Oct. 10, 1967 J. DRESNER 3,346,755

DARK CURRENT REDUCTION IN PHOTOCONDUCTIVE TARGET BY BARRIER JUNCTION BETWEEN OPPOSITE CONDUCTIVITY TYPE MATERIALS

Filed March 31, 1966

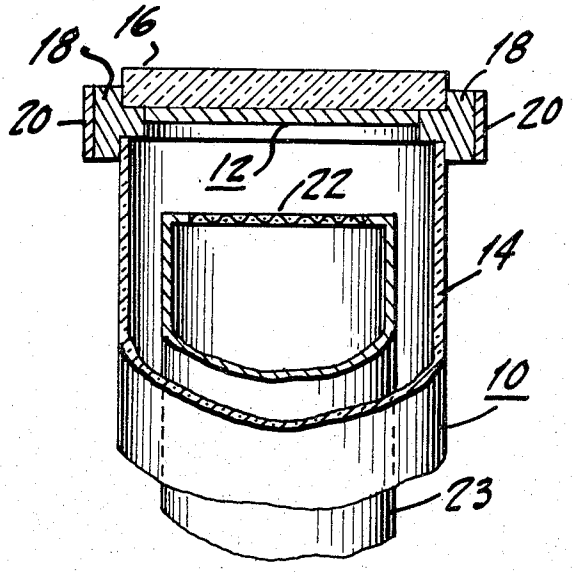



Fig. 1.

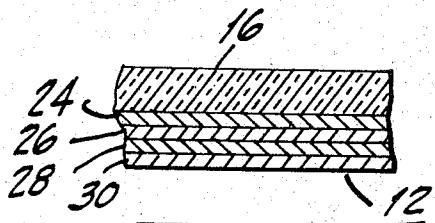



Fig. 2.

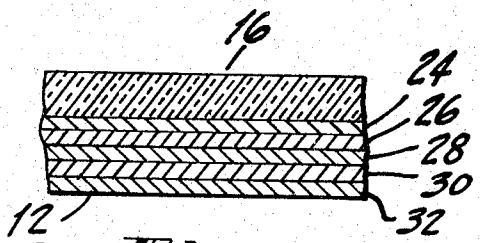



Fig. 3.

INVENTOR.
JOSEPH DRESNER
BY
L. A. Larsen
Attorney

United States Patent Office 3,346,755 Patented Oct. 10, 1967



3,346,755

# DARK CURRENT REDUCTION IN PHOTOCONDUCTIVE TARGET BY BARRIER JUNCTION BETWEEN OPPOSITE CONDUCTIVITY TYPE MATERIALS

Joseph Dresner, Princeton, N.J., assignor to Radio Corporation of America, a corporation of Delaware

Filed Mar. 31, 1966, Ser. No. 539,107
7 Claims. (Cl. 313—94)

My invention relates to targets for photoconductive devices and particularly to an improved target including vitreous selenium.

One type of photoconductive device in which the target herein disclosed is adapted to be used to advantage is a vidicon pickup tube. A vidicon pickup tube generally comprises an evacuated glass bulb within which is mounted an electron gun of any suitable construction for developing a beam of electrons. The electrons so developed are focused and deflected in a desired scanning beam over a photoconductive target.

The photoconductive target is usually supported on a light-transparent backing which may be the end wall or faceplate of a glass bulb or tube envelope. The target usually includes an electrically conductive light-transparent layer serving as a signal plate, and a layer of photoconductive material over the signal plate. The focused and deflected electrons are deposited on the face of the photoconductive target remote from the signal plate to produce a charge thereon.

One problem in connection with a photoconductor including selenium in the vitreous state is the relatively rapid reversion of the vitreous selenium to the crystalline state. Selenium is objectionably conductive in the crystalline state. Such reversion is particularly pronounced when the photoconductor is heated during fabrication and operation of a device in which it is used. While prior attempts to solve this problem have resulted in some improvement with respect to the thermal stability of a selenium-containing photoconductor, further increase in thermal stability is desirable for increased operating life and improved performance of the device.

Another problem arising where a selenium-containing photoconductor is used, concerns dark current. While prior attempts have resulted in appreciable reduction of dark current, a further reduction thereof is desirable for optimum results.

Accordingly, it is an object of the invention to improve the thermal stability of a target for a photoconductive device including vitreous selenium.

A further object is to provide an improved substrate for a photoconductive layer including vitreous selenium. in order to increase the thermal stability of the layer.

Another object is to provide a target for a photoconductive device containing vitreous selenium and tellurium and in which the dark current is appreciably reduced.

I have discovered that where vitreous selenium is used in the target of a photoconductive device, the smoothness of the substrate on which the vitreous selenium is overlaid contributes appreciably to thermal stabilization of the selenium in the vitreous state. As herein disclosed, the desired smoothness of the substrate is obtained in one example by first depositing a layer of bismuth trioxide on a relatively smooth glass faceplate, then coating the layer of bismuth trioxide with a relatively thin layer of gold, and coating the gold layer with a relatively thin layer of wide band gap N-type semiconductor material. To the relatively smooth surface of the wide band gap N-type semiconductor material is applied a photoconductive layer of vitreous selenium-tellurium alloy. The relatively thin layer of wide band gap N-type semiconductor material intermediate the bold and selenium alloy layers,



not only contributes to thermal stability of the vitreous selenium alloy outer layer but also is accompanied by an appreciable reduction in dark current.

If desired, an outer stabilizing layer may be applied to the selenium alloy layer.

Further objects and features of the invention will become apparent as the present description continues.

In the drawing, to which referece is now made for a description of an embodiment of the invention by way of example:

FIG. 1 is a fragmentary view, partly in section, of a vidicon tube having a photoconductive target including a vitreous selenium alloy characterized by increased thermal stability of the alloy and reduced dark current; and

FIGS. 2 and 3 are fragmentary sectional views of plural layer targets that may be used in the vidicon tube shown in FIG. 1.

In FIG. 1 is shown a vidicon tube **10** in which a target **12** incorporates the present invention. The tube **10** is conventional except for the target **12**. The tube **10** comprises an elongated glass envelope **14** closed at one end thereof by a transparent glass faceplate **16**. The faceplate **16** is sealed across the end referred to by means of an indium ring **18** and a clamping ring **20**. The target **12** is positioned on the inner surface of the faceplate **16**. Closely spaced from the target **12** is a mesh screen **22** mounted across one end of a tubular focusing electrode **23**. In the other end portion (not shown) of the envelope **14** is positioned an electron gun for providing an electron beam. The beam is scanned across the target **12** by suitable means such as electromagnetic coils (not shown) disposed outside of the enevelope **14**.

The target **12** is a multilayered structure that may have either of the forms illustrated in FIGS. 2 and 3.

In the form shown in FIG. 2, the target **12** comprises four layers supported on the faceplate **16**. The first layer **24** next to the faceplate **16**, comprises bismuth trioxide having a thickness of from about 10 to about 500 microns. The maximum thickness of this layer is not critical, except that it should not be so thick as to objectionably impede light transfer therethrough. On the bismuth trioxide layer **24**, is a relatively thin layer **26** of gold which serves as a signal electrode. The gold layer **26** may have a thickness of from about 10 to about 200 Angstroms. A third layer **28** of a wide band gap N-type semiconductor material covers the gold layer **26**. The layer **28** may have a thickness of from about 10 to about 500 Angstroms. Among the materials suitable for the layer **28** are cadmium sulfide, cadmium selenide, bismuth trioxide or tin dioxide. Of these materials I prefer to use cadmium selenide for best results.

A photoconductive layer **30** applied to the layer **28**, comprises a vitreous alloy of selenium and tellurium. Arsenic may also be included. Although the arsenic may be omitted for satisfactory results, its presence contributes to improved decay. The layer **30** may have a thickness of from about 4 to about 7 microns.

The layer **30** is graded so as to provide a richer concentration of tellurium at the surface of the layer adjacent to the N-type layer **28**, than at the opposite surface. The amount of tellurium in the layer **30** is preferably gradually reduced towards the surface of the layer remote from the N-type layer **28**.

For good results the vitreous alloy layer **30** may contain at its surface adjacent to the N-type layer **28**, from 70 to 82% selenium, 17 to 29% tellurium and about 1% arsenic, all by weight. However, for best results the vitreous alloy layer **30** contained about 76% selenium, about 23% tellurium and about 1% arsenic by weight at its surface adjacent to the gold layer **26**. When arsenic is not used, the selenium content may be increased by about

1% by weight. The tellurium content in the surface region of layer **30** remote from the N-type layer **28**, may be from 0 to about 10% by weight. The arsenic when used is uniformly distributed throughout the layer **30**.

The combination of layers **24**, **26** and **28** is accompanied by several important advantages. One of these advantages concerns a preservation of thermal stability of the vitreous alloy layer **30**. Another advantage relates to a reduction in dark current.

With respect to thermal stability of the vitreous alloy layer **30**, I have found that the smoothness of the substrate, i.e., the N-type layer **28** on which the vitreous alloy layer **30** is deposited, contributes to improved thermal stability of the vitreous character of the layer **30**. Such smooth surface of the layer **28** involves an appreciable reduction in surface discontinuities. Since such discontinuities induce crystal growth in the vitreous alloy layer **30**, their reduction or elimination by the smooth character of the N-type layer **28** effectively serves to restrain crystal growth and thereby preserve the vitreous form of the alloy layer **30**. I have found that the smoothness of the N-type layer **28** is appreciably enhanced by the smoothness of the layer **24** of bismuth trioxide. Such smoothness of the layer **24** of bismuth trioxide is a consequence of several factors including the natural tendency of this material to form a smooth surface and the manner in which the layer **24** is formed, as will be described in the following.

As far as reduced dark current is concerned, I have found that the junction between the N-type layer **28** and the tellurium rich surface of the vitreous alloy layer **30**, restrains hole injection in the junction when reverse biased. Such reverse bias occurs when the gold layer **26** serving as a signal electrode is connected to a positive voltage source and the vitreous selenium alloy layer **30** is rendered negative by electrons impinging on the surface thereof remote from the layer **28**. The junction formed by the N-type layer **28** and the P-type tellurium-rich surface of the layer **30** serves to block hole injection from the layer **28** when so biased and when layer **30** is in the non-conductive state as when in the dark. This junction may thus be termed a blocking junction.

For further stabilization of the vitreous alloy layer **30** a stabilizing layer **32** may be provided over the surface of the layer **30** remote from the faceplate **16**, as shown in FIG. 3. The stabilizing layer **32** may be formed of a material such as germanium, germanium oxide, antimony trisulfide or antimony trioxide. Of these materials, I have found germanium and germanium oxide to be the best.

In making the target herein disclosed I take great care to assure that the substrate **16**, which may be a glass or fused quartz faceplate and on which the layer **24** of bismuth trioxide is to be deposited, is characterized by the best obtainable smoothness and freedom from surface imperfections. One way in which such surface smoothness may be produced is by lapping or fire polishing.

Bismuth trioxide is then evaporated on the smooth substrate surface in an ambient containing oxygen and having a pressure of about 10 microns of mercury to form the layer **24**. The layer **24** should have a minimum thickness of 10 microns and may have a maximum thickness determined by its light absorption as indicated before herein. Such light absorption should be sufficiently small so as not to affect adversely a desired light energization of the target by an image to which the target is exposed. I have found that a thickness of layer **24** up to about 500 microns is not accomplished by light absorption to an objectionable degree. The bismuth trioxide may be evaporated from a heated boat, or in any ther suitable known manner.

The gold signal electrode layer **26** is next applied over the bismuth trioxide layer **24** by heating a gold coated filament to evaporate gold therefrom in known manner. The gold evaporation step may be performed in the oxygen-containing ambient in which the layer **26** was deposited, or in any other desired ambient. The gold evaporation is permitted to proceed until the resultant gold layer **26** acquires a thickness of from about 10 to about 200 Angstroms. The thickness may be monitored by a commercially available quartz thickness monitor.

After the application of the bismuth trioxide layer **24** and the gold layer **26** to the faceplate **26**, the faceplate may be removed from the evaporator in which the gold layer was formed and placed in a dust-free container and air baked at temperatures ranging from 50° C. and up to about 300° C. for approximately one hour. While this air baking step is not necessary for satisfactory results, its practice appreciably improves the operation of the finished device as a consequence of desirable changes produced in the bismuth trioxide layer **24** by this step. One of these changes is to increase the smoothness of the surface of layer **24** adjacent to the gold layer **26**.

Following the application of the gold layer **26**, and the baking step, the layer **28** of wide band gap N-type semiconductor material, such as cadmium selenide, is evaporated onto the gold layer **26** to a thickness of from about 10 to about 500 Angstroms. The evaporation may be effected in an ambient having a pressure of about $10^{-5}$ torr. The thickness of the layer **28** may be determined by a suitable light interference monitor in known manner. After evaporation of layer **28**, the coated substrate may be removed from the evaporator and air baked at temperatures from 50 to 300° C. for approximately one hour. While this step is not necessary for satisfactory results, it is desirable in that it contributes to a further reduction in dark current.

After the layer **28** has been applied, the vitreous selenium-containing alloy layer **30** is formed to a thickness of from about 4 to about 7 microns. In order to provide a desired grading of the tellurium content of the alloy of from about 17 to about 29% by weight of tellurium in the surface region of the layer **28** adjacent to layer **30**, from about 0 to about 10% by weight of tellurium in the opposite surface region of layer **28**, and about 1% by weight of arsenic, if desired, a dropping pellet technique may be employed such as is described in copending application Ser. No. 507,728 of William M. Kramer and assigned to the assignee of this application.

The final stabilizing layer **32** of material such as germanium or germanium oxide, or other material described before herein in connection with layer **32**, may be formed over the vitreous selenium alloy layer **30** by suitably evaporating the same and monitoring the thickness to a value of from about 10 to about 100 Angstroms.

It is apparent from the foregoing that I have provided an improved vitreous selenium alloy target for a photoconductive device.

I claim:

**1.** A target for a photoconductive device comprising:
(a) a light transparent substrate,
(b) a relatively thick layer of bismuth trioxide on said substrate,
(c) a relatively thin layer of gold on said bismuth trioxide layer,
(d) a relatively thin layer of wide band gap N-type semiconductor material on said gold layer, selected from the group consisting of cadmium sulfide, cadmium selenide, bismuth trioxide and tin dioxide, and
(e) a relatively thick layer containing vitreous selenium on said layer of wide band gap N-type semiconductor material.

**2.** A target for a photoconductive device according to claim **1**, and wherein said relatively thick layer containing vitreous selenium is overlaid with a stabilizing layer made of a material selected from the group consisting of germanium, germanium oxide, antimony trisulfide and antimony trioxide.

**3.** A target for a photoconductive device according to claim **1** and wherein:
(a) said layer of bismuth trioxide has a thickness of

from about 10 to about 500 microns,

(b) said layer of gold has a thickness of from about 10 to about 200 Angstroms,

(c) said layer of wide band gap N-type semiconductor material has a thickness of from about 10 to about 500 Angstroms, and

(d) said vitreous selenium-containing alloy having a thickness of from about 4 to about 7 microns.

4. A target for a photoconductive device comprising:

(a) an air-baked substrate including a support and succeeding layers of bismuth trioxide and gold on said support,

(b) a layer of cadmium selenide on said gold, and

(c) a layer of vitreous selenium-tellurium alloy on said layer of cadmium selenide,

(1) the tellurium in said vitreous alloy being graded in content from a maximum at the surface of said alloy adjacent to said layer of cadmium selenide, to a minimum in the opposite surface of said alloy layer.

5. A target for a photoconductive device according to claim 4 and wherein said vitreous selenium-tellurium alloy includes about 23% tellurium by weight at the surface thereof adjacent to said cadmium selenide layer, and from about 0 to about 10% of tellurium by weight at the opposite surface of said alloy layer.

6. A target for a photoconductive device comprising:

(a) a substrate having a relatively smooth surfaced outer signal electrode layer thereon, and a layer of bismuth trioxide having a thickness of from about 10 to about 500 microns under said signal electrode layer,

(b) a layer of wide band gap N-type semiconductor material on said signal electrode layer, selected from the group consisting of cadmium sulfide, cadmium selenide, bismuth trioxide and tin dioxide,



(1) said last-named layer having a thickness of from about 10 to about 500 Angstroms whereby the outer surface of said layer remote from said signal electrode layer is characterized by substantially the same relative smoothness as said signal electrode layer, and

(c) a relatively thick layer of a vitreous selenium-tellurium alloy on said layer of N-type semiconductor material, said vitreous alloy containing by weight about 23% tellurium in a surface thereof whereby said surface exhibits P-type conductivity, said surface being adjacent to said N-type layer for forming a blocking junction therewith,

(d) whereby said target is characterized by reduced dark current and the thermal stability of said vitreous alloy is improved.

7. A target for a photoconductive device according to claim 6 and wherein said bismuth trioxide layer is relatively smooth and said signal electrode layer is made of gold having a thickness of from about 10 to about 200 Angstroms, whereby the surface of said gold layer remote from said bismuth trioxide layer is substantially as smooth as said bismuth trioxide layer, for improving the thermal stability of said vitreous selenium-tellurium alloy layer.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,890,359 | 6/1959 | Heijne et al. | 313—65 |
| 3,310,700 | 3/1967 | Dresner et al. | 313—94 X |


JAMES W. LAWRENCE, *Primary Examiner.*

ROBERT SEGAL, *Examiner.*