another advantage of the present invention is its scalability to large areas.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0012] The present invention will be better understood from reading the following description of nonlimitative embodiments, with reference to the attached drawings, wherein:

[0013] **FIG. 1** is a schematic cross-section of a field emission device in which the emitter tips or edges formed from the process of the present invention can be used;

[0014] **FIG. 1A** is a schematic cross-section of a field emission device in which the emitter tips or edges formed from the process of an alternative of the present invention can be used;

[0015] **FIG. 2** is a schematic cross-section of the doped substrate of the present invention superjacent to which is a mask, which in this embodiment, comprises several layers;

[0016] **FIG. 2A** is a schematic cross-section of another doped substrate of the present invention superjacent to which is a mask, which in this embodiment comprises several layers;

[0017] **FIG. 3** is a schematic cross-section of the substrate of **FIG. 2**, after the substrate has been patterned and etched according to the process of the present invention;

[0018] **FIG. 3A** is a schematic cross-section of the substrate of **FIG. 2A**, after the substrate has been patterned and etched according to the process of the present invention;

[0019] **FIG. 4** is a schematic cross-section of the substrate of **FIG. 3**, after the tips or edges have been formed according to the process of the present invention;

[0020] **FIG. 4A** is a schematic cross-section of the substrate of **FIG. 3A**, after the tips or edges have been formed according to the process of the present invention;

[0021] **FIG. 5** is a schematic cross-section of the tips or edges of **FIG. 4**, after the nitride and oxide layers of the mask have been removed; and

[0022] **FIG. 5A** is a schematic cross-section of the tips or edges of **FIG. 4A**, after the nitride and oxide layers of the mask have been removed.

DETAILED DESCRIPTION OF THE INVENTION

[0023] Referring to **FIG. 1**, a field emission display employing a pixel **22** is depicted. In this embodiment, the cold cathode emitter tip **13** of the present invention is depicted as part of the pixel **22**. In an alternative embodiment, the emitter **13** is in the shape of an elongated wedge, the apex of such a wedge being referred to as a "knife edge" or "blade."

[0024] The schematic cross-sections for the alternative embodiment are substantially similar to those of the preferred embodiment in which the emitters **13** are tips. From a top view (not shown), the elongated portion of the wedge would be more apparent.

[0025] **FIG. 1** is merely illustrative of the many applications for which the emitter **13** of the present invention can be used. The present invention is described herein with respect to field emitter displays, but one having ordinary skill in the art will realize that it is equally applicable to any other device or structure employing a micro-machined point, edge, or blade, such as, but not limited to, a stylus, probe tip, fastener, or fine needle.

[0026] The substrate **11** can be comprised of glass, for example, or any of a variety of other suitable materials, onto which a conductive or semiconductive material layer, such as doped polycrystalline silicon can be deposited. In the preferred embodiment, single crystal silicon serves as a substrate **11**, from which the emitters **13** are directly formed. Other substrates may also be used including, but not limited to, macrograin polysilicon and monocrystalline silicon, the selection of which may depend on cost and availability.

[0027] If an insulative film or substrate is used with the process of the present invention, in lieu of the conductive or semiconductive film or substrate **11**, the micro-cathode **13** should be coated with a conductive or semiconductive material prior to doping.

[0028] At a field emission site, a micro-cathode **13** (also referred to herein as an emitter) has been constructed in the substrate **11**. The micro-cathode **13** is a protuberance that may have a variety of shapes, such as pyramidal, conical, wedge, or other geometry, which has a fine micro-point, edge, or blade for the emission of electrons. The micro-cathode **13** has an apex and a base. The aspect ratio (i.e., height-to-base width ratio) of the emitters **13** is preferably greater than 1:1. Hence, the preferred emitters **13** have a tall, narrow appearance.

[0029] The emitter **13** of the present invention has an impurity concentration gradient, indicated by the shaded area **13**A, in which the concentration is higher at the apex and decreases towards the base.

[0030] The emitter **13** of an alternative of the present invention has an impurity concentration gradient, indicated by the shaded area **13**A', in which the concentration is lower at the apex and increases towards the base.

[0031] Surrounding the micro-cathode **13** is an extraction grid or gate structure **15**. When a voltage differential, through source **20**, is applied between the micro-cathode **13** and the gate structure **15**, an electron stream **17** is emitted toward a phosphor-coated screen **16**. The phosphor-coated screen **16** functions as the anode. The electron stream **17** tends to be divergent, becoming wider at greater distances from the tip of micro-cathode **13**.

[0032] The electron emitter **13** is integral with the semiconductor substrate **11** and serves as a cathode conductor. Gate structure **15** serves as an extraction grid for its respective micro-cathode **13**. A dielectric insulating layer **14** is deposited on the substrate **11**. However, a conductive cathode layer (not shown) may also be disposed between the dielectric insulating layer **14** and the substrate **11**, depending upon the material selected for the substrate **11**. The dielectric insulating layer **14** also has an opening at the field emission site location.

[0033] The process of the present invention, by which the emitter **13** having the impurity concentration gradient is fabricated, is described below.

[0034] **FIG. 2** shows the substrate or film **11** which is used to fabricate a field emitter **13**. The substrate **11** is preferably single crystal silicon. An impurity concentration gradient **13**A is introduced into the substrate or film **11** in such a manner so as to create a concentration gradient from the top of the substrate **11** surface, which decreases with depth down into the film or substrate **11**. Preferably, the impurity concentration gradient **13**A is from the group including, but not limited to, boron, phosphorus, and arsenic.

[0035] **FIG. 2A** shows the substrate or film **11** which is used to fabricate a field emitter **13**. The substrate **11** is preferably single crystal silicon. An impurity concentration gradient **13**A' is introduced into the substrate or film **11** in such a manner so as to create a concentration gradient from the top of the substrate **11** surface, which increases with depth down into the film or substrate **11**. Preferably, the impurity concentration gradient **13**A' is from the group including, but not limited to boron, phosphorus, and arsenic.

[0036] The substrate **11** can be doped using a variety of available methods. The impurity concentration gradient **13**A can be obtained from a solid source diffusion disc or gas or vapor feed source, such as POC**1**, or from spin-on dopant with subsequent heat treatment or implantation or CVD film deposition with increasing dopant component in the feed stream, throughout the time of deposition, either intermittently or continuously.

[0037] In the case of a CVD or epitaxially grown film, it is possible to introduce an impurity that decreases throughout the deposition and serves as a component for retarding the consumptive process subsequently employed in the process of the present invention. An example is the combination of a silicon film or substrate **11**, doped with a boron impurity concentration gradient **13**A, and etched with an ethylene diamine pyrocatechol (EDP) etchant, where the EDP is employed after anisotropically etching pillars or fins from substrate **11**.

[**0038**] In the preferred embodiment, the substrate **11** is single crystal silicon. After doping, the film or substrate **11** is then patterned, preferably with a resist/silicon nitride/silicon oxide sandwich etch mask **24** and dry etched. Other types of materials can be used to form the sandwich etch mask **24**, as long as they provide the necessary selectivity to the substrate **11**. The resist/silicon nitride/silicon oxide sandwich etch mask **24** has been selected due to its tendency to assist in controlling the lateral consumption of silicon during thermal oxidation, which is well known in semiconductor LOCOS (Local Oxidation of Silicon) processing.

[**0039**] The structure of **FIG. 2** is then etched, preferably using a reactive ion, crystallographic etch, or other etch method well known in the art. Preferably, the etch is substantially anisotropic, i.e., having undercutting that is reduced and controlled, thereby forming "pillars" in the substrate **11**, which "pillars" will be the sites of the emitter tips **13** of the present invention.

[**0040**] The structure of **FIG. 2A** is then etched, preferably using a reactive ion, crystallographic etch, or other etch method well known in the art. Preferably, the etch is substantially anisotropic, i.e., having undercutting that is reduced and controlled, thereby forming pillars **50** in the substrate **11**, which pillars **50** are depicted in **FIG. 3A** and will be the sites of the emitter tips **13** of the present invention.

[**0041**] **FIG. 4** illustrates the substrate **11** having emitter tips **13** formed therein. The resist portion **24**A (**FIG. 2**) of the sandwich etch mask **24** has been removed. An oxidation is then performed, wherein an oxide layer **25** is disposed about the emitter tip **13** and subsequently removed.

[**0042**] **FIG. 4A** illustrates the substrate **11** having emitter tips **13** formed therein. The resist portion **24**A (**FIG. 2A**) of the sandwich etch mask **24** has been removed. An oxidation is then performed, wherein an oxide layer **25** is disposed about the emitter tip **13** and subsequently removed.

[**0043**] Alternatively, an etch is performed, the rate of which is dependent upon (i.e., a function of) the concentration of the contaminants (impurities exposed to a consumptive process, whereby the rate or degree of consumption is a function of the impurity concentration, such as the thermal oxidation of silicon which has been doped with impurity concentration gradient **13**A).

[**0044**] The etch, or oxidation, proceeds at a faster rate in areas having higher concentration of impurities. Hence, the emitters **13** are etched faster at the apex, where there is an increased impurity concentration gradient **13**A, and slower at the base, where there is a decrease in the impurity concentration gradient **13**A.

[**0045**] The etch is preferably nondirectional in nature, removing material of a selected purity level in both horizontal and vertical directions, thereby creating an undercut. The amount of undercut is related to the impurity concentration gradient **13**A, **13**A'.

[**0046**] **FIG. 5** shows the emitters **13** following the removal of the nitride **24**B and oxide **24**C layers (shown in FIGS. **2-4**); preferably by a selective wet stripping process. An example of such a stripping process involves a 1:100 solution of hydrofluoric acid (HF)/water at 20° C., followed by a water rinse. Next is a boiling phosphoric acid (H_3PO_4)/water solution at 140° C., followed by a water rinse and a 1:4 hydrofluoric acid (HF)/water solution at 20° C. The emitters **13** of the present invention are thereby exposed.

[**0047**] **FIG. 5A** shows the emitters **13** following the removal of the nitride **24**B and oxide **24**C layers (shown in **FIG. 2A**); preferably by a selective wet stripping process. An example of such a stripping process involves a 1:100 solution of hydrofluoric acid (HF)/water at 20° C., followed by a water rinse. Next is a boiling phosphoric acid (H_3PO_4)/water solution at 140° C., followed by a water rinse and a 1:4 hydrofluoric acid (HF)/water solution at 20° C. The emitters **13** of the present invention are thereby exposed.

[**0048**] All of the U.S. patents cited herein are hereby incorporated by reference herein as if set forth in their entirety.

[**0049**] While the particular process as herein shown and disclosed in detail is fully capable of obtaining the objects and advantages herein before stated, it is to be understood that it is merely illustrative of the presently preferred embodiments of the invention and that no limitations are intended to the details of construction or design herein shown other than as described in the appended claims. For example, one having ordinary skill in the art will realize that the emitters can be used in a number of different devices, including but not limited to field emission devices, cold cathode electron emission devices, and micro-tip cold cathode vacuum triodes.

What is claimed is:

1. A field emission site, comprising:

an electron emitter having a base and an apex and defining a decreasing range of widths from said base to said apex;

a dopant in said emitter having a density generally inversely proportional to said range of widths; and

a generally undoped film under said electron emitter.

2. The field emission site in claim 1, wherein said dopant has a concentration generally inversely proportional to said range of widths.

3. The field emission site in claim 2, wherein said generally undoped film is directly under said electron emitter.

4. A field emission site, comprising:

a generally pure substrate; and

a cathode on said substrate having an apex and a base and defining an increasing range of widths from said apex to said base and having a purity generally directly proportional to said range of widths.

5. A cathode conductor system, comprising:

a tip further comprising:

an apex, and

a base under said apex;

a substrate indivisibly extending from said base; and

a dopant in said tip defining a concentration gradient from said apex to said base and further defining a uniform concentration under said base.

6. The electrode conductor system in claim 5, wherein said dopant defines a concentration of generally zero within said substrate.

7. An electron-source site, comprising:

a film having a generally constant first conductivity; and

an emitter over said film, having a base and an apex, and further having a plurality of conductivities including a low conductivity at said base and a high conductivity at said apex.

8. The electron-source site in claim 7, wherein said first conductivity is at most generally equal to said low conductivity.

9. The electron-source site in claim 8, wherein said film is more conductive than resistive.

10. The electron-source site in claim 9, wherein said emitter further comprises a portion between said apex and said base and having a second conductivity between said high conductivity and said low conductivity.

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