ABSTRACT
A transparent conductive coating overlaps a transparent substrate. A layer of an electroluminescent material, such as zinc sulfide doped with manganese and copper, partially covers the conductive coating. A resistive cermet film overlaps the electroluminescent layer and an electrode is attached to the cermet film. The cermet is of a composition so as to exhibit a non-linear current-voltage characteristic and includes conductor particles therein which have an average size of from about 10A to about 20A.

14 Claims, 8 Drawing Figures
(a) 73 VOLUME PERCENT Au

(b) 48 VOLUME PERCENT Au

(c) 35 VOLUME PERCENT Au

(d) 18 VOLUME PERCENT Au

Fig. 3.
ELECTROLUMINESCENT CELL WITH A CURRENT-LIMITING LAYER OF HIGH RESISTIVITY

Background of the Invention

The invention herein described was made in the course of or under a contract or subcontract with the Department of Army. This application is a continuation-in-part of application Ser. No. 348,623 filed Apr. 6, 1973, and now abandoned.

This invention relates to electroluminescent cells and particularly to electroluminescent cells made with resistive cermet films with the cermet films exhibiting nonlinear current-voltage characteristics.

It has been long recognized that the use of electroluminescent materials may provide the simplest means for obtaining a flat panel display, such as for use in television receivers. However, the future of electroluminescent displays depends on continued progress in the development of materials and electroluminescent cell structures.

One invention that greatly advanced the development of electroluminescent devices is disclosed in U.S. Pat. No. 2,880,346 issued to Nicoll et al. on Mar. 31, 1959. That patent disclosed the use of a resistance in series with the electroluminescent particles. The resistance limited current flow to a value below that which would cause the particles to burn out. Therefore, if an individual electroluminescent particle broke down under the influence of the applied voltage, the resistance in series with the particle would limit the current flow through the particle to a value that would prevent burnout of the particle and thereby prevent the shorting of the applied voltage through that particle and around the remaining particles.

The present invention provides a decided improvement in the efficiency, life expectancy, and light output of electroluminescent cells that use resistive layers.

SUMMARY OF THE INVENTION

An electroluminescent cell includes a substantially transparent first electrode and a layer of an electroluminescent material on the first electrode. A resistive film of cermet is on the layer of electroluminescent material. A second electrode is attached to the resistive film. The cermet film has a percent conductor volume such that the film exhibits a non-linear current-voltage characteristic. The conductor particles in the cermet film have an average size of from about 10 A to about 20 A.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an edge view of an electroluminescent cell constructed in accordance with the present invention.

FIG. 2 is a graph showing the average conductor particle size as a function of the cermet composition.

FIG. 3 is an electron micrograph of cermet resistive films of varying compositions including one suitable for use in the electroluminescent cell of the present invention.

FIG. 4 is a graph which indicates the current-voltage characteristic of resistive cermet films which are suitable for use in the electroluminescent cell of the present invention.

FIGS. 5, 6, 7, and 8 are graphs which indicate the characteristics of the electroluminescent cell of FIG. 1 as a function of the cermet composition.

DETAILED DESCRIPTION OF THE INVENTION

The electroluminescent cell structure of the present invention is designed primarily for dc or pulsed dc operation. In such a cell structure, upon the application of a voltage between two electrodes which are disposed on opposite sides of an electroluminescent layer, an electric current, i.e., a transport current, flows through all layers of the cell between the electrodes. The current continues to flow until the applied voltage is removed. The intensity of the light emitted from the cell is proportional to the current. Generally, the dc electroluminescent cell performs only with one polarity of applied voltage. With the opposite polarity, the cell is too conducting to produce electroluminescence and tends to burn out with high applied voltages, i.e., poor ac performance. The dc electroluminescent cell structure is to be distinguished from one designed for ac operation in which an electrically insulating layer is disposed between the electroluminescent layer and the electrode on one or both sides of the electroluminescent layer. When a voltage is applied to the ac cell structure, there is no transport current through the cell, as in the dc cell structure. When the electric field becomes sufficiently large, a displacement current only is established through the electroluminescent layer. The displacement current flows only during a short time during each half-cycle, i.e., if a longer pulse is applied, the displacement current terminates. Electroluminescent cells designed for ac operation, i.e., utilizing the previously described insulating layer, cannot be successfully operated with dc current in view of the previous discussion.

Referring partially to FIG. 1, one form of an electroluminescent cell of the present invention is generally designated as 10. The cell 10 includes a transparent substrate 12 covered by a transparent conductive coating 14. A layer 16 of an electroluminescent material partially covers the conductive coating 14 and a first electrode 18 is attached to a noncoated portion of the conductive coating 14. The layer 16 of electroluminescent material is covered with a resistive cermet film 20 and a second electrode 22 is attached to the film 20.

Although the basic structure of the electroluminescent cell 10 is well known in the art, it is believed that the present invention is the first use of a resistive cermet film to provide the current limiting function for the cell.

In a preferred embodiment, the electroluminescent cell 10 comprises a transparent glass plate substrate 12 coated with a transparent conductive coating 14, such as InO₃, SnO₂, or a mixture thereof. A thin, e.g., 1.5 micron, electroluminescent layer 16 of zinc sulfide (ZnS) doped with manganese (Mn) and copper (Cu) partially covers the conductive coating 14. The electroluminescent layer 16 is covered with a thin, e.g., 3.0 micron, cermet film 20 comprising SiO₂ and Ag or SiO₂ and Ni. The percentage of Ag in the Agₓ(SiO₂)₁₋ₓ cermet by volume can range from about 5% to about 15% with about 11% being preferred. The percentage of Ni in the Niₓ(SiO₂)₁₋ₓ cermet by volume can range from about 9% to about 12%. It is preferred that the cermet thickness is greater than the electroluminescent layer thickness. It has been found that the electroluminescent cells of the present invention are most successful when the conductor particles in the cermet resistive film are of a size such that they are disposed as substantially separate particles in an insulating matrix. An av-
average conductor particle size of about 10Å to about 20Å and a conductor volume of from about 2% to about 20% have been found to give good results. Metal electrodes 18 and 22, such as Al, or Al coated with Cr, or Cr coated with Cr and Au, are deposited on the conductive coating 14 and the cermet film 20, respectively.

It is important to note that the electroluminescent cell of the present invention requires a film type cermet, i.e., such that the composition and particle size can be controlled. It is known in the art that a sputtered or evaporated cermet film can be deposited with the precision necessary to obtain a 2% to 20% volume of conductor with the conductor particles therein having an average size of from about 10Å to about 20Å. For example, U.S. Pat. No. 3,843,420, issued Oct. 22, 1974, to Gittleman et al. describes a method of sputtering which is useful in obtaining cermet films for the electroluminescent cells of the present invention. However, it is preferable to heat the substrate to approximately 200°C to 300°C during the deposition of the cermet film so as to promote film to electroluminescent layer adherence. Thus, the method enables one to obtain the desired cermet resistive film as shown in FIG. 2 in which the average conductor particle size d is shown as a function of the volume fraction x of the conductor in the cermet.

In construction of the preferred embodiment, the conductive coating may be applied by any one of several known techniques, such as by painting, evaporation, or sputtering, although evaporation is preferred. Preferably, the electroluminescent layer is applied to a coated glass.

It is presently believed that the reason the cermet resistive films of the present invention perform better than the resistive layers of the prior art involves the presence of “hot” electrons. Electroluminescence in ZnS films has been shown to be caused by “hot” electrons. Hot electrons are electrons which are generated by high electric fields applied across materials with a large band gap, such as ZnS, D.C. Krupka, Journal of Applied Physics, 43 476 (1972). The energy of these hot electrons may range from a few tenths to a few electron volts. As these electrons pass through an electroluminescent layer, e.g., ZnS, which contains luminous centers such as Mn, Tb, Er, Dy, etc., the electrons impact and ionize the centers, thereby displacing an electron from a given energy level. When another electron falls back into this level, light is emitted from the center.

In addition to the hot electrons it is presently believed that there are also “thermal” electrons passing through the electroluminescent layer with an energy of kT, where T is the temperature in degrees Kelvin, which is less than that of the hot electrons and which is of insufficient energy to produce electroluminescence. It is also believed that the thermal electrons are in majority, especially at high current densities, and that they account for the low power efficiency in conventional electroluminescent cells, e.g., ordinarily much less than 0.1%. The thermal electrons are not only wasteful of power, but are also detrimental to the life of the cells by causing local heating and burnout.

Therefore, it is presently believed that the improved results obtained in the electroluminescent cells of the present invention are due to the presence of the cermet resistive film, i.e., the cermet film favors the conductance of the previously described hot electrons in preference to the thermal electrons so as to function as a thermal electron filter.

It has been found that there are different kinds of conductivity in cermet films which depend upon the film composition, temperature, and applied electric field, e.g., P. Sheng, B. Abeles, and Y. Arte, Physics Review Letters, 31, 44 (1973) and P. Sheng and B. Abeles, Physics Review Letters, 28, 34 (1972). When prepared by sputtering or by evaporation, it is possible to obtain cermet films having extremely small conductor particles, e.g., down to about 5Å, finely dispersed in an insulating medium. The size of the conductor particles and the thickness of the insulating medium separating them are of critical importance in determining the conductivity mechanism.

When the fraction of the conductor in the cermet is large, e.g., 1.0 to 0.4, the conductor particles touch each other, as in FIGS. 3a and 3b in which an electron micrograph of an Al(AlO2)x cermet film is shown, and the conductivity is similar to that of a conductor, i.e., the current voltage characteristic is linear. When the fraction of the conductor falls below about 0.4, the conductor particles begin to break apart to clusters as shown in FIG. 3c. Upon further decrease of the conductor content, the conductor particles become completely separated, as in FIG. 3d, and the conductivity becomes similar to that of a semiconductor, e.g., the current-voltage characteristic for a Ni3O(SiO2)1-x cermet becomes non-linear, as shown in FIG. 4.

Within this last range of composition, two types of conductivity have been found to exist, low field and high field conductivity. Low-field conductivity is the conductivity associated with the conduction of thermal electrons and high-field conductivity is associated with the conduction of higher energy electrons, i.e., hot electrons. The high-field conductivity is promoted by decreasing the conductor content and/or by decreasing the temperature. Thus, it is possible to preferentially conduct either hot electrons or thermal electrons through the cermet film merely by selecting the appropriate cermet composition and temperature, i.e., a resistive cermet film can act as a filter for the unwanted thermal electrons. It is this mechanism which appears to be responsible for the unexpected improvement in the electroluminescent cells of the present invention.

It has been found that the ideal cermet composition may vary for different types of electroluminescent layers. Therefore, in order to optimize the performance of the electroluminescent cell of the present invention, a decision must be made as to what is the best composition of cermet for a particular electroluminescent layer. Since many materials may be used in constructing an electroluminescent cell in accordance with the present invention and all possible combinations of electroluminescent materials, electrode materials and cermet compositions have not been tried, the following procedure, which was used in constructing the preferred embodiments, may be utilized. Basically, the method comprises forming a plurality of electroluminescent cells in a row on a single substrate bearing a film of electroluminescent material, e.g., ZnS:Mn:Cu or ZnS:Mn, of constant composition deposited on a layer of transparent conductive coating. In the construction of the plurality of cells, the composition of the cermet in each cell is varied by the method described by J. J. Hanak et al. in Journal of Applied Physics, 43, 1666, (1972), and J. J. Hanak et al. in Journal of Applied Physics, 44, 5142, (1973). Each of the cells can
then be tested for light output, life expectancy, and efficiency to determine which composition of cermet provides the optimum cell. Once this composition is determined, further cells may be constructed of the same materials and compositions as used in the optimum cell. The results obtained indicated that some cermet compositions unexpectedly worked better than the resistors of the prior art.

Several electroluminescent cells of the present invention were fabricated having a sputtered electroluminescent layer with a constant composition and thickness. The electroluminescent layer was a 1 μm thick ZnS layer, doped with 0.88 mole per cent of Mn. The electroluminescent layer was coated with a layer of a Ni₄(SiO₂)ₓ-x cermet, having a thickness of about 2.5 μm with x ranging from 0.04 to 0.19 for different electroluminescent cells. The cells were tested at a constant brightness of approximately 5 footlamberts as a function of the cermet composition as shown in FIGS. 5-8.

The operating characteristics of the electroluminescent cells of the present invention are shown in FIGS. 5, 6, 7, and 8 as a function of the conductor content in the cermet. The applied voltage, shown in FIG. 5, is dominated largely by the electroluminescent layer at high conductor content in the cermet. For low conductor content, the cermet film has a strong effect on the voltage required to maintain constant brightness. This variation in the applied voltage is due to the relative electrical resistivity of the cermet and the electroluminescent layer, as shown in FIG. 6.

Very high current was required for the highest conductor content (19%) in the cermet layer, as shown in FIG. 7. However, the current required to maintain constant brightness decreased rapidly with decreasing conductor content and then leveled off. The power efficiency of the electroluminescent cells, shown in FIG. 8, increased correspondingly and reached a maximum at about 12% Ni. According to FIG. 6, it is preferable for the electrical resistivity of the cermet film to vary from about 0.3 to about 0.01 of the resistivity of the electroluminescent layer over the range of optimum efficiency.

The use of cermet films, as in the present invention, has unexpectedly improved the performance of the electroluminescent cells to a much greater degree than the use of conventional resistors such as painted carbon, nichrome, or silver paints, e.g., a factor of one or more orders of magnitude, as shown in Table I. The data of Table I was obtained with a sputtered electroluminescent layer of ZnS:TbF₃ containing about 1.5 mole per cent TbF₃ and having a thickness of about 1.2 μm. The electroluminescent layer was coated with various prior art resistive layers including a sputtered cermet film of the present invention which consisted of a 2 μm thick layer of Ni₄(SiO₂)ₓ-x containing about 10% Ni by volume. For purposes of comparison, the electroluminescent layer was also coated with a cermet resistor composition such as one described in U.S. Pat. Nos. 2,924,540 and 3,052,573, which is commercially available as Dupont Resistor Composition 7828 from E. I. DuPont De Nemours and Co. (Inc.). Such a resistor has a sheet resistivity of 10⁴ ohm per square. The cells were tested with a pulsed dc voltage using a pulse width of 40 μsec and a repetition rate of 480 μsec, i.e., 5% duty cycle. The maximum brightness was tested at the maximum applied voltage above which the cell burned out. As can be observed from the test results shown in Table I, the large difference in electroluminescent performance of the electroluminescent cells indicates that the cermet film prepared in accordance with the present invention is not functioning merely as a resistor.

<table>
<thead>
<tr>
<th>Resistive Layer</th>
<th>Maximum Brightness at 215V (fl.)</th>
<th>Brightness at 215V (fl.)</th>
<th>Power Efficiency (%)</th>
<th>Cell Half Life at 215V (h.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtered Ni₄(SiO₂)ₓ-x (prepared in accordance with the present invention)</td>
<td>320</td>
<td>27</td>
<td>4.0 x 10⁻⁴</td>
<td>400 hrs.</td>
</tr>
<tr>
<td>Cermet Resistor Composition</td>
<td>8</td>
<td>5</td>
<td>1.3 x 10⁻⁴</td>
<td>2 min.</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.9</td>
<td>0.7</td>
<td>9.1 x 10⁻⁵</td>
<td>&lt;1 min.</td>
</tr>
<tr>
<td>Silver paint</td>
<td>1.1</td>
<td>0.7</td>
<td>5.1 x 10⁻⁵</td>
<td>&lt;1 min.</td>
</tr>
<tr>
<td>Nichrome</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

Referring again to Table I, it is important to note the Cermet Resistor Composition, e.g., Dupont Resistor 7828, includes conductor particles therein which have an average particle size of 0.1 to 50 microns, where 1 micron is equal to 10,000A. As shown in Table I, the performance of the electroluminescent cell with a cermet film prepared in accordance with the present invention, i.e., 2% to 20% conductor volume and 10A to 20A conductor particle size, greatly surpasses the performance of the electroluminescent cell with the Cermet Resistor Composition in which the conductor particles are of larger size. Also, the electroluminescent cells of the present invention produced more uniform light than the other electroluminescent cells. As previously stated, for different electroluminescent layers, different ranges of cermet composition and hence of particle size may be necessary. However, the cermet composition should be such as to exhibit a non-linear current-voltage characteristic.

Although the electroluminescent cell of the present invention is preferably operated in a dc mode, at least in the sense that a current actually passes through the cell as previously described, the electroluminescent cells of the present invention operate similarly well with both polarities. In addition, the cells operate well under ac excitation. In fact, the ac electroluminescent cell life is improved over the dc cell life. With ac excitation, transport current flows through the entire cell during each half cycle so as to permit pulse width modulation of gray scale.

It should be pointed out that the results obtained in the electroluminescent cells of the present invention are unexpected in view of the prior art which typically suggests that the resistive layer in the electroluminescent cell should have a resistivity in the range of from...
about 10^6 ohm-cm to 10^7 ohm-cm and a sheet resistivity of from about 10^6 ohm per square to about 10^7 ohm per square, e.g., U.S. Pat. No. 3,350,596 and U.S. Pat. No. 2,800,346. In contrast, the electroluminescent cells of the present invention preferably employ cermet resistive films having a resistivity of about 10^6 ohm-cm to about 10^7 ohm-cm and a sheet resistivity of from about 10^6 ohm per square to about 10^7 ohm per square.

In addition, an advantage of the cermet film of the present invention was a noticable improvement in contrast. This advantage probably occurred because the optimum cermet composition yielded a somewhat non-transparent dark brown film that provided a dark background for the emitted light. Also, the dark material, being a good heat radiator, helps to maintain low temperature operation so as to favor the conduction of the hot electrons, as previously mentioned. This advantage, however, must be balanced with the fact that some of the light produced is lost due to absorption by the cermet.

In broad terms, the cermet film of the present invention is a mixture of an electrical insulator and an electrical conductor. One type of cermet within this definition is a mixture of metal particles embedded in a dielectric matrix, such as ceramic. Cermet materials made of ceramic and metal show little solubility between the metallic phase and the ceramic phase at temperatures of preparation and thus are heterogeneous materials wherein small metal grains are embedded in an amorphous insulating matrix. As such, the properties of cermet, such as electrical resistivity and magnetic permeability, generally vary with the relative proportion of metal and insulator present in the composition.

Materials that can be used as electrical insulators in the cermet film of the present invention include borosilicate glasses, aluminum oxide (Al₂O₃), silicon dioxide (SiO₂), magnesium oxide (MgO), titanium dioxide (TiO₂), barium titanate (BaTiO₃), and calcium fluoride (CaF₂). Similarly, materials that can be used as the metal in the cermet include gold (Au), nickel (Ni), tungsten (W), platinum (Pt), chromium (Cr), copper (Cu), aluminum (Al), magnesium (Mg), and silver (Ag). A conductive metal oxide can be used in place of a metal in the cermet. For example, the cermet can comprise a metal oxide, such as indium oxide (In₂O₃), and a ceramic, such as SiO₂. Small changes in cermet composition have large effects on cermet resistivity. While the magnitude of resistivity is important in bringing about optimum performance of electroluminescent cells, it appears unimportant which conductor is used.

Although the electroluminescent cell of the present invention has been described as having a ZnS electroluminescent layer doped with Mn and/or Cu and a ZnS layer doped with TbF₃, it is apparent that similar results would be observed with any other known electroluminescent material as long as the proper cermet composition was utilized. For example, electroluminescent materials suitable for use in the electroluminescent cell of the present invention include ZnS:ErF₃, Ba₂ZnS₃:Mn, and GaN:Zn. Thus, the electroluminescent cell of the present invention provides greater brightness, efficiency, and life expectancy than the electroluminescent cells which employ conventional resistive films.

1. An electroluminescent cell comprising:
   a. a substantially transparent first electrode,
   b. a layer of an electroluminescent material on said first electrode,
   c. a resistive film of cermet on said layer having a percentage conductor volume of from about 2% to about 20% such that said film exhibits a non-linear current-voltage characteristic and said conductor includes particles having an average size of from about 10Å to about 20Å, and
   d. a second electrode attached to said film.

2. The electroluminescent cell as defined in claim 1, wherein said transparent electrode is disposed on a substantially transparent substrate.

3. The electroluminescent cell as defined in claim 2, wherein said first electrode comprises a conductive oxide compound.

4. The electroluminescent cell as defined in claim 2, wherein said layer of electroluminescent material comprises zinc sulfide doped with manganese and copper.

5. The electroluminescent cell as defined in claim 4, wherein the composition of said cermet resistive film comprises a conductive metal oxide and an electrical insulator.

6. The electroluminescent cell as defined in claim 5, wherein said metal oxide is In₂O₃ or SnO₂.

7. The electroluminescent cell as defined in claim 4, wherein the composition of said cermet resistive film comprises a metal and an electrical insulator.

8. The electroluminescent cell as defined in claim 7, wherein said metal is Au, Pt, Cr, Ni, Al, Mg, W or Ag.

9. The electroluminescent cell as defined in claim 8, wherein said metal is Ag.

10. The electroluminescent cell as defined in claim 9, wherein said insulator is silicon dioxide.

11. The electroluminescent cell as defined in claim 10, wherein the composition of Ag in said cermet ranges from about 5% to about 15% of said cermet by volume.

12. The electroluminescent cell as defined in claim 11, wherein the composition of Ag in said cermet is about 11% of said cermet by volume.

13. The electroluminescent cell as defined in claim 8, wherein said metal is Ni and the composition of Ni in said cermet ranges from about 9% to about 12% of said cermet by volume.

14. The electroluminescent cell as defined in claim 7, wherein said electrical insulator is borosilicate glass, Al₂O₃, SiO₂, MgO, TiO₂, BaTiO₃, or CaF₂.