

[54] **METHOD OF MAKING A DIRECT
CURRENT ELECTROLUMINESCENT
DEVICE**

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117/201

[56] **References Cited**

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[57]

ABSTRACT

A method of making a direct-current electroluminescent device in which an electroluminescent film is deposited onto a heated substrate coated with an optically transparent electrode by means of vacuum evaporation of a first substance comprising zinc sulphide doped with Mn, Cu and Cl and a second substance comprising metallic zinc in a quasi-closed volume, both substances being evaporated simultaneously and each substance being evaporated from a separate evaporator. The temperature of the evaporator containing the first substance comprising zinc sulphide doped with Mn, Cu and Cl is maintained within a range enabling the first substance to evaporate at a specified rate, while the temperature of the separate evaporator containing the second substance of metallic zinc is maintained within a range enabling the second substance to evaporate at a specified rate, thereby enabling the desired concentration of zinc to be deposited onto said film. A metal electrode is deposited onto the obtained film by means of vacuum evaporation.

3 Claims, No Drawings

METHOD OF MAKING A DIRECT CURRENT ELECTROLUMINESCENT DEVICE

The present invention relates to methods of manufacture of electroluminescent devices and, more particularly, to methods of making direct-current electroluminescent devices utilized in optoelectronics, automatic systems, and computers.

Known in the art is a method of making a direct-current electroluminescent device.

According to the known method, the electroluminescent devices are manufactured by (1) depositing an electroluminescent film onto a substrate heated to a temperature of 290°–500°C, which substrate is coated with a layer of SnO₂ (optically transparent electrode), by means of vacuum evaporation of zinc sulphide doped with manganese; and then (2) depositing a metal electrode onto the obtained film by means of vacuum evaporation. The evaporated substance is usually either in the form of (1) a powdery ZnS doped with Mn forming an excess of Zn obtained by firing a mechanical mixture of ZnS and metallic manganese in a flow of nitrogen at 1,110°C during 3 hours, and then adding 1% of metallic zinc to the powder after the firing, or (2) crystals of ZnS doped with Mn grown from a melt and containing excessive zinc.

In such films the electroluminophore is not uniformly doped with zinc throughout the film thickness. This is explained by the fact that Zn and ZnS have different evaporation temperatures (400° and 1,100°C, respectively), and that during the evaporation of a mixture of these substances from a single evaporator the first portions of the evaporated substance contain mainly zinc, while the last portions thereof contain substantially ZnS. The non-uniform distribution of zinc throughout the thickness of the film and its uncontrollable content in the film—as in the case of evaporating crystals or a powdery, mechanical mixture of ZnS doped with Mn and Zn—are responsible for the uncontrollable and poor reproducible properties of the film.

The electroluminescent films obtained by means of the known method feature extremely low brightness (10⁻⁸ foot-lamberts 3.5 10⁻⁸ nits) even at a considerable voltage (up to 100 volts), and, therefore, as a practical matter, they cannot be used in the manufacture of electroluminescent devices.

In addition, the known method is disadvantageous in that production costs are higher because a number of labor consuming operations are necessary to make the material to be evaporated. Moreover, the present method permits the temperature of the substrate to be reduced from 290°–500°C to 250°–300°C.

An object of the present invention is to provide a method of making a direct-current electroluminescent device which allows one to increase the reproducibility of the parameters of the manufactured devices, to increase the brightness thereof, and to increase the life of the electroluminescent devices within the range of rated brightness (~20 nits).

This object is attained by the present invention, which provides a method of making a direct-current electroluminescent device in which, zinc sulphide doped with Mn, Cu and Cl and metallic zinc are simultaneously evaporated in a quasi-closed volume, each substance being evaporated from a separate evaporator, whereby the temperature of the evaporator in which the zinc sulphide doped with Mn, Cu and Cl is

contained is maintained within that range commensurate with the specified rate desired of this substance, while the temperature of the evaporator in which the metallic zinc is contained is maintained within that range required to provide a predetermined concentration of zinc in the luminophore film.

Thus, according to a preferred embodiment of the present invention, an electroluminescent film is deposited by means of vacuum evaporation — onto a heated, 250°–300°C substrate covered with a conductive layer and disposed in a quasi-closed volume — of vaporous: zinc sulphide doped with manganese, copper, and chlorine from an evaporator, or of a previously prepared powdery electroluminophore of like composition, and, simultaneously, of vaporous zinc evaporated from another evaporator separate from that in which the ZnS doped with Mn, Cu, and Cl are evaporated.

The temperature of the evaporator containing the zinc sulphide doped with Mn, Cu and Cl is preferably kept within the range of 1,050°–1,250°C while the temperature of the evaporator containing the metallic zinc is kept within the range of 360°–400°C.

The proposed method of making a direct-current electroluminescent device is advantageous in that it makes it possible to increase the reproducibility of the parameters of the devices, as well as their life (to 400–600 hours at a constant voltage), and to intensify the brightness of the device for more than nine orders of magnitude at an operating voltage not exceeding 20 volts.

The proposed method consists substantially of depositing a luminophore film with excessive zinc by simultaneously evaporating, under vacuum, a powdery luminophorescent substance comprising ZnS doped with Mn, Cu, and Cl, and metallic zinc substance, each substance being evaporated from a separate evaporator.

The entire process of evaporation is carried out in a quasi-closed volume, i.e. in a vacuum device containing a vertical tubular furnace with a closed upper end arranged under the cap of this device and accommodating the substrate to be processed, the evaporators being mounted at the lower end of the furnace.

The temperature of the evaporator containing the zinc sulphide doped with manganese, copper and zinc chloride is maintained within the range of 1,050°–1,250°C, thereby providing for a specified rate of evaporation of this substance, whereas the temperature of the evaporator containing the metallic zinc is maintained within the range of 360°–400°C to provide for a predetermined concentration of zinc in the electroluminophore film.

The evaporation of zinc from a separate evaporator under the correct conditions of evaporation makes it possible to obtain a constant predetermined ratio of the rates of evaporation of ZnS doped with Mn, Cu and Cl, and Zn, thereby enabling one to obtain uniform doping of the electroluminophore film with zinc throughout the entire volume of this film to ensure a specified concentration of zinc in said film, and to increase the reproducibility of the method. The use of the quasi-closed volume improves the conditions of growth of the film, the reproducibility of the results, and reduces the consumption of the substance, since the rate of condensation of ZnS is increased due to the low rate of evaporation of the particles from the heated substrate.

Given below is an example of carrying the proposed method into effect.

EXAMPLE

A substrate with an optically transparent, current-conducting layer of SnO_2 is purified in a glow discharge and is heated to $250^\circ\text{--}300^\circ\text{C}$ in a tubular furnace under a vacuum of 2.10^{-5} mm Hg. The tubular furnace is equipped with several evaporators having a flap placed between them and the substrate. When the flap is closed, the powdery luminophore comprising ZnS doped with Mn, Cu, and Cl is degassed by smoothly increasing the temperature of the evaporator with said powdery luminophore to $1,050^\circ\text{C}$. Then the temperature of another separate evaporator with metallic zinc therein is raised to $360^\circ\text{--}400^\circ\text{C}$, and the flap is opened. The zinc is evaporated from a quartz crucible having a heater with a heating element of tungsten. In the process of evaporation the temperature of the evaporator with containing the powdery luminophore comprising ZnS doped with Mn, Cu, and Cl is raised from $1,050^\circ$ to $1,250^\circ\text{C}$, while the rate of evaporation of the ZnS doped with Mn, Cu, and Cl is maintained approximately constant and equal to 0.5 to 0.6 microns per minute.

The temperature of the evaporator containing the metallic zinc during the entire cycle of evaporation is kept constant and equal to $360^\circ\text{--}400^\circ\text{C}$.

The evaporation is maintained until the thickness of the electroluminophore layer reaches 10 microns. After this the evaporator and the furnace are de-energized. The obtained film is cooled down in a vacuum. A metal electrode is deposited onto the cooled film by means of vacuum evaporation.

The specimens obtained by the proposed method radiate yellow-orange light with maximum intensity within the region of 585 nm when applying a negative

voltage on the metal electrode. A brightness of 20–30 nits is obtained at a voltage of 15–20 volts and a current density of $0.6\text{--}1.0\text{ mA/mm}^2$. The life (the time of half-decay of the brightness from the initial level of 20 nits) is equal to 1,000–2,000 hours at a slight increase in the applied voltage during the process of operation (by 25–30%). The life of the direct-current luminescent devices obtained by the present method is considerably higher than that of the direct-current luminescent devices obtained by any known method.

We claim:

1. A method of making a direct-current electroluminescent device, in which an electroluminescent film is deposited onto a heated substrate covered with an optically transparent electrode, comprising vacuum evaporating zinc sulphide doped with manganese, copper, and chlorine from a first evaporator at a temperature between $1,050^\circ\text{C}$ – $1,250^\circ\text{C}$ and simultaneously vacuum evaporating metallic zinc from a second evaporator at a temperature between 360°C – 400°C , thereby enabling the desired concentration of zinc to be obtained in said film; and vacuum evaporating a metal onto said film to form an electrode on said film.

2. A method of making a direct-current electroluminescent device according to claim 2, wherein said first and second substances are evaporated in separate evaporators contained in a quasi-closed volume having said substrate at the upper end thereof and said evaporators at the lower end thereof, thereby enabling an excess of zinc of a predetermined concentration to be uniformly distributed throughout the entire thickness of said film.

3. A method of making a direct-current electroluminescent device according to claim 3, wherein the temperature of said substrate is maintained between $250^\circ\text{--}300^\circ\text{C}$.

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