PATENT SPECIFICATION

(11) 1 568 111

(21) Application Nos. 30590/75 30591/75 (22) Filed 22 July 1975 (19)

(23) Complete Specification filed 22 July 1976

(44) Complete Specification published 29 May 1980

(51) INT. CL.³ H05B 33/10

(52) Index at acceptance
H1K 1EA 2R3B 2R3E 2R3F 2S17 2S19 2S1C 2S20 2S21 2S27 2S9 2SU2 9M1 9N3 EAL.

(72) Inventors ARON VECHT
RAYMOND ELLIS

1 568 111

(54) ELECTROLUMINESCENT DEVICES

(71) We, PHOSPHOR PRODUCTS COMPANY LIMITED, a British Company of 10D Dawkins Road, Hamworthy, Poole, Dorset, BH15 4JP, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electroluminescent devices and, more particularly, to electroluminescent devices employing electroluminescence material of the type which is required to undergo a forming process in order to render it electroluminescent.

Such electroluminescent devices may be constructed by depositing on a surface of a transparent substrate of, for example, glass, a transparent layer of an electrically-conductive material such as tin oxide. The unwanted portions of this layer are then removed to provide an electrode of the desired configuration having areas defining the parts of the electroluminescent device which may be required to emit, light, a conductive strip adjacent an edge of the substrate and leads appropriately connecting the conductive strip to the said areas of the electrode. The electroluminescent layer is applied to the exposed surface of the electrode in the form of paint comprising an electroluminescent powder mixed with a suitable binder. After curing or drying of this paint, it is covered by an electrically-conductive layer of, for example, aluminium to provide the other electrode of the device and the device is then encapsulated for protection purposes. At this stage the device will not emit light and to cause such electroluminescence it must undergo a forming process which changes appropriately the structure of the electroluminescent layer. This is achieved by applying a unidirectional voltage to the device using a transparent layer as the positive electrode until the required structure is provided, causing the resistance of specific portions of the electroluminescent layer to increase, the current flow to fall and light to be emitted from the said parts. Thereafter the application of a suitably relatively low voltage cross the electrodes will cause immediate emission of light.

The function and construction of the electroluminescent layer, the process use to form the electroluminescent layer and the operation of the electroluminescent devices has been described in detail in a number of articles and other publications. Two such articles are an article entitled "Direct-Current Electroluminescence in Zinc Sulphide : State of the Art" in Proceedings of the IEEE, Vol. 61, No. 7, July 1973 at pages 902 to 907, and an article entitled "Materials control and d.c. electroluminescence in ZnS: Mn, Cu, Cl powder phosphors" in Brit. J. Appl. Phys. (J.Phys.D), 1969, Ser. 2, Vol. 2, at pages 953 to 966.

Typical forming currents are in the region of 100mA/sq.cm. with voltages of the order of 15 to 80 volts depending upon the construction and shape of the layers of the device and, in particular, the shape of the transparent electrode. For example, higher forming voltages are necessary especially when the transparent electrode has relatively long leads connecting its conducting strip to the areas of that electrode defining the light emitting parts of the device, and in these circumstances the heat dissipated in the connecting leads can cause overheating and/or cracking of the substrate, especially when the light emitting parts are relatively large, as well as burning of the transparent electrode and the electroluminescent layer.

It is an object of the present invention to provide a method of manufacturing an electroluminescent device in which the said forming thereof is achieved with relatively lower power and, in particular, substantially lower currents.

According to one aspect of the present invention a method of manufacturing an electroluminescent device comprises the steps of providing on a transparent substrate a first electrode which is transparent and on which is to be disposed a layer of electroluminescent material of the type which is electrically-conductive and which is required to undergo a forming process in order to render it electroluminescent and simultaneously increase its resistance, the said first electrode having a surface portion whose surface area remote from the substrate is to define a part of the layer of electroluminescent material that eventually will be required to emit light, the said surface portion of the first electrode having discrete regions dispersed therein within which current flow through the said surface portion is substantially confined, disposing a layer of electroluminescent material of the said type on said surface portion of said first electrode, whereby the part of said layer of electroluminescent material is to emit light is defined by said surface portion, disposing a second electrode on the surface of said layer of electroluminescent material remote from said first electrode, and applying between said first and second electrodes a unidirectional voltage to cause current to flow through the said discrete regions of the said surface portion of the first electrode and the part of the layer of elcetroluminescent material defined by the surface portion to form that part of electroluminescent material whereby that part increases in resistance and emits light.

It has been found that by providing a said surface portion less electric power than aforesaid is required to form the electroluminescent material thereby reducing the risk of damaging the substrate, the electroluminescent material and the transparent electrode during the said forming process.

The said surface portion may be at least partially of a semiconducting or insulating material.

The said surface portion may have characteristics substantially to inhibit the flow of impurities therethrough.

The said first electrode may comprise a first layer of electrically-conductive material adjacent the said substrate and a second layer of semiconductive or insulating material. In these circumstances the second layer may have apertures therein defining the said discrete regions. Alternatively, the second layer may completely cover the first layer.

In another form of the device the first electrode may comprise a metal oxide, the discrete regions thereof being provided by reducing the metal oxide. The metal oxide may be doped, the level of such dopant in the said surface portion of the first electrode being different from that in the remainder of the electrode.

Three forms of direct current electroluminescent devices and methods for their manufacture, in accordance with the present intention will now be described, by way of example, with reference to the accompanying drawsng in which:—

Figure 1 is a sectional side view of a first form of the electroluminescent device;

Figures 2 and 3 are fragmentary sectional views used to explain different constructions of the first form of the device;

Figure 4 is a sectional side view of an assembly used in the manufacture of a second form of the device;

Figure 5 is a fragmentary sectional view used to describe the second form of the device; and

Figure 6 is a diagram to explain a method of manufacturing a third form of the device.

Referring to Figure 1, the direct current electroluminescent device includes a transparent substrate 10 of glass or a polymeric material on one surface of which is provided a transparent electrically-conductive layer 11 to form the positive electrode for the device. The layer 11 may be of, for example, tin oxide doped with antimony, indium oxide, titanium dioxide, cadmium oxide doped with tin, carmium stannate, or bismuth oxide coated with gold. The tin oxide layer 11 may be formed by any of the known processes such as evaporation, sputtering or chemical vapour deposition. Alternatively electrolytic processes may be used to form the layer 11 by anodising a metal layer deposited on the substrate 10. The unwanted portions of the layer 11 are then removed by a conventional etching process to provide an electrode having areas defining the parts of the electroluminescent device which may be required to emit light, one or more conductive strips adjacent the edges of the substrate 10 and conductive tracks appropriately interconnecting the said electrode areas and the conductive strip(s).

Thereafter, in order to permit the said forming process to be achieved with reduced electric power, there is formed on the exposed surface of the electrode layer 11, by an evaporisation process, a continuous layer 12 of copper sulphide. The thickness of the layer 12 is less than 5 micron and preferably of the order of 1 micron.

Various other semiconducting or insulating materials may be used to constitute the layer 12. For example, this layer may be of zinc sulphide, copper oxide, zinc oxide, copper selenide, zinc selenide, aluminium oxide, silicone monoxide or Yttrium oxysulphide. The layer 12 is preferably one having a work function between 2ev and 6ev.

The layer 12 is covered by electroluminescent layer 13 of a powder phosphor mixture having a thickness of the order of, for example, 30 to 50 microns. This mixture comprises phosphor particles individually coated with copper and mixed with a binder, the mixture being painted on to the layer 12 to the required thickness and then cured or allow to dry. More particularly, this mixture is of the kind described in the articles referred to previously.

When this has been completed an electrically-conductive material of, for example, aluminium or copper is formed on the exposed surface of the electroluminescent layer to provide a layer 14 constituting the other electrode for the electroluminescent device.

As shown in Figure 1, the substrate 10, the electrode 11 and the layer 12 project beyond the electroluminescent layer 13 and the electrode 14 to provide a step with the upper surface of the layer 12 exposed. The electroluminescent layer 13 and the electrode 14 are covered by a sheet 16 of glass mounted on strips 17 of butyl rubber which are in turn mounted on the layer 12 to define a closed volume in which the electroluminescent layer 13 and the electrode 14 are disposed. A dessicent is disposed within this volume and the external surfaces of the sheet 16 and the strips 17 are covered by layer 18 of a suitable encapsulation material.

At this stage the electroluminescent device will not emit light when a direct voltage is applied to the electrodes constituted by the layers 11 and 14 and it is necessary to form the electroluminescent layer 13. To this end a unidirectional voltage is applied to the device using the layer 11 as the positive electrode and the layer 14 as a negative electrode to cause the required structure to be provided in the electroluminescent layer 13. At this time the resistance of the electroluminescent layer 13 increases, the current flow through the layer 13 decreases and light is emitted from the said parts of the layer 13 defined by the layer 11. Thereafter the application of a suitable relatively low unidirectional voltage of continuous or pulse form will cause immediate emission of light by the device. Conveniently when pulses are used having a mark to space ratio of the order of 1 to 200 and a repetition frequency of the order of 125KHz.

By providing between the electrode layer 11 and the electroluminescent layer 13, the layer 12 (which effectively constitutes an additional layer of the electrode) it has been found that less electric power is required to form the electroluminescent layer. As a result the risk of overheating and damaging of the substrate 10 and the layers 11 and 13 during the forming process, as herein before described, is substantially reduced. It has been found that this is due to the fact that the semiconducting or insulating layer 12 tends to modify the surface portion of the electrode 11 and confine the current flow into the surface of the electrode layer 11 to discrete regions thereof. These regions may be very small having, say, a maximum cross-sectional dimension of the order of a few microns but this dimension may be as low as 1/10 micron or even lower.

The surface of the electrode 11 remote from the substrate 10 is undulating having peaks which project towards the electroluminescent layer 13, and the continuous layer 12 may be of the two different forms shown in Figures 2 and 3. In Figure 2 the continuous layer 12 covers only the minor peaks provided by the undulating surface of the electrode 11 and has apertures through which major peaks 20 of the electrode 11 extend and electrically engage with the electroluminescent material. In this form the current flow is confined to the peaks 20. In the form of Figure 3 the continuous layer 12 completely covers the electrode 11 and the layer 12 serves to confined the current flow to the discrete regions by providing a blocking contact between the electrode 11 and the electroluminescent layer 13. The thin resistive regions of the layer 12 between the electroluminescent layer 13 and the major peaks 20 of the layer 11 constitute the discrete regions and provide preferential high field regions on the initial application of the forming voltage between the electrodes 11 and 14.

It has further been found that the layer 12 also serves to increase the life of the electroluminescent devices by inhibiting diffusion into the electroluminescent layer 13 of impurities in the substrate 10 and the electrode 11.

Although the insulating or semiconducting material constituting the layer 12 may be of many different forms, this material may be any metal chalcogenide compound, the metal of the compound being different from the metal on the electrode 11 and being compatible with the electroluminescent material. More particularly, the material of the layer 12 may be a metal chalcogenide compound comprising a metal and a chalcogenide selected from the group consisting of oxygen, sulphur and selenium.

Although in this particular form of the electroluminescent device the semiconducting or insulating layer 12 is formed separately from the layer 11, it is visualised that the layers 11 and 12 may be integral with one another. For example, the transparent electrode 11 may be deposited on the substrate 10 and then be treated so as appropriately to change the properties of the surface of the layer 11 remote from the substrate 10 so that that surface of the layer 11 exhibits the properties or characteristics of the layer 12. Alternatively the layer 11 may be formed in two distinct steps, the first step involving the forming on the substrate 10, by, for example, deposition, of a first part of the layer 11 having the necessary properties to provide a transparent electrode for the device, and the second step involving the forming of the other part of the layer 11 under the necessary conditions so that the surface portion of the layer 11 formed in this latter step has the properties or characteristics previously provided by the separate layer 12.

In a second form of the electroluminescent device a layer 11 of tin oxide doped with antimony is formed on the glass substrate 10 and a layer of aluminium is then evaporated into the surface of the layer 11. This is shown in Figure 4 in which the layer of aluminium is referenced 21. This layer 21 is then removed using a solution of stannous chloride by immersing the device in the solution. It has been found that during the removal of the aluminium layer 21, an insulation layer of aluminium oxide is formed on the surface of the tin oxide. Referring to Figure 5, which shows a portion of the assembly of Figure 4 enlarged, this insulating layer is shown at 22, the layer 22 completely covering the electrode 11 and being of constant thickness.

In a third form of the electroluminescent device a layer 11 of tin oxide doped with antimony is formed on the glass substrate 10 and the so-formed device is then immersed in an electrolyte 23 as shown in Figure 6 of, for example, tap water or a slightly acidified, distilled water. The tin oxide layer 11 is connected to a negative electrode of a power supply source (not shown) whose positive electrode is connected to an electrode 24 immersed in the electrolyte to cause an electrolytic current to flow from the electrode 24 to the layer 11. The electrode 24 is of a suitable inert material such as graphite, platinum or tin oxide.

It has been found that during both the removal of the aluminium layer 21 and the electrolytic action used respectively in the second and third forms of the electroluminescent device, discrete portions of the tin oxide layer 11 adjacent the surface thereof remote from the substrate 10 are reduced to tin to form the said discrete regions within which the current is substantially confined during the said forming process. Furthermore it is believed that during both of the reduction processes of the second and third forms of the device the ratio of antimony dopant in the surface of the layer 11 remote from the substrate 10 is changed to form an insulating surface portion on the layer 11 which seeks to inhibit the flow of impurities into the electroluminescent layer 13 from the substrate 10 and the layer 11. Also in the second form of the device this flow of impurities is further inhibited by the insulation layer 22 of aluminium oxide.

When the methods of the second and third forms of the device has been completed, the electroluminescent and conductor layers 13 and 14 are formed as previously described.

The parts of the electroluminescent devices which are to be illuminated may be excited simultaneously or sequentially. In the former case the areas of the layer 11 defining the said parts are each connected by conductive tracks to a conductive strip provided adjacent the edge of the substrate 10.

In the latter case the conductive strip may be dispensed with, individual conductive tracks being provided for the said areas of the layer 11, the tracks extending to the edge of the device to permit individual connection of the tracks to respective terminals of a voltage supply source. However, when the areas of the layer 11 are to be excited in groups, conductive strips may be provided for each group with the areas being connected to appropriate ones of the strips by conductive tracks.

Although the invention has been described with reference to d.c. electroluminescent devices it will be appreciated that the invention is equally applicable to a.c. electroluminescent devices.

WHAT WE CLAIM IS:—

1. A method of manufacturing an electroluminescent device comprising the steps of providing on a transparent substrate a first electrode which is transparent and on which is to be disposed a layer of electroluminescent material of the type which is electrically-conductive and which is required to undergo a forming process in order to render it electroluminescent and simultaneously increase its resistance, the said first electrode having a surface portion whose surface area remote from

the substrate is to define a part of the layer of electroluminescent material that eventually will be required to emit light, the said surface portion of the first electrode having discrete regions dispersed therein within which current flow through the said surface portion is substantially confined, disposing a layer of electroluminescent material of the said type on said surface portion of said first electrode, whereby the part of said layer of electroluminescent material which is to emit light is defined by said surface portion, disposing a second electrode on the surface of said layer of electroluminescent material remote from said first electrode, and applying between said first and second electrodes a unidirectional voltage to cause current to flow through the said discrete regions of the said surface portion of the first electrode and the part of the layer of electroluminescent material defined by the surface portion to form that part of electroluminescent material whereby that part increases in resistance and emits light.

2. A method according to Claim 1, wherein the said surface portion is at least partially of a semiconducting or insulating material.

3. A method according to Claim 1 or 2, wherein the said surface portion substantially inhibits the flow of impurities therethrough.

4. A method according to any one of the preceding claims, wherein the said first electrode comprises a first layer of electrically-conductive material adjacent the said substrate and a second layer of semiconducting or insulating material.

5. A method according to Claim 4, wherein the second layer has apertures therein defining the said discrete regions.

6. A method according to Claim 5, wherein the first layer projects through the said apertures.

7. A method according to Claim 4, wherein the second layer completely covers the first layer.

8. A method according to Claim 7, wherein the second layer has a work function substantially between 2ev and 6ev.

9. A method according to any one of Claims 4 to 8, wherein the second layer comprises copper sulphide.

10. A method according to any one of Claims 4 to 8, wherein the second layer comprises zinc sulphide.

11. A method according to any one of Claims 4 to 8, wherein the second layer comprises copper oxide.

12. A method according to any one of Claims 4 to 8, wherein the second layer comprises zinc oxide.

13. A method according to any one of Claims 4 to 8, wherein the second layer comprises copper selenide.

14. A method according to any one of Claims 4 to 8, wherein the second layer comprises zinc selenide.

15. A method according to any one of Claims 4 to 8, wherein the second layer comprises aluminium oxide.

16. A method according to any one of Claims 4 to 8, wherein the second layer comprises silicone monoxide.

17. A method according to any one of Claims 4 to 8, wherein the second layer comprises Yttrium oxysulphide.

18. A method according to any one of Claims 4 to 17, wherein the second layer has a thickness less than 5 microns.

19. A method according to Claim 1, wherein the said first electrode comprises a metal oxide, the discrete regions thereof being provided by reducing the metal oxide.

20. A method according to Claim 19, wherein the metal oxide is doped, the levels of such dopant in the said surface portion of the first electrode being different from that in the remainder of the first electrode.

21. A method according to Claim 19 or Claim 20, wherein the surface of the first electrode remote from the substrate is covered by a layer of insulating material.

22. A method according to any one of Claims 19 to 21, wherein the first electrode is formed by providing a transparent layer of metal oxide on the substrate, disposing a metal layer on the exposed surface of the metal oxide layer, and chemically removing that metal layer.

23. A method according to Claim 22, wherein the metal oxide is tin oxide and the said metal layer is of aluminium.

24. A method according to Claim 19 or Claim 20, wherein said first electrode is formed by immersing the substrate with the metal oxide thereon in an electrolyte and passing a current through the electrolyte from a positive electrode to the metal oxide.

25. A method according to Claim 4, wherein the said second layer of the said transparent first electrode comprises a metal chalcogenide compound, the metal of that compound being different from the metal in the said first layer and being compatible with the electroluminescent material.

26. A method according to any one of the preceding claims, wherein the electroluminescent material is of particulate form.

27. A method according to Claim 26, wherein the electroluminescent material comprises particles coated with an electrically-conductive material.

28. A method according to Claim 27, wherein the electrically-conductive material is copper.

29. A method of manufacturing an electroluminescent device substantially as hereinbefore described with reference to the accompanying drawings.

30. An electroluminescent device when manufactured by a method in accordance with any preceding claim.

For the Applicants,
E. SWINBANK,
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1980. Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained

Fig.1.

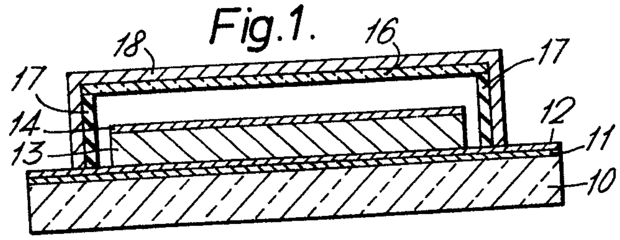

Fig.2.

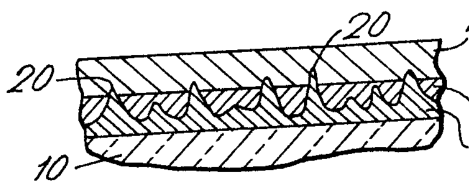

Fig.3.

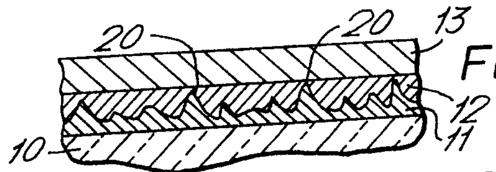

Fig.4.

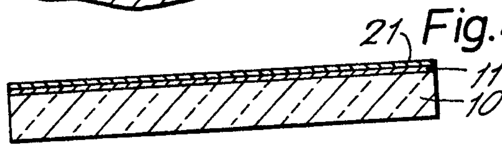

Fig.5.

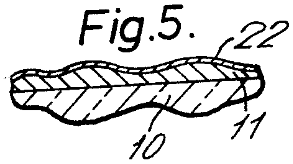

Fig.6.