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M. WASSERMAN
PHOTOCONDUCTIVE DEVICES

2,937,353

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Fig. 1

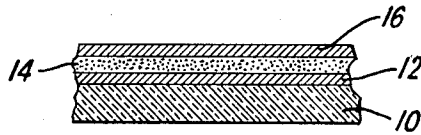


Fig. 2

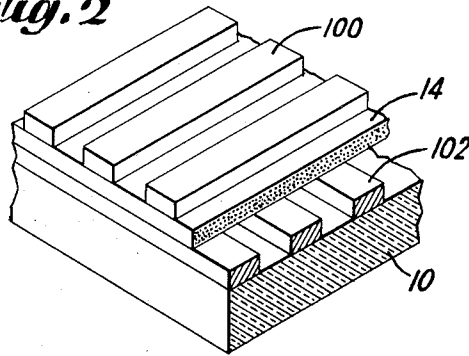
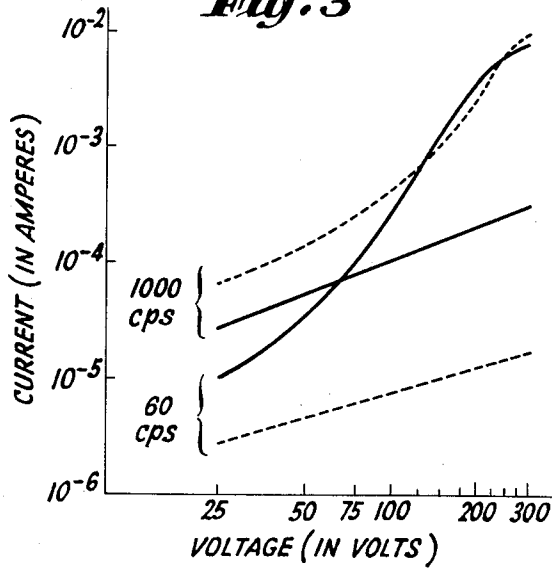


Fig. 3



INVENTOR
MOE WASSERMAN
BY *Isidor Jay*
ATTORNEY

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PHOTOCONDUCTIVE DEVICES

Moe Wasserman, Massapequa Park, N.Y., assignor to Sylvania Electric Products Inc., a corporation of Massachusetts

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14 Claims. (Cl. 338-15)

My invention relates to photoconductive devices.

One known type of photoconductive device comprises a photoconductive layer subtended between two transparent electrodes. A first or alternating voltage is applied between the electrodes. When light is directed upon one or both electrodes, the electrical resistance of the layer is reduced to a low value, and a photocurrent flows through the device. Upon interruption of incident light, the resistance of the layer is increased to a high value, and a much smaller current, the dark current, flows through the device.

For many applications, this type of known device possesses certain severe limitations. For example, the photocurrent is relatively low and normally requires subsequent amplification. Further, the photoconductive sensitivity of the device (i.e. the ratio of the photocurrent to the dark current) is low.

I have invented several new types of photoconductive devices characterized by sharply increased photocurrents and photoconductive sensitivities. In addition, this device possesses greater uniformity over large areas and exhibits less sensitivity to changes in atmospheric conditions. Moreover, I have developed a new process for producing such devices.

In accordance with the principles of my invention, I employ, as a photoconductive powder, cadmium sulfide activated with copper and coactivated with chloride. This material can be produced, for example, in the manner taught in the copending application of Morrison et al., filed February 13, 1959, Serial No. 792,977.

This powder is mixed with a glass frit (i.e. powdered glass). A coating of this mixture is applied to one surface of an electrically conductive glass substrate. The coated substrate is then heated to fuse the frit and bond the powder to the substrate. An electrode, as for example transparent tin oxide, is then applied over the fused coating.

When an alternating or direct voltage is applied between the electrodes, and light is directed upon one of the electrodes, the resultant photoconductive sensitivities and photocurrents were found to be substantially in excess of values heretofore obtainable in a device of this geometry.

A matrix of photoconductive devices can be produced by forming the substrate into a first set of separate, parallel, transparent conductors extending in a first direction, and by forming the electrode into a second set of separate, parallel, transparent conductors extending in a second and non-parallel direction. More particularly, a photoconductive device is formed at each point where any conductor in the second set crosses over any conductor in the first set. Any one of these devices can be electrically or optically excited separately as described in more detail hereinafter.

Moreover, I have found that the adhesion of the photoconductive coating to the substrate can be enhanced, and further, the electrode or the conductors can be more

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easily and securely applied over the coating, when the coating is constituted by a plurality of successively applied thin layers, rather than one relatively thick layer.

Illustrative embodiments of my invention will now be described both with reference to the example which follows and with reference to the accompanying drawings wherein:

Fig. 1 illustrates a photoconductive device in accordance with my invention;

Fig. 2 illustrates a photoconductive matrix in accordance with my invention; and

Fig. 3 is a graph of certain current-voltage characteristics of the devices of Fig. 1 and Fig. 2.

One device in accordance with the invention is shown in cross section in Fig. 1. More particularly, there is shown a glass plate 10, one surface of which is covered with a transparent electrically conductive film 12. A photoconductive layer 14 is applied over the conductive film and a second electrically conductive film 16 is applied over the photoconductive layer. The photoconductive layer comprises a sintered mixture of cadmium sulfide powder and a glass frit (i.e. the powder is embedded in a glass enamel), there being between 50%-85% by weight of cadmium sulfide and between 50%-15% by weight of glass. Layer 14 has a thickness which normally ranges between 3-15 mils.

Referring now to Fig. 2, there is shown a device comprising a photoconductive matrix. More particularly, a continuous transparent electrically conductive film is applied over a layer of window glass. Using sandblasting or other known graphic arts techniques, the electrode is divided into a first set of separate parallel conductors 102 extending in a given direction. The photoconductive layer is then applied in a manner previously indicated and a second electrically conductive film is applied thereover. Again, this film is subdivided into a second set of separate parallel conductors 100 which extend in a second and non-parallel direction. (In this example, the conductors in the first set extend in a direction approximately perpendicular to the conductors in the second set.)

The continuous photoconductive layer can then act as a square array of elements, for example $\frac{1}{16}$ " square. Any one of these elements can be electrically excited by applying a voltage to a selected one of electrodes 100 and a selected one of conductors 102. Further, any of the elements can be optically excited by illumination directed either from a small light source or through an aperture.

EXAMPLE

An illustrative process for preparing the device of Fig. 1 is as follows.

The starting material is photoconductive cadmium sulfide activated with between 2.5×10^{-4} - 20×10^{-4} gram atoms of copper per mole of sulfide and coactivated with chloride, the chloride-copper mole ratio normally falling within the range 2-0.05. A typical ratio is about 1 and a typical concentration is 9.2×10^{-4} . A suspension of this material with a glass frit is formed, the suspension being dispersed in a mixture of hexylene glycol and isopropyl alcohol. Two mixtures of this suspension, 80% by weight of powder to 20% by weight of frit and the other containing 60% by weight of the powder and 40% by weight of the frit, are prepared.

The first mixture is sprayed onto window glass which has been previously coated with a continuous transparent tin oxide film. The coated glass is then heated to a temperature of about 200° C. to dry the coating which then has a weight of about 100 mg. per square inch. The coated glass is then heated in an electrical furnace to a temperature of 650° C. for four minutes and then re-

moved immediately. After the coated glass has cooled to room temperature, a second coating of the same mixture as the first is sprayed over the first fired coating. The coating weight of the second step is about 260 mg. per square inch.

After drying, a third coating (using the second mixture) is sprayed over the second coating. The panel is heated to 700° C. for a period of four minutes. (The dry coating weight of the second mixture is 100 mg. per square inch.) Immediately upon removal from the furnace, the surface is sprayed with a conventional stannic chloride solution to form the second transparent tin oxide electrode.

Under these circumstances, the photoconductive layer is approximately 9 mils. thick. When an alternating voltage of 60 cycles per second is applied between the electrodes (the root mean square value of the applied voltage establishing an electric field intensity of 20 volts per mil.), and the device is illuminated by a green electroluminescent lamp of 10 foot lambert brightness, the photoelectric sensitivity was found to be 1500.

A graph of the voltage-current characteristics for the various applied voltages at separate fixed frequencies of 60 cycles per second and 1000 cycles per second will be found in Fig. 3.

The dotted and solid lines for the higher frequency respectively represent the photocurrent and the dark current. The dotted and solid lines for the lower frequency respectively represent the dark current and the photocurrent.

Further, if 2% by weight of anhydrous cadmium chloride (as expressed in percentage by weight of cadmium sulfide) is added to all spraying suspensions, it was found that a further increase in sensitivity was obtained. More particularly, the sensitivity was increased by a factor of 2 or 3. The decay period, i.e. the response time, of the device produced utilizing the anhydrous cadmium chloride was approximately five times as long as that without it.

The glass frit utilized can be of any type that does not react unfavorably with the photoconductive material. One typical frit has the composition appearing in Table I below.

Table I

Material:	Mole percent
Silicon dioxide -----	23
Titanium dioxide -----	2
Boron oxide -----	23
Zinc oxide -----	25
Barium oxide -----	4
Sodium oxide -----	8.5
Calcium oxide -----	5
Aluminum oxide -----	4
Lithium oxide -----	0.5
Fluorine -----	3

The firing temperatures employed can be varied within the range 575°-700° C., depending upon the firing period, the type of frit, the weight of frit and powder and the like.

What is claimed is:

1. A photoconductive device comprising a layer including photoconductive cadmium sulfide powder mixed with a glass enamel, said powder being activated with copper and coactivated with a chloride; and first and second electrodes secured to opposite surfaces of said layer, at least one of said electrodes being transparent.

2. A photoconductive device comprising a layer of photoconductive cadmium sulfide powder embedded in a glass enamel, said powder being activated with copper and coactivated with a chloride; first and second electrodes secured to opposite surfaces of said layer, at least one of said electrodes being transparent, each of said electrodes consisting of a plurality of separate parallel electrical conductors, the first electrode conductors and

the second electrode conductors extending in different directions.

3. A photoconductive device comprising a layer including photoconductive cadmium sulfide powder mixed with a glass enamel, said powder being activated with copper and coactivated with a chloride, said layer containing 50%-15% by weight of enamel and 50%-85% by weight of powder; and first and second electrodes secured to opposite surfaces of said layer, at least one of said electrodes being transparent.

4. A photoconductive device comprising a layer including photoconductive cadmium sulfide powder mixed with a glass enamel, said powder being activated with copper and coactivated with a chloride, the copper concentration falling within the approximate range 2.5×10^{-4} to 20×10^{-4} gram atoms of copper per mole of sulfide, the coactivator-activator mole ratio falling within the range 2-0.05.

5. A photoconductive device comprising a layer including photoconductive cadmium sulfide powder mixed with a glass enamel, said powder being activated with copper and coactivated with a chloride, the copper concentration falling within the approximate range 2.5×10^{-4} to 20×10^{-4} gram atoms of copper per mole of sulfide, the coactivator-activator mole ratio falling within the range 2-0.05, said layer containing 50%-15% by weight of enamel and 50%-85% by weight of powder.

6. A photoconductive device comprising a first set of coplanar, parallel, separate, electrical conductors extending in a first direction; a second set of coplanar, parallel, separate, electrical conductors extending in a second and non-parallel direction, said first and second sets lying in different parallel planes; and a layer of photoconductive cadmium sulfide powder embedded in a glass enamel interposed between said first and second sets and in contact with the conductors of both sets.

7. A method for producing a photoconductive device comprising the steps of applying a coating to an electrically conductive glass substrate, said coating consisting of a mixture of photoconductive cadmium sulfide powder and a glass frit; firing said coated substrate to a temperature falling within the range 575°-700° C. to fuse said frit and bond said powder to said substrate; and applying an electrically conductive film over said fused coating.

8. The method as set forth in claim 7, wherein prior to the application of said film, at least one additional like coating is applied over the original coating and fired to a temperature falling within said range.

9. A method for producing a photoconductive device which comprises the steps of applying to an electrically conductive glass substrate a coating consisting of a mixture of photoconductive cadmium sulfide and glass frit, said coating containing 50-15% by weight of frit and 50%-85% by weight of sulfide; firing said coated substrate to a temperature falling within the range 575°-700° C.; applying a second like coating to said fired coating; again firing the coated substrate to a temperature falling within said range; and applying an electrically conductive film over said second fired substrate.

10. A method for producing a photoconductive device which comprises the steps of applying to an electrically conductive glass substrate a coating consisting of a mixture of photoconductive cadmium sulfide and glass frit, said coating containing 50%-15% by weight of frit and 50%-85% by weight of sulfide; said powder being activated with copper and coactivated with a chloride, the copper concentration falling within the range 2.5×10^{-4} to 20×10^{-4} gram atoms of copper per mole of sulfide, the coactivator-activator ratio falling within the range 2-0.05; firing said coated substrate to a temperature falling within the range 575°-700° C. to fuse said frit and bond said powder to said substrate; and applying an electrically conductive film over said fired coating.

11. A method for producing a photoconductive device comprising the steps of applying a coating to an electrical-

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ly conductive glass substrate, said coating consisting of a mixture of photoconductive cadmium sulfide powder, cadmium chloride, and a glass frit; firing said coated substrate to a temperature falling within the range 575-700° C. to fuse said frit and bond said cadmium sulfide and cadmium chloride coating to said substrate; and applying an electrically conductive film over said fused coating.

12. The method as set forth in claim 11, wherein the amount of cadmium chloride in said coating is approximately 2% by weight and wherein prior to the application of said film at least one additional like coating is applied over the original coating and fired to a temperature falling within said range.

13. A photoconductive device comprising a layer including photoconductive cadmium sulfide powder mixed with a glass enamel, said powder being activated with copper and coactivated with a chloride, said layer containing 50-15% by weight of enamel and 50-85% by

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weight of powder; and first and second electrodes secured to opposite surfaces of said layer, at least one of said electrodes being transparent, each of said electrodes consisting of a plurality of separate, parallel, electrical conductors, the first electrode conductors and the second electrode conductors extending in different directions.

14. A photoconductive device as defined in claim 13, wherein the copper concentration falls within the approximate range 2.5×10^{-4} to 20×10^{-4} gram atoms per mole of sulfide and the coactivator-activator mole ratio falls within the range 2-0.05.

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