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3,466,183

METHOD OF MANUFACTURE PHOTOCONDUCTIVE LAYERS

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FIG. 1

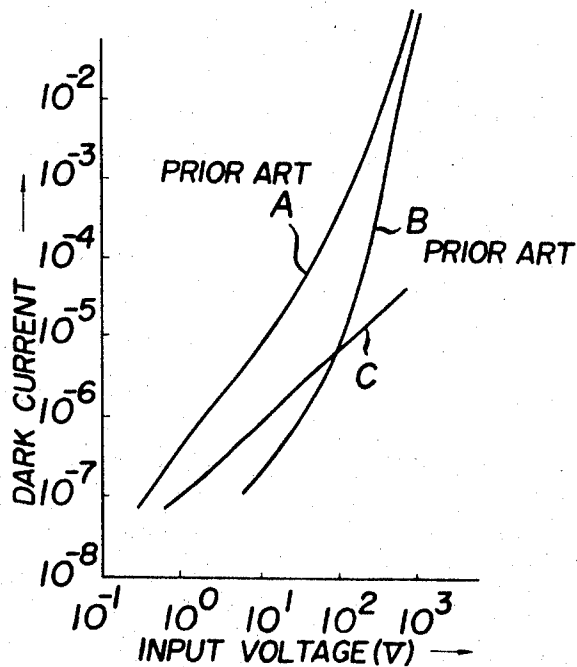


FIG. 2

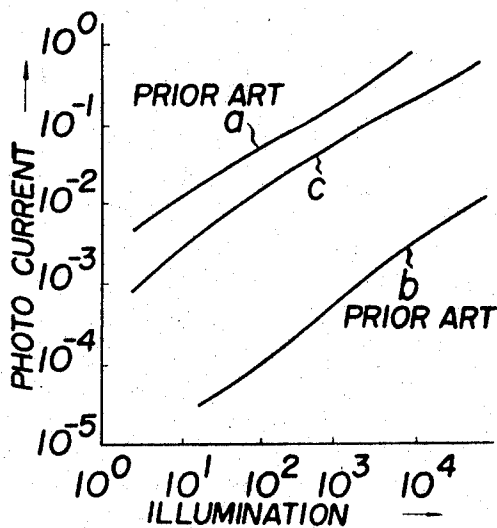
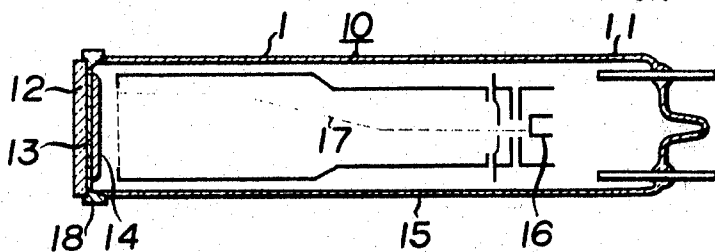


FIG. 3



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METHOD OF MANUFACTURING PHOTO-
CONDUCTIVE LAYERS

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3 Claims

ABSTRACT OF THE DISCLOSURE

A method of manufacturing a photoconductive target for use in an image pickup tube by vaporizing a powdery mixture formed by adding minute amounts of thallium to cadmium selenide and cadmium chloride to form a photoconductive layer on a transparent conductive layer which is on a substrate, and heat treating the formed layer at a temperature of from 425° C. to 700° C. in an inert atmosphere containing selenium vapor.

This invention relates to a method of manufacturing photoconductive layers of chalcogenated cadmium of improved characteristics, especially suitable for use as targets of image pickup tubes.

As an example of photoconductive devices utilizing a photoconductive material consisting of chalcogenated cadmium, i.e., cadmium sulphide, cadmium selenide, or cadmium telluride or mixtures of two or more of them there have been proposed devices having a photoconductive layer essentially consisting of said photoconductive material and formed on a transparent electrode layer which is deposited on one surface of an electric insulating sheet or on a glass substrate. Notwithstanding numerous efforts to improve the photosensitivity of the photoconductive layer of the prior art device, in practice there are a number of unsolved problems.

Photoconductive layers of high photosensitivity can be obtained by depositing a photoconductive material upon a substrate by vapor-deposition method, for example, and then heating the deposited material in an inert atmosphere or by heating a vapor-deposited photoconductive layer under the state of coexistence with an activator such as a halogenated compound, copper, silver and the like. For example, a mixture of cadmium selenide, 10% of cadmium chloride and 0.01% of copper chloride, based on the weight of cadmium selenide was deposited in a vapor-depositing apparatus on a glass substrate to form a photoconductive layer and then the deposited layer was fired in a nitrogen atmosphere for one hour at 500° C. Hereinafter the photoconductive layer thus obtained will be referred to as the "reference Example No. 1." This layer was cut to have a width of 10 mm. and indium was deposited upon the surface of the photoconductive layer at a spacing of 0.5 mm. to provide a counter electrode. At an applied voltage of one volt, the ratio between the photocurrent and dark current was measured to be 1000 at 1000 luxes which shows that the photosensitivity of the layer is excellent. Such a highly sensitized photoconductive layer exhibits a high dark resistance and a high photosensitivity when used with a low applied voltage but when it is applied with such a high voltage that will produce a high electric field of more than 2×10^3 v./cm., for example, it was found that the dark resistance had decreased rapidly, as shown by curve A, FIG. 1, thus greatly increasing the dark current. This causes a decrease in the photosensitivity to such an extent that the photoconductive layer can not be used practically.

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In order to prevent this rapid decrease of the dark resistance it was attempted to treat the photoconductive at about 400° C. in an atmosphere of gaseous sulfur at a reduced pressure but the problem is not yet completely solved. For example, when the photoconductive layer of the above mentioned reference Example 1 is treated in a sulfur atmosphere of reduced pressure for one hour at 400° C. the dark resistance of the so-treated photoconductive layer (reference Example No. 2) is somewhat improved as shown by curve B in FIG. 1. However, the tendency of rapidly increasing the dark current at high voltages still remains. The sample used in this test was identical with said reference Example 1. Yet the photocurrent-light intensity characteristic is inferior to that of the reference Example 1 (curve A) as shown by curve B in FIG. 2. Such a rapid change in the dark resistance of the photoconductive layer greatly hinders practical use of the devices utilizing photoconductive layers of the type referred to above.

In pickup tubes, especially of the vidicon type, for television cameras, photoconductors are being used for their targets. These photoconductors are required to have a dark resistance of more than 10^{12} ohm-centimeters and an image timelag shorter than one period of the television frame, for example $\frac{1}{30}$ second. While the above mentioned photoconductor consisting of a cadmium compound is known in the art as a photoconductor having high sensitivity it has been considered that it is not suitable for use as a target of a pickup tube because of its low dark resistance and variation thereof mentioned above.

It is therefore an object of this invention to provide a method of manufacturing a photoconductive layer having high sensitivity and stable dark resistance.

Another object of this invention is to provide a novel method of manufacturing a photoconductive layer having a high dark resistance and hence is suitable for use as targets of pickup tubes.

Further objects and advantages of the present invention will become apparent and this invention will be better understood from the following description, reference being made to the accompanying drawing. The features of the novelty which characterize this invention are set forth in the claims annexed to and forming part of this specification.

In the drawings:

FIGS. 1 and 2 are graphs to compare the characteristics of a photoconductive layer prepared in accordance with a preferred embodiment of this invention and one prepared by a prior method wherein FIG. 1 shows the dark current-voltage characteristic and FIG. 2 the photocurrent-light intensity characteristic; and

FIG. 3 shows a longitudinal cross section of a pickup tube utilizing the photoconductive layer prepared in accordance with this invention.

According to this invention the characteristics of a photoconductive layer formed by vapor-deposition and sintering are improved without affecting the photosensitivity thereof by heat treatment carried out in an atmosphere maintained at normal pressure and containing one or more of sulfur, selenium and tellurium at a temperature of from 425° to 700° C., preferably from 500° to 650° C.

Referring now to the accompanying drawing there is shown in FIG. 3 a pickup tube 10 including a target which utilizes a photoconductive layer prepared in accordance with this invention. The tube 10 shown is of the vidicon type and a transparent electric conductive layer 13 which may be made of tin oxide is deposited upon the inner surface of a face plate 12 provided at one end of an evacuated tubular envelope 11. A target 14 made of a photoconductive layer is formed on the transparent conductive layer 13. An electron gun 15 is dis-

posed in the envelope to oppose the target whereby an electron beam emitted from a cathode electrode 16 of the electron gun is caused to scan across the surface of the target 14. When an optical image is projected upon the target 14 an electrostatic charge pattern corresponding to the optical image will be formed on the target and the charge is then discharged and erased by the scanning action of the electron beam 17 while at the same time the discharge current obtainable from the electric conductive layer 13 is obtained from the tube through a signal ring 18 as the output signal. The target is manufactured as fully described in the following examples of this invention.

EXAMPLE 1

A powdery mixture consisting of about 20%, by weight, of cadmium chloride, from 0.05 to 0.2%, by weight of thallium and the balance of cadmium selenide was put in a vaporizing crucible made of quartz which is equipped with a tungsten heater and located in an evacuated vessel maintained in a vacuum of about 10^{-5} mm. Hg. A glass substrate coated with a transparent electric conductive layer of tin oxide was disposed above the crucible to oppose thereto. When the tungsten heater was energized said powder was heated to vaporize and was deposited upon the transparent conductive layer on the substrate. During the vapor-deposition process the substrate was maintained at a constant temperature, for example, 100° C.

The thickness of the deposited layer was controlled to be in a range of from 0.1 to 10 microns in order that the layer may be utilized as targets for pickup tubes. The deposited layer was then heat treated in an inert atmosphere containing selenium vapors for about 30 minutes at 500° C. while being maintained at normal pressure, thus providing a photoconductive layer target of high sensitivity.

In the above described process although the resistance of the photoconductor can be increased by increasing the quantity of the impurity such as copper, thallium and the like, an increase in the quantity of copper results in non-uniform diffusion whereas with thallium even when the quantity thereof is increased it is possible to form layers of uniform quality. In television pickup tubes this is important in order to provide a uniform background. Although the residual image can be reduced by increasing the quantity of thallium, too much thallium would result in a decrease of the sensitivity and it has been found by experience that the preferably quantity of thallium is in a range of from 0.05 to 0.2%.

With regard to the thickness of the photoconductive layer it has been found that too thick layer decreases the sensitivity at a short wave length whereas too thin a layer results in a decrease in the absorption of light, thus again decreasing the sensitivity. At the same time the image timelag is increased. By this reason the thickness of the photoconductive layer should be in a range of from 0.1 to 10 microns as described above.

The substrate deposited with a photoconductive layer in the manner described above can be immediately utilized as the face plate 12 of the image pickup tube shown in FIG. 3 in which case the photoconductive layer serves as the target 14.

EXAMPLE 2

A photoconductive layer was formed on a glass substrate by simultaneous vapor deposition of cadmium selenide, 10% by weight, of cadmium chloride and 0.01%, by weight, of copper chloride based on the weight of cadmium selenide by a conventional method and then the photoconductive layer was baked for one hour at 500° C. in a nitrogen atmosphere. The photoconductive layer thus prepared was then heat treated for 30 minutes at 500° C. in a nitrogen atmosphere containing selenium. The width of the photoconductive layer was adjusted to be 10 millimeters and indium was deposited upon the surface of the layer at a spacing of 0.5 mm. to provide a counter-electrode.

The result of measurement of its dark current-voltage characteristic is indicated by the curve C in FIG. 1. As can be noted from this curve the dark current-voltage characteristic is a straight line until a field strength of about 2×10^4 volt/cm. is reached, thus showing no rapid increase in the dark current under low voltages as well as under high voltages. It can be clearly noted that the dark current characteristic of the photoconductive layer is greatly improved when one compared the curve C (the photoconductive layer prepared by the novel method) with curves A and B respectively representing the dark current-voltage characteristics of said Examples 1 and 2 of the prior art. Other characteristics, for example, the photo-current-light intensity characteristic represented by the curve c of FIG. 2 are comparable with those of the reference Example 1 represented by a curve a which means that the deterioration of this characteristic is not large.

In this manner, according to the novel method the dark current characteristic of the photoconductive layer can be readily improved without sacrificing the photocurrent characteristic thereof. Thus, it is possible to apply the photoconductive layer in much wider field of application.

Although in the above examples this invention has been embodied in the fabrication of a photoconductive layer wherein cadmium selenide, cadmium chloride and copper chloride are to be vapor-deposited simultaneously and then the deposited layer is to be baked in the nitrogen atmosphere. It is to be understood that this invention is also applicable with equal results to photoconductive layers of the following compositions and treating atmosphere. For example, the photoconductive layer may be prepared by vapor deposition of chalcogenated cadmium, i.e., cadmium sulfide, cadmium telluride, cadmium selenide or mixtures or solid solutions comprising two or more of them, the photoconductive layer thus formed may be baked in an inert gas or air. A suitable amount of one or more of halogen compounds, copper, silver, gold and thallium may be incorporated to said vapor deposited layer which can be baked in air or inert gas, if desired. Instead of chalcogen, i.e., selenium, sulfur, tellurium or a mixture of them may be added to the heat treating atmosphere which may be composed of nitrogen, other inert gas, air, hydrogen or the like. The pressure of the treating atmosphere is preferably of the order of normal pressure in view of the heat treating temperature or vaporization. The temperature and time of the heat treatment are suitably selected dependent upon the type, field of application and the like of the photoconductive layer to be treated. However the treating temperature should be higher than 425° C. because below this value a longer period of time is required to obtain the desired result, or the result often is not obtained. A treating temperature above 700° C. results in the vaporization of the deposited photoconductive layer, so that the treating temperature should be maintained below 700° C.

The measured values in the following examples were obtained by adjusting the width of the photoconductive layer to 10 millimeters, and by vapor-depositing indium upon the surface of the layer at a spacing of 0.5 mm. to form the counter electrode which was used for measurement.

EXAMPLE 3

A photoconductive material comprising a mixture of cadmium sulfide and cadmium selenide in equal weight ratio, 10% of cadmium chloride and 0.1% of thallium, based on the weight of said photoconductive material were simultaneously vapor-deposited by a conventional method upon two glass substrates and the photoconductive layers thus formed were baked for 10 minutes at 650° C. in an argon atmosphere. One of the photoconductive layers thus obtained was heat treated for 2 hours at 425° C. in the argon atmosphere containing sulfur and its dark current-voltage characteristic was measured. With applied voltages less than about 100 v. the value of the dark current

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was nearly equal to that of said reference examples. Even with an applied voltage of about 100 v. the current-voltage characteristic was a straight line without any electric breakdown. In the case of the other photoconductive layer which had not been subjected to the above mentioned treatment, the dark current was rapidly increased as the applied voltage was increased above 100 v., and at about 1000 v. an electric breakdown was noted.

EXAMPLE 4

After vapor-depositing carmium telluride upon each of two glass substrates, the deposited layers were baked for 15 minutes at 600° C. in a nitrogen atmosphere to form photoconductive layers. One of the photoconductive layers thus obtained was heated for 15 minutes at 650° C. in the nitrogen atmosphere containing tellurium and its photo-sensitivity was measured. The ratio between the dark current a and photocurrent was 100 with an applied voltage of one volt and a light intensity of 1000 luxes. With regard to the dark current-voltage characteristic the value of current was substantially equal to that of the contrast mentioned below with applied voltages up to 200 volts and the current voltage characteristic was linear with applied voltages up to about 1000 v. On the other hand the photo-sensitivity of the other photoconductive layer, or the contrast which had not been treated as above was found that the ratio between the dark current and the photoelectric current was 100, or the same as that of the treated layer with an applied voltage of one volt and a light intensity of 1000 luxes. However, the dark current-voltage characteristic was different and a rapid increase in the dark current was noted at about 200 v. and above.

As can be noted from the examples described herein-above this invention provides a method of manufacturing a photoconductive layer wherein a photoconductive layer comprising at least one of chalcogenated cadmiums as the principal composition is heated at a temperature of from 425° C. to 700° C., preferably from 500° C. to 650° C., in an atmosphere containing at least one of chalcogens,

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thus obtaining a photoconductive layer of high sensitivity and having excellent dark resistance characteristic, which is extremely useful as a photoconductive target in a pickup tube or as a solid image amplifier.

What is claimed is:

1. A method of manufacturing a photoconductive target for use in an image pickup tube comprising the steps of vaporizing a powdery mixture consisting of about 20%, by weight, of cadmium chloride, from 0.05 to 0.2%, by weight of thallium and the balance of cadmium selenide to form a photoconductive layer on a substrate, said layer being made to have a thickness of from 0.1 to 10 microns and heat treating said photoconductive layer at a temperature of from 425° to 700° C. in an atmosphere containing selenium vapor.

2. The method according to claim 1 wherein the period of heat treatment carried out in said atmosphere is less than two hours.

3. The method according to claim 1 wherein the other gas component of said atmosphere is principally nitrogen.

References Cited

UNITED STATES PATENTS

2,685,530	8/1954	Cusano et al.	117—106 X
2,688,564	9/1954	Forgue	117—106 X
2,710,813	6/1955	Forgue	117—106 X
2,810,087	10/1957	Forgue	117—106 X
2,829,074	4/1958	Lubszynski	117—106 X
2,681,903	11/1958	Heimann	117—106 X
2,879,362	3/1959	Meyer	117—34 X
3,127,282	3/1964	Hershinger	117—106 X
3,142,586	7/1964	Colman	117—106 X

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