March 14, 1972 KAZUNOBU TANAKA ET AL 3,649,553

SEMICONDUCTIVE ELECTRO-LUMINESCENT ELEMENT

Filed Nov. 21, 1967

FIG. 1a

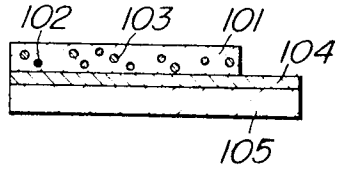


FIG. 1b PRIOR ART

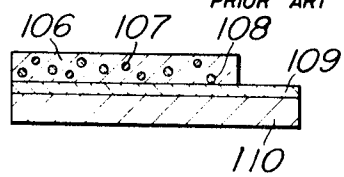


FIG. 2

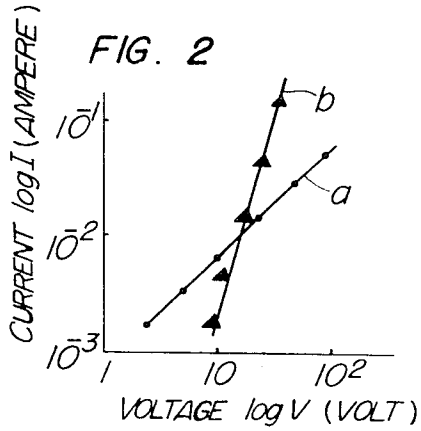


FIG. 4

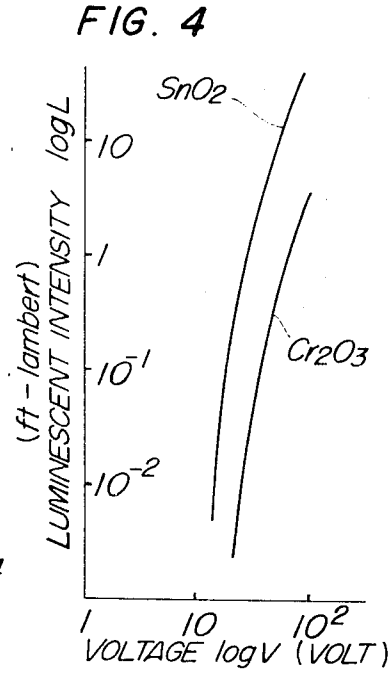
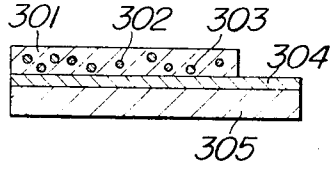


FIG. 3



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SEMICONDUCTIVE ELECTRO-LUMINESCENT ELEMENT

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Int. Cl. C09k 1/12
U.S. Cl. 252—301.5 4 Claims

ABSTRACT OF THE DISCLOSURE

A semiconductive electro-luminescent element having an ohmic resistivity of from 10^5 to 10^8 ohm-cm. wherein a mixture of electroluminescent powder metal oxide powder having a good reflectivity to the light emitted by the electro-luminescent powder and glassy binding agent powder is applied to a nesa glass plate. The grain size of the glassy powder is smaller than that of the metal oxide powder which in turn is smaller than that of the electro-luminescent powder. The softening point of the glassy binding agent is lower than the firing temperature which in turn is lower than the softening point of the glass plate. The element is useful as an electro-luminescent element for a solid state image intensifier.

The present invention relates to electro-luminescent elements and more particularly to electro-luminescent elements endowed with semi-electroconductivity.

In the past as a technique of endowing a solid layer formed of a high resisitive material such as plastic glass, or the like with electro-conductivity it was proposed to disperse an electro-resistive material in the glass, plastic, or the like. However, such a technique has been only utilized to produce either conductive solid elements of very low resistivity or elements whose resistivities are allowed to be not identical over a wide range. There was no semiconductive solid layer, the resistivity of which was of the order of 10^5 to 10^8 ohm-cm., and which had the ohmic characteristic up to a fairly high electric field. Carbon black is a comparatively good resistive material, but, since it absorbs electro-luminescent light, it cannot be mixed with electro-luminescent powder. Metal powder as the resistive material is subject to oxidation or degeneration due to high temperature for firing. Moreover metal is difficult to be pulverized due to its malleability. In addition, the control of the resistance of the solid layer is difficult due to the fact that the metal powder has a very low resistivity, and when the binding agent is plastic, the ohmic characteristic of the solid layer can hardly be maintained up to a high electric field because of the poor thermal resistivity of the plastic. For these reasons, the conventional technique could not be applied to endowing the electro-luminescent layers of certain kinds of solid state imaging plates which necessitate D.C. control with electro-conductivity.

Therefore, it is an object of the present invention to provide a semiconductive electro-luminescent element having ohmic characteristic up to a high electric field.

According to the present invention there is provided a semiconductive electro-luminescent element characterized in that electro-luminescent powder and metal oxide powder are intermingled with each other in a vitreous binding agent.

In the present invention, a novel semiconductive electro-luminescent element with a resistivity of from 10^5 to 10^8 ohm-cm., having ohmic characteristic up to a fairly high electric field, stable on heating, withstanding abrasion and having a high luminescent efficiency is obtained by the processes of preparing, as an electro-resistive material, powder of a semiconductive metal oxide which is stable in the air up to fairly high temperatures and easy to be made into fine powder, and preferably having a particularly large reflectivity to the light emitted by the electro-luminescent powder employed such as SnO_2, WO_3, Sb_2O_5 or TiO_2, controlling voluminal ratios of the powders, selecting the grain size of fine powder of glass as a binding agent to be smaller than those of the powders of the metal oxide and the electro-luminescent material in order to improve the binding between the powders themselves and a substrate and to obtain a smooth layer, mixing the powders with an appropriate liquor into a homogeneous and well dispersed mixture, and firing the mixture on the heat proof substrate having a softening point higher than that of the glass powder and a coefficient of voluminal expansion equal to that of the mixture, for example a glass plate onto which a light transmissive electroconductive layer consisting of a metal oxide such as SnO_2 is deposited (nesa glass).

The present invention will be described in more detail with reference to the accompanying drawing, in which:

FIG. 1*a* is a cross-section of an embodiment of this invention;

FIG. 1*b* is a cross-section of a known solid layer;

FIG. 2 is the voltage versus current characteristics of the embodiments of FIGS. 1*a* and 1*b*;

FIG. 3 is a cross-section of a reference sample; and

FIG. 4 is the luminescent characteristics of the embodiment of FIG. 1*a* and the sample of FIG. 3.

Now, referring to FIG. 1*a*, a mixture of powder **102** of an electro-resistive material such as SnO_2, TiO_2, WO_3, Sb_2O_5 or the like, powder **103** of an electro-luminescent material such as ZnS:CuAl or the like, and a glassy binding agent **101** is provided on a transparent electrode (nesa electrode) **104** deposited on a transparent glass plate **105** as a heat proof substrate. FIG. 1*b* shows a known solid layer in which a plastic **106** such as epoxy resin is employed as the binding agent. Reference numerals **107**, **108**, **109** and **110** correspond to **102**, **103**, **104** and **105** in FIG. 1*a*, respectively. The composition of these semiconductive electro-luminescent layers is as shown in Table I, for example. The voluminal mixture ratio of SnO_2 (or TiO_2, WO_3, Sb_2O_5 etc.) can be varied within the range of approximately from 10 to 20%, that is, not exceeding 20% depending on the desired resistance, and the content of the electro-luminescent powder can also be varied within the range of from 15 to 30%.

Table 1

Component:	Voluminal ratio, percent
Vitreous binding agent	65
SnO_2(TiO_2 etc.) fine powder	15
ZnS:CuAl powder	20

Now a method of manufacturing a semiconductive electro-luminescent layer employing a vitreous binding agent as shown in FIG. 1*a* will be described. In order to simplify the description, vitreous binding agent powder SnO_2 (or TiO_2, WO_3, Sb_2O_5) powder, and electro-luminescent powder are put as A, B, and C, respectively. As regards the grain sizes of the powders, it is desired that the mean diameter of the grain of A is 1μ or less, that of B is 5μ or less and that of C is 10μ or less. If the diameters of the powder grains are greater than these values, the degrees of dispersion of the electro-resistive material becomes lower, lamination is difficult, and the layer is apt to become porous. Making the powders finer has the advantage that the degree of dispersion of the resistive material is better, the resistance is more stable, and the

lamination is easier, even at which time the diameters of the powder grains must have the relation $A<B,C$, because of $A>B,C$ the finer powder of the resistive material SnO_2, TiO_2, WO_3, or Sb_2O_5, covers the peripheries of the glass grains which are a binding agent, and hence even if subjected to a firing, not only the binding to a substrate but also the binding between the glass grains will be prevented, resulting in no formation of layer.

A mixture of A, B, and C selected and weighed in such a manner that the abovementioned condition was satisfied was sufficiently intermingled and dispersed by means of an appropriate mixer. As the mixer a ball mill was employed in this embodiment. When employing the ball mill for the purpose of mixing only, a polyethylene vessel is employed as a mixer vessel and the number of balls is decreased to greatly reduce the powder of fracture in order to avoid the fracture of the electro-luminescent powder.

By the use of this special ball mill a mixture of A, B, and C together with an approximately equivalent weight of an appropriate volatile liquor such as diacetone alcohol or octyl alcohol added thereto is operated for several hours in wet blending.

The powders thus mixed and stirred are almost in a state of sol, the liquor serving as a dispersion medium. As a method of applying this mixture to a nesa glass (consisting of the glass plate **105** and the stannic oxide coating **104** as a heat-proof substrate the screen coating method such as the silk screen method is preferable, but the method is not limited to the screen coating method.

The purpose of the operation of baking and lamination is to melt the vitreous binding agent **101** without perfectly melting the resistive material SnO_2 (or TiO_2, WO_3, Sb_2O_5) into the glassy material **101** and to bond the mixture to the substrate to form a smooth layer. The composition of the glass powder **101**, the metal oxide powder **102**, and the electro-luminescent (EL) powder **103** and the melting point or softening point thereof are selected so that the EL powder **103** does not change in quality, does not melt into the glassy material **101** or metal oxide powder **102**, or does not undergo an influence by these materials **101** and **102** and hence the luminescent characteristic thereof is not so impaired. Since as low a working temperature as possible is better, as the vitreous binding agent one having a low viscosity at low temperatures or one having a low softening point should be selected.

As the heat-proof substrate a nesa glass which consists of a common glass plate **105** and a transparent electrode (nesa electrode) **104** provided thereon is employed. In the past as a substrate to which a glassy material is baked only a few materials such as a metal plate, for example iron plate, or ceramics are employed. However, the present invention has made it possible to bake a glassy material to a glassy substrate without changing the quality of the glassy substrate by satisfying the following two conditions. One of the two conditions is that the softening point of the glassy binding agent is lower than that of the glass substrate. This is an indispensable condition because, if the substrate softens first at the time of firing, the formation of the layer is impossible. The other of the conditions is that the coefficients of voluminal expansion of the glass substrate and the glassy binding agent are substantially the same. If the coefficients of voluminal expansion of the two are greatly different, there arises a strain when cooling, and the substrate may fracture. At this time, even if the substrate may not be fractured, the transparent nesa electro deposited on the substrate loses electro-conductivity due to the strain. An example of the composition of the glassy binding agent employed in this embodiment is shown in Table II, and the coefficients of voluminal expansion and softening points of the glassy binding agent and the glass substrate are shown in Table III. Although the composition of the glassy binding agent is not limited to that shown in Table II, a material containing at least SiO_2, B_2O_3, ZnO, BaO, and Na_2O preferably in an amount of more than 10 weight percent each as shown in Table II was suitable for obtaining a good thermal characteristic and a good EL luminescent characteristic.

TABLE II

Component	Weight percent	Component	Weight percent
SiO_2	20.01	Na_2O	10.84
B_2O_3	28.58	K_2O	4.05
ZnO	18.33	TiO_2	2.31
BaO	14.34	Al_2O_3	0.41
CaO	0.74	Fe_2O_3	0.009
MgO	0.016	PbO	0.012

TABLE III

	Coefficient of voluminal expansion	Softening point, °C.
Glassy binding agent	270×10^{-7}	600~630
Glass substrate	$(270\sim300)\times10^{-7}$	680~700

In this embodiment, although the baking temperature was set at 640° C., the operation of the process was very simple, because, since the metal oxide SnO_2 (or TiO_2, WO_3, Sb_2O_5) employed as an electro-resistive material and ZnS: CuAl employed as an EL material are very stable even in the air at a temperature of the order of 640° C., the baking in the air is possible, and moreover, the coefficients of thermal expansion of the heat-proof substrate and the glassy binding agent are selected substantially the same. After the nesa glass coated with the mixture of A, B, and C is inserted in an electric furnace the temperature of the furnace is raised to 650° C. in about twenty minutes, during which process the liquor employed for mixing, A, B and C vaporizes leaving the mixture powder only. The temperature of the furnace is maintained at 650° C. for five minutes, and then the furnace is cooled. After a lapse of twenty minutes from the beginning of the cooling process the firing finishes. When the grain diameter of the mixture powder is 1μ, a layer about 20μ thick is formed by one firing by employing a silk screen of 130 mesh. Depending on purposes the lamination of a further layer is possible by a further firing. The viscosity of glass is fairly high, and hence the first glassy layer does not flow nor the thickness thereof changes in such a short time as five minutes at temperatures of about 640° C. The nesa electrode also hardly loses its electro-conductivity and transparency.

A method of manufacturing a semiconductive EL layer employing a plastic as a binding agent as shown in FIG. 1*b* is almost the same as the conventional method except that the mixing of the resistive powder is performed sufficiently, and hence no further description thereof is given here. The D.C. current versus voltage characteristics *a* and *b* of the semiconductive EL layers shown in FIGS. 1*a* and 1*b* thus formed, respectively, in a direction of thickness thereof are shown in FIG. 2. It is noted from FIG. 2 that the resistance is ohmic independent of the electric field and stable up to a high electric field and that the semiconductive EL layer employing the glassy binding agent shown in FIG. 1*a* is by far more excellent than that employing the plastic binding agent shown in FIG. 1*b*. Thus, the characteristic of the EL element of FIG. 1*a* is the most suitable for an EL layer for a D.C. controlled type solid state imaging plate.

FIG. 3 shows an EL element employing Cr_2O_3, which is also a semiconductive metal oxide, instead of SnO_2, TiO_2, WO_3, or Sb_2O_5 as the resistive material. Reference numerals **301**, **302**, **303**, **304**, and **305** designate a glassy binding agent, Cr_2O_3 powder, EL powder such as ZnS: CuAl powder, a transparent nesa electrode, and a transparent glass plate, respectively. The method of manufacturing this element is all the same as that of the element of FIG. 1*a*. The only difference between the elements of FIG. 1*a* and FIG. 3 is that the element of FIG. 3 employs the semiconductive metal oxide Cr_2O_3 which has a poor reflectivity to the light emitted by the EL powder in contrast to SnO_2, TiO_2, WO_3, or Sb_2O_5 employed in the ele-

ment of FIG. 1*a*. From the viewpoint of light reflectivity, a comparison of the luminescent characteristics of the element of FIG. 1*a* which employs the good light reflective material SnO_2, TiO_2, WO_3, or Sb_2O_5 and the element of FIG. 3 which employs the poor light reflective material CrD_3 is given in FIG. 4. Apparently the element employing SnO_2, TiO_2, WO_3, or Sb_2O_5 has a higher luminescent efficiency than that employing Cr_2O_3.

From the foregoing description it is understood that glassy material is excellent as a binding agent for semiconductive EL layers, the baking of glassy material to glass substrates is possible, and SnO_2, TiO_2, WO_3, or Sb_2O_5 is excellent as an electro-resistive material. The configuration of the EL layer can of course be modified depending on purposes. Moreover, it is not always necessary to provide the EL layer directly on the nesa glass.

Since the substrate of the EL element of the present invention is a light transmissive glass plate having a light transmissive electrode thereon, the EL element of the present invention can be employed as an EL element for a solid state image amplifying element by combining with a photoconductive element.

What we claim is:

1. A semiconductive electro-luminescent element having an electro-luminescent layer having a resistivity of 10^5 to 10^8 ohm-cm., which comprises powder of an electro-luminescent material and powder of a semiconductive metal oxide which is highly reflective to the light emitted from said powder of electro-luminescent material, said powders being embedded in a vitreous binding agent, and the proportion of said semiconductive metal oxide being in the range of from 10 to 20% by volume.

2. A semiconductive electro-luminescent element as defined in claim **1**, wherein the proportion of said electro-luminescent material is from 15 to 30% by volume.

3. A semiconductive electro-luminescent element as defined in claim **1**, wherein said powder of semiconductive metal oxide is selected from the group consisting of SnO_2, TiO_2, Sb_2O_5 and WO_3.

4. A semiconductive electro-luminescent element as defined in claim **1**, wherein said vitreous binding agent is glass enamel material selected from the group consisting of SiO_2, B_2O_3, ZnO, BaO and Na_2O.

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D. J. FRITSCH, Assistant Examiner

U.S. Cl. X.R.

117—211, 221; 161—193; 252—301.6 S; 313—108

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,649,553 Dated March 14, 1972

Inventor(s) Kazunoba TANAKA et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Claim for Convention Priority, one of three applications is omitted and should be listed as follows:

--Japan, Appln. N° 41/80698 filed December 7, 1966--.

Signed and sealed this 22nd day of August 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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