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Dresner et al.

[11] **3,710,167**

[45] **Jan. 9, 1973**

[54] **ORGANIC ELECTROLUMINESCENT CELLS HAVING A TUNNEL INJECTION CATHODE**

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[73] Assignee: **RCA Corporation**

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[52] **U.S. Cl.** ....**313/108 A,** 313/109.5

[51] **Int. Cl.** **H05b 33/02**

[58] **Field of Search**.........313/108 A, 109.5 108 D, 108 R

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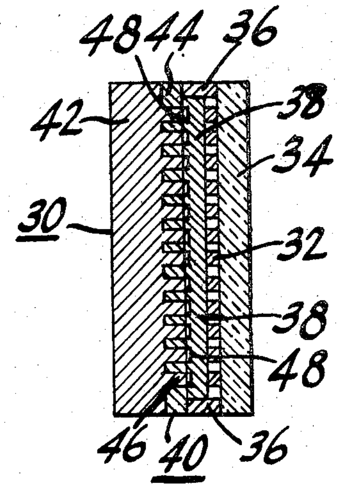
[57] **ABSTRACT**

An electroluminescent cell comprises an anthracene layer having an anode and cathode thereon. The cathode of the novel cell is of the tunnel injection type. A typical cathode consists of a 10–100 A. thick layer of silicon dioxide deposited over a degenerate n type silicon body. The silicon dioxide layer of the cathode is placed in contact with the anthracence layer. The anode should provide hole injection into the anthracence layer. A preferred anode is a film of copper oxide and copper iodide.

14 Claims, 4 Drawing Figures



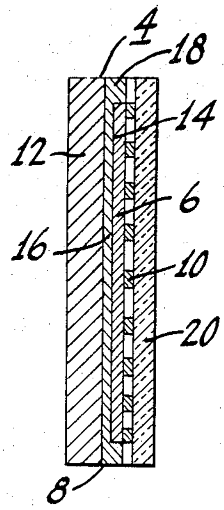


Fig. 1.

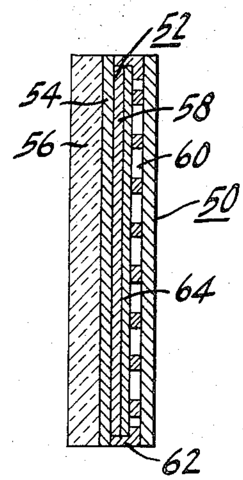


Fig. 4.

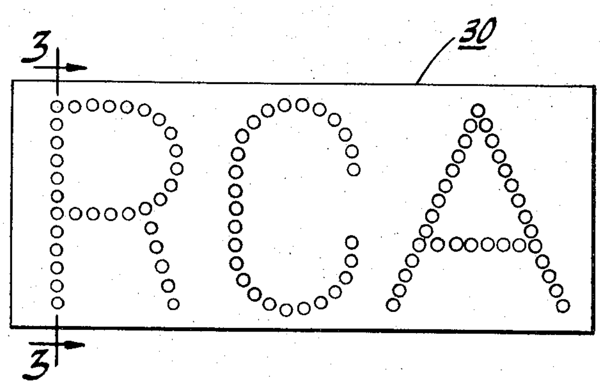


Fig. 2.

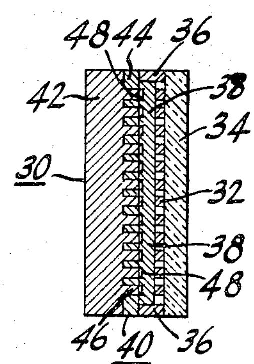


Fig. 3.

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ORGANIC ELECTROLUMINESCENT CELLS HAVING A TUNNEL INJECTION CATHODE

BACKGROUND OF THE INVENTIONO

This invention relates to improved electroluminescent cells useful as simple light sources or in display devices. It more particularly relates to electroluminescent cells which employ organic phosphors as the luminescent material.

Organic phosphor electroluminescent cells are known in the art. These prior art cells are formed from admixtures of anthracene or other organic phosphor compositions with electrically conductive materials such as metals, graphite or other forms of carbon. The admixture is deposited as a thin layer on a conductive surface. The conductive surface is typically a tin oxide coating applied to a glass substrate. The admixture is coated with an insulating layer such as glycerin and a metal electrode is provided to make electrical contact with the glycerin. Examples of these prior art cells can be found with reference to U.S. Pat. No. 3,173,050 issued to E. F. Gurnee.

Although the voltage and frequency requirements for operating the cells as described above are stated therein to offer an improvement in the then existing art, this improvement has not been sufficient to result in low cost, low voltage cells emitting a brightness which would approach commercial utility.

In order to approach commercial utility the electroluminescent cell should have a long life, improved brightness, simple construction free of shorts and for many device applications, it should be compatible with silicon technology.

SUMMARY OF THE INVENTION

An electroluminescent cell comprises a layer of an organic phosphor composition, an anode upon one surface of the layer and a tunnel-injection type cathode upon the other surface of the layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a novel electroluminescent cell.

FIG. 2 is a front elevational view of an embodiment of an electroluminescent cell having a desired luminescent pattern therein.

FIG. 3 is a cross-sectional view of the embodiment shown in FIG. 2 taken along line 3—3 thereof.

FIG. 4 is a cross-sectional view of an electroluminescent cell employing a glass support for the anode.

DETAILED DESCRIPTION OF THE INVENTION

The organic phosphor layers utilized in the present invention comprise a conjugated organic compound of condensed benzene rings. Examples of useful phosphors are anthracene, naphthalene, methyl derivatives of anthracene and anthracene doped with tetracene or other similar fluorescent dyes.

Preferably, the phosphor should be of high purity. For example, a preferred phosphor is anthracene having an electron trap density in the order of $<10^{14}$ traps/cc. The thickness of the phosphor layer should be less than 10 micrometers (μm) and preferably between 1 and 5 μm.

Unlike the cited prior art devices of Gurnee, the phosphor layer of the novel device is free of dispersed conductive particles. Such particles, if they were to exist in the novel device, would induce shorts and absorb light from the phosphor and thereby reduce the efficiency and life of the novel device.

Preferably, the phosphor layer comprises phosphor grains which are mono-crystalline in the direction of current flow. This results in a more efficient cell.

A feature of the novel cells is the use of a tunnel injection cathode for injecting electrons into the phosphor. Such a cathode comprises a base electrode material having a dielectric film of a thickness of less than about 100 A., and generally between **10–100** A., on the surface thereof. The dielectric film is in contact with the phosphor layer of the cell. Preferably the dielectric material has a dielectric constant of less than 5, but higher dielectric constant films are also suitable.

A preferred tunnel injection cathode has as the electrode material a wafer of n type silicon, preferably degenerate n type silicon. The dielectric film of this cathode is a 10–100 A. thick silicon dioxide layer on a surface of the silicon wafer. This cathode is hereinafter designated as n type $Si—SiO_2$. Another useful tunnel injection cathode consists of aluminum, such as an evaporated layer of aluminum, having a 10–100 A. thick aluminum oxide layer thereon. This cathode is hereinafter designated as $Al—Al_2O_3$.

The use of such cathodes results in devices which are easy to construct, are compatible with silicon technology, are long-lived and have improved brightness.

The anode of the device, which is a hole injecting contact, may consist of a conductive oxide, such as tin oxide, indium oxide, or a mixture of cuprous oxide and cuprous iodide; a metal, such as gold or platinum; an alloy, such as selenium-tellurium alloy; or a tunnel injecting contact such as p type silicon having a 10–100 A. thick layers of silicon dioxide thereon. Preferred anodes comprise a transparent copper oxide and copper iodide layer or a conductive oxide such as tin oxide or indium oxide coated with a very thin transparent layer of Te. A Te layer which is a few atoms thick is sufficient.

Although edge emission is possible, for most purposes and in order for the device to emit a greater amount of light, it is preferred that either the anode or the cathode or both be transparent.

Examples of a transparent anode are films of tin oxide coated with a very thin layer of tellurium (preferably a few atoms thick) or tin oxide coated with a thin layer of a copper oxide-copper iodide mixture. A transparent electrode can be obtained by forming it in a mesh-like configuration so that light is freely transmitted through the spaces in the mesh.

In order to control the thickness of the phosphor layer, spacers defining this thickness may be employed. The novel devices make possible the use of spacers which are an integral part of the electrode structure. For example, the silicon dioxide layer of the tunnel injecting cathode can be built up around the periphery of the electroluminescent cell so as to provide a spacer of several microns in thickness which is integral with the tunnel injection area (less than 100 A. thick) of the cell.

Alternatively, the cathode or anode may be formed on a glass support, either with or without a transparent conductive coating thereon, and the spacer evaporated, sputtered or otherwise formed on this structure.

Referring now to FIG. 1 there is shown a preferred novel electroluminescent cell **4**. The novel cell **4** comprises an anthracene layer **6** sandwiched between a cathode **8** and an anode **10**. The cathode comprises a degenerate n type silicon wafer **12** having a silicon dioxide coating **14** thereon. The degenerate silicon wafer typically has a resistivity in the range of 6×10^{-4} to $1\times10^{-}$ohm-cm. The silicon dioxide coating, which may be formed by any of the techniques which are well known in the art, is provided with a thin central region **16** where electron injection occurs by a tunneling mechanism. This thin region is in the order of 10 to 100 A. thick and is preferably less than 50 A. thick. The outer periphery **18** of the silicon dioxide layer is thicker than the central portion **16**. This outer periphery **18**, which has a typical uniform thickness of from 1 to 5 μm., functions as a spacer to determine the thickness of the anthracene phosphor layer **6** of the cell and to prevent shorts. A preferred technique for forming the silicon dioxide coating for tunnel injection comprises the steps of (1) cleaning the silicon wafer in a boiling ammoniated solution of hydrogen peroxide, (2) etching the cleaned wafer in concentrated HF, (3) oxidizing the etched wafer in a steam atmosphere at 1,100° C., (4) recleaning and re-etching the oxidized wafer, (5) heating the wafer for several minutes at 150° C., (6) oxidizing the wafer with water vapor at 600° C., and (7) annealing the oxidized wafer at 500° C. in a pure hydrogen atmosphere. This technique is the subject of a U.S. Patent Application filed by Alvin M. Goodman and James M. Breece.

The anthracene layer **6** may be formed by melting finely divided anthracene on the central portion **16** of the silicon dioxide layer **14** and allowing this molten material to crystallize.

The anode **10**, is provided on the anthracene layer **6** on the side opposite the cathode **8**. The anode **10** consists of a thin coating of a copper oxide-copper iodide film. This film may be deposited directly on the anthracene or alternatively it is deposited on one surface of a conducting glass flat **20** as shown. The copper oxide-copper iodide film is less than 100 A. thick. If the copper oxide-copper iodide film exceeds about 500 A. in thickness, the transmission of light therethrough is reduced such that it is preferably formed in a mesh or crossed-grid pattern so as to allow light to be efficiently emitted from the cell.

In operation, the silicon wafer **12** is connected to negative terminal of a battery and the copper oxide-copper iodide anode layer **10** is connected to the positive terminal of the battery. Electrons are injected into the anthracene layer **6** through the silicon dioxide layer **14** and holes are injected into the anthracene layer **6** from the copper oxide-copper iodide layer **10**. Recombination of electron-hole pairs occurs in the anthracene layer **6** resulting in the emission of blue light.

Although the injecting tunnel cathode is shown to comprise n type silicon, p type silicon can also be used. In fact, p type silicon has the advantage that it is easier to deposit p type silicon on glass than n type silicon, and, hence, may offer a cost advantage where the cathode is formed on a glass substrate. There is however, the disadvantage that it requires a somewhat higher voltage to operate a cell of a given configuration where the silicon is p type as compared with n type.

In FIGS. 2 and 3 there is shown another embodiment of the invention. In this embodiment, an electroluminescent cell **30** comprises a grid-like anode **32** formed on a transparent glass support **34**, and a silicon dioxide spacer **36** around the periphery of the anode support **34**. A 2–3 μm layer **38** of anthracene phosphor is disposed on the anode **32**. A cathode structure **40** is positioned over the anthracene to form the complete cell. This cathode structure **40** consists of a wafer **42** of n type silicon having a 2–3 μm thick SiO_2 layer **44** thereon. The SiO_2 layer **44** is in contact with the anthracene layer **38**. The SiO_2 layer **44** has **1** mil. diameter plugs **46** of the n type silicon extending completely therethrough. A 10–50 A. thick dielectric SiO_2 layer **48** is provided on the outer surface of each of the silicon plugs **46** so as to contact the anthracene layer **38**. The plugs are formed in a desired pattern, for example, to portray RCA as shown in FIG. 2. Electron injection into this device takes place by tunneling through the dielectric SiO_2 layer **48** on each of the silicon plugs **46**. An alternative and somewhat similar structure to that described with reference to FIGS. **2** and **3** is one in which the silicon dioxide layer **36** has an array of holes therein extending therethrough rather than silicon plugs extending through the SiO_2 layer as shown in the FIGURES. In this alternative structure, the Si layer is provided with a thin SiO_2 coating (10–100 A.) in the region of each hole and the anthracene then fills each hole.

The cell **50** shown in FIG. **4** employs an Al—Al_2O_3 cathode structure **52**. The cathode may be formed by vacuum evaporating a layer **54** of aluminum onto a glass substrate **56** and anodizing the surface of the aluminum layer **54** to form an Al_2O_3 layer **58** which is preferably from 10–50 A. thick. The cell **50** is also provided with an anode **60** having spacers **62** the same as that described with reference to FIG. **3**. An organic phosphor layer **64** is disposed between and in contact with the anode and cathode.

Where one desires light emission from the cathode side of the cell, the cathode can be formed in a thin line or mesh pattern. Such a pattern can be formed, for example, by evaporating the cathode material onto a glass substrate by standard flash evaporation or electron beam evaporation techniques through an appropriate mask.

Although the examples indicate tunnel injection cathodes comprising Al—Al_2O_3 and Si—SiO_2, it should be understood that other metal-metal oxide tunnel injection cathodes may also be useful, for example, tantalum-tantalum oxide and magnesium-magnesium oxide.

Electroluminescent cells made in accordance with the invention comprising anthracene containing tetracene therein in an amount not exceeding 5 ppm were operated at applied average fields of only approximately 2×10^5 volts/cm. across the phosphor layer. Light emission was observed at wavelengths between 4,100–5,400 A. These cells comprised a cathode consisting of a fine grid of aluminum having about a 50 A.

thick film of Al_2O_3 thereover and an anode consisting of either colloidal platinum paste, copper-copper iodide paste, silver-silver iodide paste, an evaporated conductive selenium-tellurium alloy or a conductive arsenic-tellurium alloy containing a small percentage of selenium therein. The choice of anode did not have a major effect on the efficiency of light emission from the cell but it does affect the speed of response to the applied field. For the applied fields stated above, current densities ranging from 5×10^{-3} to 5×10^{-2} amp/cm^2 have been observed. The higher current densities correspond to measured surface brightnesses of 60 foot-lamberts. This may be compared to a brightness of only 10 foot-lamberts for the blue light of a commercial color television kinescope. The quantum efficiency of these cells is between about 0.01–0.04 photons/electron.

Cells having a cathode consisting of n^+ silicon, either as a wafer or a vacuum deposited film, covered with a 20–40 A. thick film of SiO_2 and an evaporated transparent Cu_2O—CuI anode were also operated at an average field of about 2.5×10^5 volts/cm. These cells had a current density of 1.8×10^{-2} amp./cm.^{2} and a quantum efficiency of from about 0.01–0.03 photons/electron. The surface brightness of these cells was estimated to exceed 10 foot-lamberts.

What is claimed is:

1. An electroluminescent cell comprising

1. a cathode structure consisting of a base of an electrode material selected from the group consisting of silicon and aluminum and having a thick dielectric insulating layer on one surface thereof, said dielectric layer being an oxide of said electrode material, said electrode material extending through said oxide layer to the surface thereof to form a plurality of plug-like protrusions in a predetermined pattern through said oxide layer, and a thin oxide tunnel injection layer over the exposed surfaces of said plug-like protrusions, said oxide being an oxide of said electrode material,
2. a layer of an organic phosphor over and in contact with said tunnel injection layer, and
3. a light transmitting anode structure over and in contact with said phosphor layer and spaced from said cathode structure.

2. The electroluminescent cell recited in claim **1** wherein said organic phosphor composition comprises an organic compound having conjugated condensed benzene rings selected from the group consisting of anthracene, naphthalene, methyl derivatives of anthracene and anthracene doped with a fluorescent dye.

3. The electroluminescent cell recited in claim **1** wherein said organic phosphor has an electron trap density in the order of 10^{14} traps/cc. or less.

4. The electroluminescent cell recited in claim **1** wherein said phosphor layer consists of phosphor grains which are monocrystalline in the direction of current flow.

5. The electroluminescent cell recited in claim **1** wherein said dielectric has dielectric constant of less than 5.

6. The electroluminescent cell recited in claim **1** wherein said electrode material is n-type degenerate silicon and wherein said dielectric layer is SiO_2 having a thickness of from 10–100 A.

7. The electroluminescent cell recited in claim **1** wherein said anode comprises a member selected from the group consisting of a tin oxide, indium oxide, a mixture of cuprous oxide and cuprous iodide, gold, platinum, a selenium-tellurium alloy and p type silicon having a 10–100 A. thick layer of silicon dioxide thereon.

8. The electroluminescent cell recited in claim **1** wherein said anode comprises a transparent film selected from a member of the group consisting of a mixture of copper oxide and copper iodide, tin oxide and indium oxide, said film having a transparent film of tellurium thereover, said tellurium film being no more than several atomic layers thick.

9. The electroluminescent cell recited in claim **1** wherein said anode has a mesh-like configuration.

10. A cell according to claim **1** wherein said phosphor layer is less than 10 micrometers in thickness.

11. A cell according to claim **1** wherein said phosphor layer contains anthracene.

12. A cell according to claim **1** wherein said cathode is spaced from said anode by an additional thickness of the dielectric layer around the periphery of said cell, which thickness defines the thickness of said phosphor layer.

13. A cell according to claim **12** wherein said peripheral dielectric thickness is from 1 to 10 micrometers.

14. An electroluminescent devise comprising:

1. a cathode structure consisting of
   a. n type silicon having a thick silicon dioxide dielectric insulating layer on one surface thereof, said silicon extending through said silicon dioxide layer to the surface thereof to form a plurality of plug-like protrusions in a predetermined pattern through said silicon dioxide,
   b. a thin silicon dioxide tunnel injection layer over the exposed surfaces of said plug-like protrusions,
2. a layer of an organic phosphor over said tunnel-injection layer and,
3. a light transmitting anode structure over and in contact with said phosphor layer and spaced from said cathode structure.

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