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Robertson

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[54] **METHOD OF MAKING A SINGLE LAYER MULTI-COLOR LUMINESCENT DISPLAY**

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[*] Notice: The portion of the term of this patent subsequent to Apr. 14, 2009 has been disclaimed.

[21] Appl. No.: **858,176**

[22] Filed: **Mar. 24, 1992**

Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 693,049, Apr. 30, 1991, Pat. No. 5,104,683, which is a continuation of Ser. No. 337,768, Apr. 13, 1989, abandoned, which is a division of Ser. No. 140,185, Dec. 31, 1987, Pat. No. 5,047,686.

[51] **Int. Cl.**[5] **B05D 3/06**; B05D 5/06

[52] **U.S. Cl.** **427/526**; 427/66; 427/68; 427/108; 427/109; 427/126.1; 427/282; 427/372.2; 427/126.2

[58] **Field of Search** 427/38, 68, 282, 372.2, 427/108, 126.1, 109, 126.2

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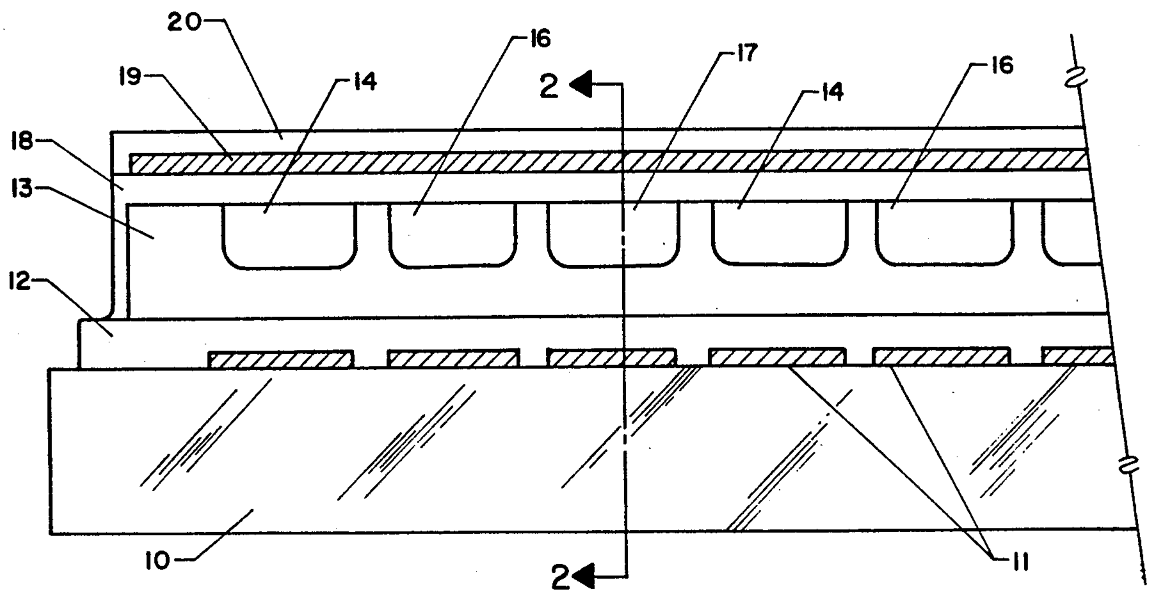
[57] **ABSTRACT**

The invention is method of forming a multi-color luminescent display including the steps of depositing on an insulator substrate a smooth single layer of host material which itself may be a phosphor with the properties to host varying quantities of different impurities and introducing one or more of said different impurities into selected areas of the single layer of host material via an appropriately positioned mask as by thermal diffusion or ion-implantation to form a pattern of phosphors of different colors in the single layer of host material such that the top surface of the host layer remains smooth. Red phosphors are formed by adding impurities selected from the group consisting of Sm, SmF_3, Eu, EuF_3, and ZnS:$MnTbF_3$ to a ZnS host; green phosphors by adding impurities selected from the group consisting of Tb and TbF_3 to a ZnS host; and blue phosphors by adding impurities selected from the group consisting of Tm, Al, Ag and Mg to a ZnS host.

20 Claims, 3 Drawing Sheets



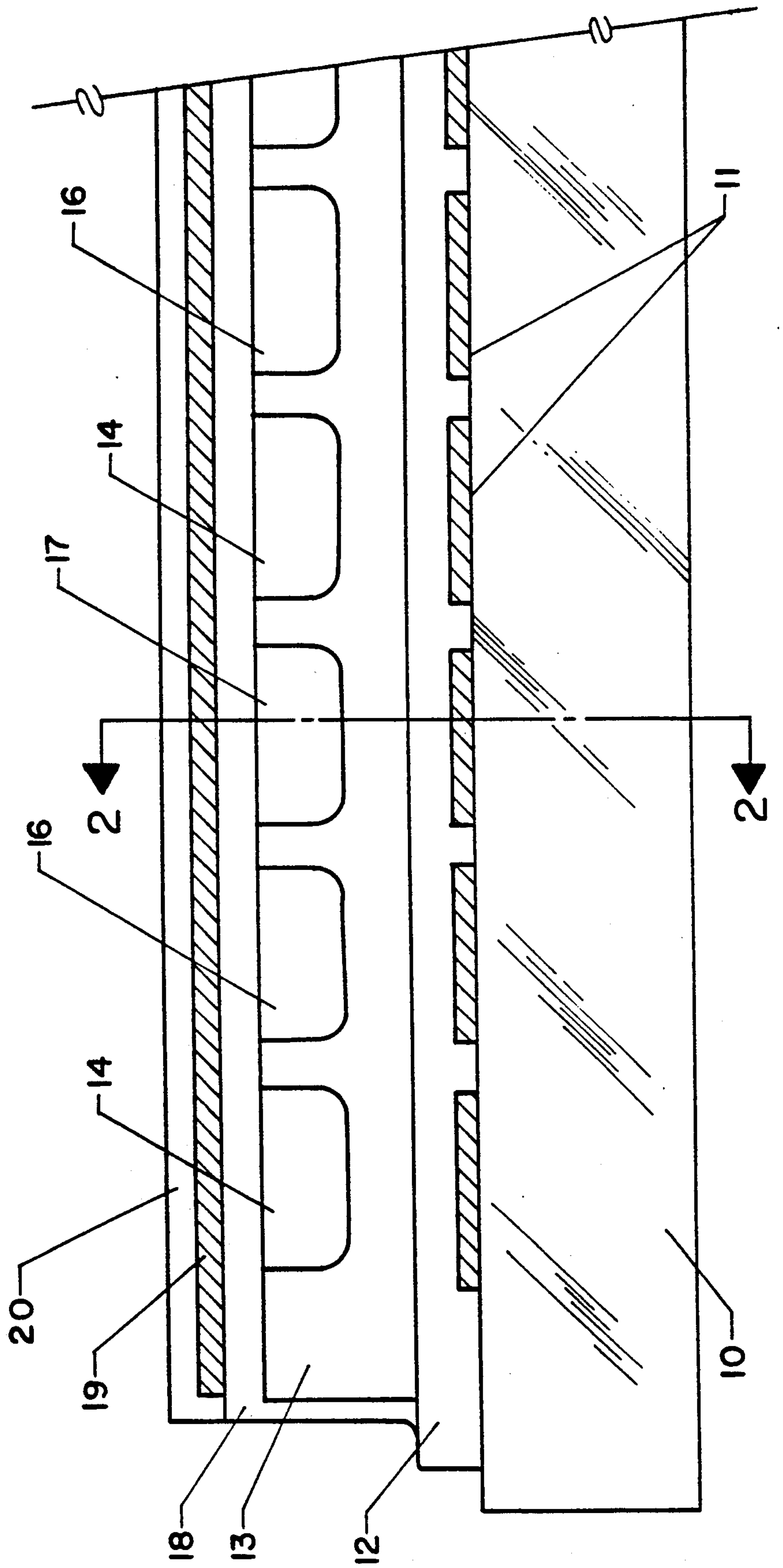


FIGURE 1

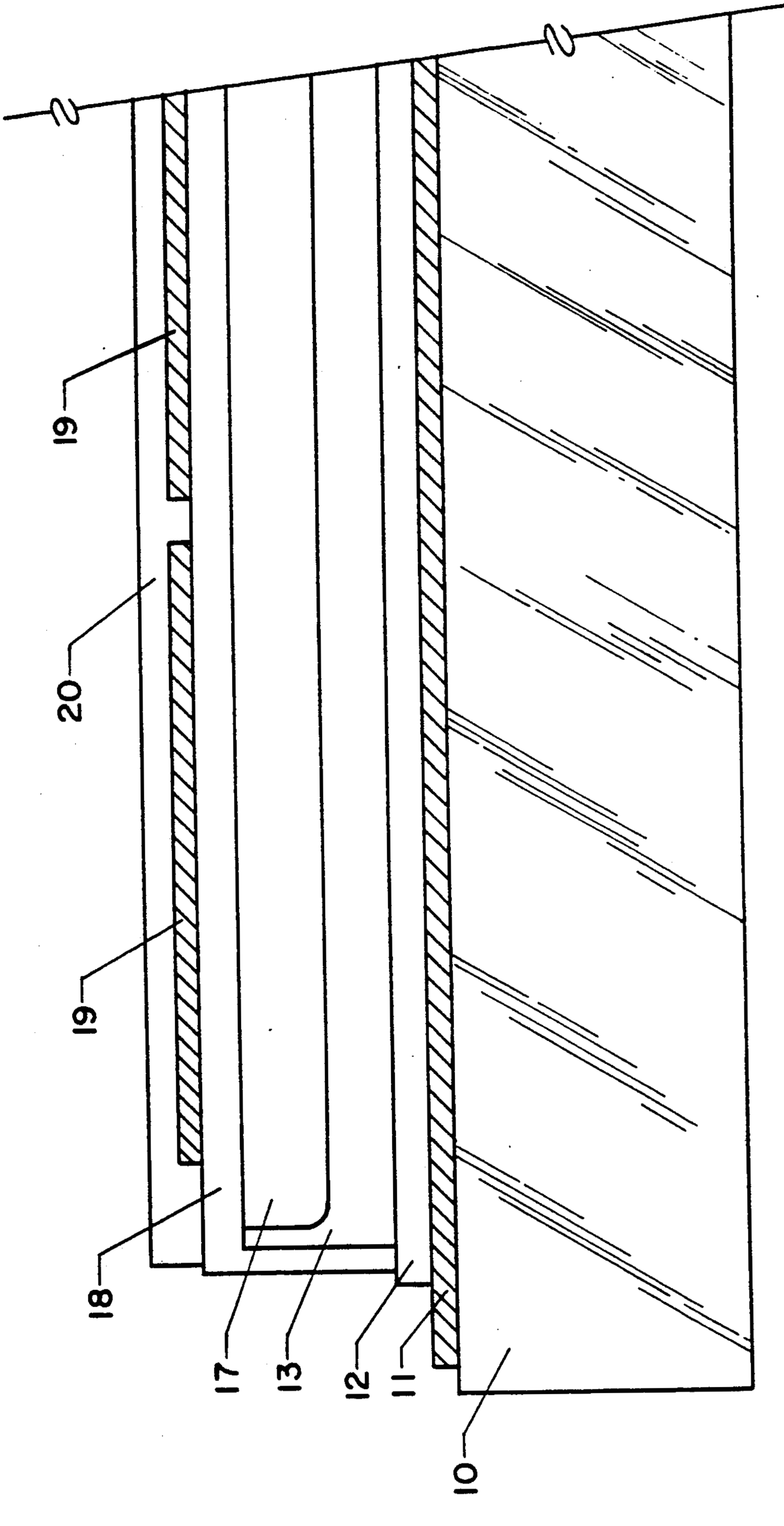


FIGURE 2

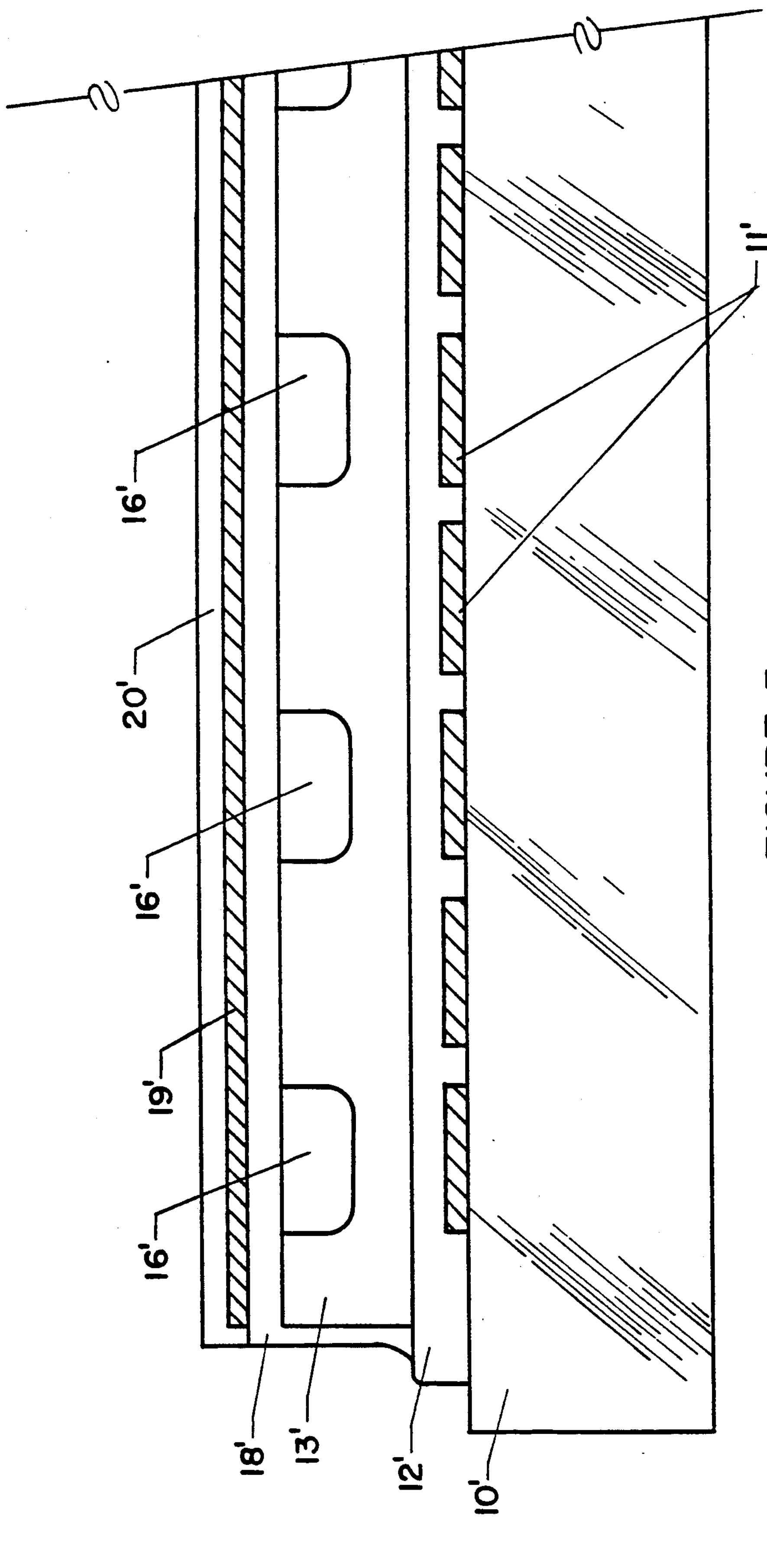


FIGURE 3

METHOD OF MAKING A SINGLE LAYER MULTI-COLOR LUMINESCENT DISPLAY

ORGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part application of allowed application Ser. No. 07/693,049, filed Apr. 30, 1991, now Pat. No. 5,104,683 which is a continuation application of Ser. No. 07/337,768, filed Apr. 13, 1989, now abandoned, which in turn is a divisional application of Ser. No. 140,185 filed Dec. 31, 1987, now U.S. Pat. No. 5,047,686.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention is a single layer multi-color luminescent display and method of making and more particularly to thin- film electroluminescent displays.

Thin-film, multi-color electroluminescent (TFEL) flat-panel displays, because of their potential to provide improved flexibility and reliability, reduce weight, space, power consumption and degration characteristics, are finding greater use in the control panels of air, space and ground vehicles and many other applications requiring thin, flat, multi-colored displays.

2. Description of the Related Art

Full-colored electroluminescent displays formed of patterned and stacked layers of phosphors separated by insulating layers and transparent conductors and frequently filters are generally known. For instance, see U.S. Pat. No. 4,689,522, dated Aug. 25, 1987 which discloses a full-color, thin-film electroluminescent device with two stacked substrates and color filters. Multicolor electroluminescent displays formed by depositing side-by-side stripes of different colored phosphors on a common insulator substrate are also known.

Conventional electroluminescent (EL) displays are generally divided into two major types according to the manner or form in which the phosphors are applied to the necessary substrate. These are thin-film electroluminescent (TFEL) and powder electroluminescent (powder EL) devices.

Powder EL devices are formed by grinding the phosphor crystals to be used into a powder, mixing the powder with a binder and a solvent, and then spreading the mixture (single color) onto a substrate by spraying or blading. TFEL devices are formed by growing the phosphors (single color) on a substrate using conventional techniques such as vapor deposition or sputtering.

Typically, the thickness of the phosphors layer in powder EL devices is about 20 to 40 μM while the thickness of the phosphors layer in a TFEL device is 0.4 to 0.5 μM. As is known the luminescence in a TFEL device is produced by a different mechanism than in a powder EL device.

To display the full color spectrum including white, a conventional TFEL device will typically have the three primary and separate colors, blue, green and red phosphors, placed close together either side-by-side on the same substrate; on separate superimposed layers, or in some combination of these two fabrication techniques.

Typically, the three phosphors are applied to the substrate or substrates (in thicknesses of 2000 to 5000 Angstroms) by vacuum deposition. In conventional single layer TFEL devices alternating stripes of blue, green and red phosphors are grown on a glass substrate. In a two-layer TFEL device such as disclosed in U.S. Pat. No. 4,689,522, a single layer of blue phosphor is superimposed over a single layer of side-by-side alternating stripes of green and red phosphors.

The fabrication of a conventional multi-color TFEL device is generally as follows: After depositing a pattern of transparent electrodes on the surface of a glass substrate and covering it with a transparent layer of insulation, the following steps are performed: (1) a red phosphor is deposited as previously described over the insulated surface of the substrate: (2) the phosphor coated surface is masked with a striped pattern (commonly with photo-resist); (3) plasma etching of the red phosphor; (4) removal of the photo-resist; (5) deposition of a green phosphor; (6) the addition of an insulating layer; (7) the repetition of steps (2), (3), and (4), after the deposition of each additional colored phosphor; and (8) annealing of the phosphors. Variations in this process may be made by changing the order and repetition of the above steps or by ion-beam etching instead of plasma etching.

As is apparent, a disadvantage of the prior art is the necessity of the etching steps, the depths and locations of which must be precisely controlled. For instance, in the first etching step, the etching must continue through the full depth of the red phosphor layer but must be stopped before going into the insulating layer. In the second etching step, the etching must continue through the full depth of the green phosphor but stop before entering the red phosphor layer. The etching also leaves an uneven surface on the underlying phosphor layer that is believed to promote dielectric breakdown in the covering insulating layer applied after etching is completed.

OBJECTS AND SUMMARY OF THE INVENTION

An object of this invention is to provide a single-layer, multi-color luminescent display and method of making same.

Another object is to provide a multi-color luminescent display using a single-layer of a host material that may be a phosphor material with the properties to serve as a host to different impurities that form different colored phosphors in the single-layer of host material.

The above and numerous other objects are achieved by the invention which is a full colored, luminescent display that includes a single layer of a host material that itself may be a phosphor on an insulating substrate, the host layer serving as host to different impurities that combine therewith in selected areas of said single host layer to form a pattern of phosphors of different colors. The impurities may be introduced into the host and single-layer of material, which also may be a phosphor, by thermal diffusion, ion implantation or the like. The number of phosphors of different colors that may be provided is determined by the number and quantity of different impurities to which the single-layer of host material can serve as a host.

BRIEF DESCRIPTION OF THE DRAWING

The above and numerous other objects and advantages of the invention will become apparent from the following detailed description when read in view of the appended drawing wherein:

FIG. 1 is a sectional view illustrating a preferred embodiment of a single layer, three-color electroluminescent display and the method of making same in accordance with the invention;

FIG. 2 is a cross-sectional view taken along the lines 2—2 in FIG. 1; and

FIG. 3 is a sectional view illustrating a single layer, two-color display and method of making same in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As shown in FIG. 1, a preferred embodiment of the invention includes an insulating substrate **10** of glass or the like upon which a pattern of individual transparent column electrical conductors **11** is deposited before an insulating covering or layer **12** of SiO_2 or other suitable dielectric is applied over the column conductors **11** as is well known. Next, a single layer **13** of a host material such as ZnS is deposited by evaporation, sputtering, or other known thin film deposition technique.

The single layer of host material **13** serves as a common host to two or more different impurities that when introduced into the common host material **13** in selected areas form a pattern of stripes, dots or other indicia of different colored phosphors in the single-layer of host material **13**. As will be explained the single layer of host material **13** may be either luminescent or non-luminescent provided it has the properties to serve as a common host to different phosphor forming impurities.

For instance, as shown in FIG. **1**, a green phosphor strip **14** is produced by introducing the impurity TbF_3 to form ZnS:TbF_3. A red phosphor stripe **16** is achieved by introducing the impurities TbF_3 and Mn into the host layer **13** of ZnS. A blue phosphor stripe **17** results by introducing the impurity Mg to the host layer **13** of ZnS to form ZnS:Mg. Thus, by adding different impurities to a single-layer of a host material **13** in selected areas, a pattern of phosphors of different colors is provided in the single layer of host material.

After annealing the layer of host material **13** and the phosphors **14, 16,** and **17** formed therein, a second transparent layer **18** of SiO_2 or other suitable dielectric is applied over the layer of host material **13**. A pattern of row electrical conductors **19** is deposited over the dielectric layer **18**. The column and row conductors **11** and **19** form a matrix permitting selected portions of the layer of host material **13** to be subjected to an electric field established between the column and row conductors as is well known.

A preferred method of making a single layer electroluminescent display begins with a glass substrate **10** upon which a pattern of transparent and individual column conductors **11** of indium-tin oxide is deposited and over which a covering insulator layer **12** of SiO_2 or other suitable dielectric is deposited as by sputtering or other conventional deposition techniques.

Thereafter a single layer of host material **13** of ZnS or a phosphor of a selected color capable of hosting one or more impurities to form phosphors of different colors is deposited by evaporation, sputtering or other known thin film deposition technique over the entire surface of the insulator layer **12**. The host layer **13** of ZnS is then covered with a metal mask to form a predetermined pattern of exposed and unexposed surface areas on the host layer **13** as required to form the desired electroluminescent display. Thereafter the impurity TbF_3 is introduced in sufficient quantity through the mask or photoresist into the host layer **13** of ZnS to produce one or more stripes **14** of green phosphor ZnS:TbF_3. The mask is then repositioned on the surface of the host layer **13** of ZnS to form the next required pattern of exposed and unexposed surface areas on the host layer **13** of ZnS before the impurities TbF_3 and Mn are introduced into the newly exposed areas of the host layer **13** in sufficient quantity to form one or more stripes **16** of red phosphor ZnS:TbF_3:Mn.

Again the metal mask is repositioned to form a third pattern of exposed areas on the surface of the host layer **13** of ZnS. Thereafter the impurity Mg is introduced into the newly exposed areas of the host layer **13** in sufficient quantity to form one or more stripes **17** of blue phosphor ZnS:Mg. Thus, a full-color luminescent display surface is achieved. The impurities may be introduced into the host layer **13** by thermal diffusion, ion-implantation or other suitable techniques.

After annealing the host layer **13** and the phosphor stripes **14, 16** and **17** therein, a pattern of individual, transparent row electrical conductors **19** embedded in a second transparent layer **18** of SiO_2 or other suitable dielectric material is applied over the host layer **13**, the SiO_2 forming an insulator between the phosphor stripes **14, 16** and **17** and the row electrical conductors **19** which with the column electrical conductors **11** form a matrix for subjecting selected portions of the phosphor stripes **14, 16** and **17** to an electric field to provide an electroluminescent display.

Other impurities may be hosted by the ZnS layer to form the desired colored stripes. For example, the impurities Sm, SmF_3, Eu and EuF_3 form red phosphor stripes **16** of ZnS:Sm, ZnS:SmF_3, ZnS:Eu and ZnS:EuF_3, respectively. The impurities Tm, Al, and Ag form blue phosphor stripes **17** of ZnS:Tm, ZnS:Al and ZnS:Ag, respectively. The impurities Tb and TbF_3, form green phosphor stripes **14** of ZnS:Tb and ZnS:TbF_3, respectively. The respective impurities which form red, green and blue phosphors when hosted by ZnS just described can be interchanged in any desired combination with the previously described impurities Mg, TbF_3 and Mn. Fabrication of an electroluminescent display using these impurities parallels the steps detailed above and below.

As mentioned luminescent and electroluminescent displays can be made in accordance with the invention using any single layer **13** of host material into which impurities can be introduced to form phosphors of different colors in the single layer of host material. For example, the phosphors SrS:Ce_2S_3 (red) and SrS:CeF_3 (green) may be formed in a single host layer **13** of SrS to provide two distinct colors.

As shown in FIG. **3**, luminescent and electroluminescent displays of two or more colors may be made in accordance with the invention using the green phosphor ZnS:TbF_3 as the single layer **13'** of host material into which the impurity Mn is introduced as previously described to form stripes **16'** of the red phosphor ZnS:TbF_3:Mn. The number of phosphors of different colors that can be formed again is determined by the number of different impurities the single layer 13' of phosphor is able to host as previously explained.

As shown in FIG. 3, an electroluminescent display may be fabricated as shown in FIGS. 1 and 2, like elements having the same reference numeral except for the prime (') symbol—thus, 13 and 13' identifying the different single layers of host material in the two embodiments. As is shown, the method of this invention eliminates the need for the difficult and costly steps of etching, thereby increasing the yield while reducing the cost of making full or multi-color thin film luminescent and electroluminescent displays.

Depositing only a single layer of host material on an insulator substrate, leaves a smooth top surface on the single layer. This eliminates the sharp corners and edges left by the overlapping layers of phosphor in conventional, multi-layer TFEL displays. Such an irregular, rough surface may cause corresponding sharp corners in the succeeding layers of insulation and transparent conductors leading to a dielectric breakdown of the insulating layers.

While the invention has been described as a multi-color, single layer electroluminescent display device (TFEL) and a method of making the same, the method of this invention may be used to make a multi-color, single phosphor layer substrate for use in cathode ray tubes and other similar applications requiring a multi-color phosphor display surface.

While preferred embodiments of a multi-color, single phosphor layer electroluminescent display and methods of making same have been described in detail, numerous changes and modifications can be made within the principles of the inventions which are to be limited only by the appended claims.

What is claimed is:

1. A method of forming a multi-color electroluminescent surface on a substrate comprising the steps of:

depositing a single layer of host material formed of ZnS having a smooth top surface on said substrate; and

introducing sufficient quantities of impurities selected from the group consisting of Sm, SmF_3, Eu and EuF_3 within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of red phosphors, namely ZnS:Sm, ZnS:SmF_3, ZnS:Eu and ZnS:EuF_3, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

2. The method according to claim 1, wherein the impurities are introduced into said single layer of host material via thermal diffusion.

3. The method according to claim 1, wherein the impurities are introduced via ion-implantation.

4. The method as defined in claim 1, further comprising depositing an insulating layer over said smooth top surface of said single layer of host material.

5. The method according to claim 1, further comprising introducing sufficient quantities of impurities selected from the group consisting of Tb and TbF_3 within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of green phosphors, namely ZnS:Tb and ZnS:TbF_3, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

6. The method according to claim 1, comprising introducing sufficient quantities of impurities selected from the group consisting of Tm, Al, Ag, and Mg within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of blue phosphors, namely, ZnS:Tm, ZnS:Al, ZnS:Ag and ZnS:Mg, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

7. The method according to claim 6, comprising introducing sufficient quantities of impurities selected from the group consisting of Tm, Al, Ag, and Mg within selected areas of said single layer of ZnS host material via an approriately positioned mask to form a pattern of blue phosphors, namely, ZnS:Tm, ZnS:Al, ZnS:Ag and ZnS:Mg, within said single layer of Zns host material such that the top surface of said single layer of host material remains smooth.

8. A method of forming a multi-color electroluminescent surface on a substrate comprising the steps of:

depositing a single layer of host material formed of ZnS having a smooth top surface on said substrate; and

introducing sufficient quantities of impurities selected from the group consisting of Tm, Al, and Ag within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of blue phosphors, namely ZnS:Tm, ZnS:Al and Zns:Ag, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

9. The method according to claim 8, wherein the impurities are introduced into said single layer of host material via thermal diffusion.

10. The method according to claim 8, wherein the impurities are introduced via ion-implantation.

11. The method as defined in claim 8, further comprising depositing an insulating layer over said smooth top surface of said single layer of host material.

12. The method according to claim 8, further comprising introducing sufficient quantities of impurities selected from the group consisting of Tb and TbF_3 within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of green phosphors, namely ZnS:Tb and ZnS:TbF_3, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

13. The method according to claim 8, further comprising introducing sufficient quantities of impurities selected from the group consisting of Sm, SmF_3, Eu, EuF_3, and Mn:TbF_3 within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of red phosphors, namely ZnS:Sm, ZnS:SmF_3, ZnS:Eu, ZnS:EuF_3 and ZnS:Mn:TbF_3 within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

14. The method according to claim 12, further comprising introducing sufficient quantities of impurities selected from the group consisting of Sm, SmF_3, Eu, EuF_3, and Mn:TbF_3 within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of red phosphors, namely ZnS:Sm, ZnS:SmF_3, ZnS:Eu, ZnS:EuF_3 and ZnS:Mn:TbF_3 within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

15. A method of forming a multi-color electroluminescent surface on a substrate comprising the steps of:

depositing a single layer of host material formed of ZnS having a smooth top surface on said substrate; and

introducing sufficient quantities of Tb within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of green phosphors, namely ZnS:Tb, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

16. The method according to claim **15**, wherein the impurities are introduced into said single layer of host material via thermal diffusion.

17. The method according to claim **15**, wherein the impurities are introduced via ion-implantation.

18. The method as defined in claim **15**, further comprising depositing an insulating layer over said smooth top surface of said single layer of host material.

19. The method according to claim **15**, comprising introducing sufficient quantities of impurities selected from the group consisting of Tm, Al, Ag, and Mg within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of blue phosphors, namely, ZnS:Tm, ZnS:Al, ZnS:Ag and ZnS:Mg, within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

20. The method according to claim **15**, further comprising introducing sufficient quantities of impurities selected from the group consisting of Sm, SmF_3, Eu, EuF_3, and Mn:TbF_3 within selected areas of said single layer of ZnS host material via an appropriately positioned mask to form a pattern of red phosphors, namely ZnS:Sm, ZnS:SmF_3, ZnS:Eu, ZnS:EuF_3 and ZnS:Mn:TbF_3 within said single layer of ZnS host material such that the top surface of said single layer of host material remains smooth.

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