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PHOTOCONDUCTIVE DEVICE INCORPORATING STABILIZING LAYERS ON THE FACE OF THE SELENIUM LAYER

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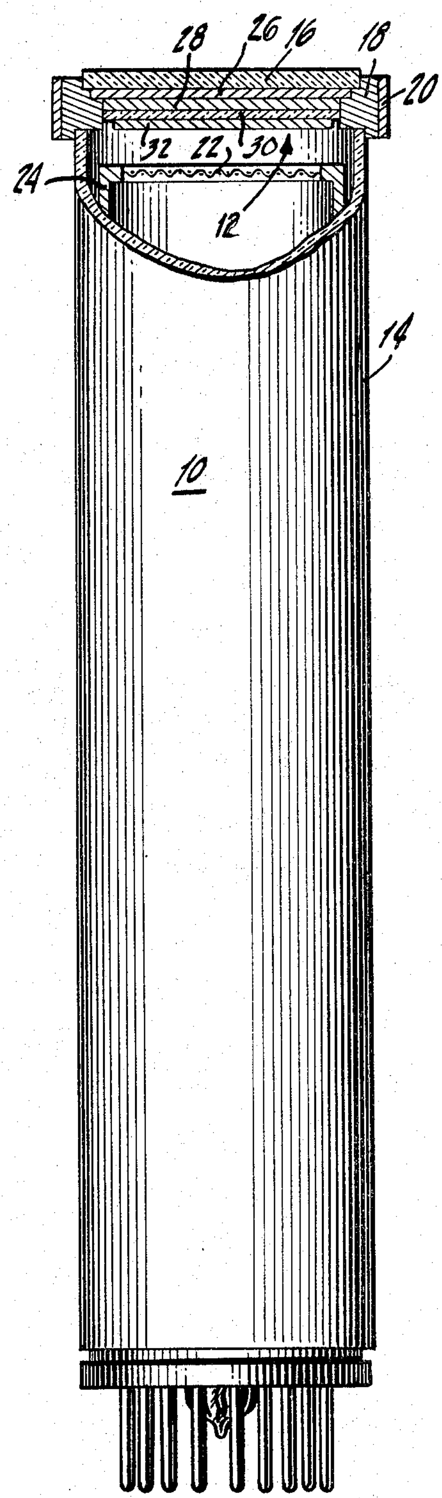

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PHOTOCONDUCTIVE DEVICE INCORPORATING STABILIZING LAYERS ON THE FACE OF THE SELENIUM LAYER

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This invention relates to photoconductive devices and particularly to a photoconductive device incorporating a photoconductive layer of amorphous selenium or alloys thereof.

One type of photoconductive device in which the invention is particularly useful is the vidicon pickup tube. Vidicon pickup tubes generally comprise an evacuated glass bulb within which is mounted an electron gun of any suitable construction for developing a deflectable beam of electrons. These electrons are focused and deflected in a desired scanning pattern over a photoconductive target. The photoconductive target has the property of coacting with the scanning electron beam and with the light impinging on each successive element area of the target. The impinging light causes the elemental areas of the target to change their conductivity proportionately to the light intensity and this change in conductivity produces signal currents under control of the scanning beam.

The photoconductive target is usually supported on a light-transparent backing which may be the end wall or faceplate of the glass bulb or tube envelope. The target usually consists of a highly conductive light-transparent layer or signal plate, which is applied to the inner surface of the faceplate facing the electron gun, and a layer of photoconductive material applied over the transparent conducting layer.

One photoconductive material heretofore used in targets for vidicon tubes is selenium or a suitable alloy thereof. When used in the vitreous (amorphous) state, the selenium or its alloy exhibits a desirable fast speed of response and high sensitivity.

However, vitreous selenium is thermally unstable, converting slowly to the gray crystalline form at room temperature. This process is accelerated when the temperature of the selenium is increased. The same process occurs with the alloy used. The conversion of the vitreous selenium and its alloys, to the crystalline state is especially objectionable in a vidicon tube because its electrical conductivity in this state is much greater than when in the vitreous state. Such greater electrical conductivity of the photoconductor has several objectionable consequences, such as a dark current having an objectionable high level and loss in photosensitivity and image resolution.

No effective means have heretofore been suggested for preserving the vitreous character of the selenium of selenium alloy during manufacture of the tube and during its storage and subsequent use.

Accordingly, it is an object of the invention to provide an improved photoconductive device including thermally stabilized selenium or selenium alloy in the photoconductor thereof.

A further object is to provide a selenium-containing target for a vidicon wherein the selenium in vitreous form possesses thermal stability over longer periods of time.

Another object is to preserve an initial vitreous state of a selenium photoconductor at temperatures encountered during use of a device in which it is incorporated.

In accordance with the invention, a selenium-containing layer for a photoconductive device is provided in

which the temperture-induced conversion to the crystalline state is greatly retarded by means of one or more stabilizing layers on one or both sides of the selenium-containing material. Crystallization of vitreous selenium originates at definite nucleation centers which are located predominantly at the surfaces of a layer of this material. In the structure, according to the invention, both the density of the nucleation centers as well as the rate of crystal growth at these centers are greatly reduced. To restrain crystallization at the surfaces of the selenium layers, we provide thin films intimately engaging these surfaces. These thin films are made of materials that mechanically engage the selenium surfaces and are themselves free from temperature-induced change in their structure. In this way, the intimate bonds between the films and the two surfaces of the selenium layer are effective to preserve mechanically an incomplete crystal development of the selenium in the vitreous state, in ambients of varying temperature.

The stabilizing films that we employ for retarding crystal development or growth at the surfaces of the selenium layer, are extremely thin. They do not affect adversely the desired action of the target of changing its electrical conductivity therethrough when the elemental areas are exposed to a light pattern. The films are made of materials that effectively restrain crystal growth at the surfaces of the vitreous selenium layer and can be made thin enough to be transparent to light.

We have found that a stabilizing film applied to only one surface of the selenium layer, greatly improves its thermal stability. However, for best thermal stability, both surfaces should be so treated. In certain instances, however, it may be desirable to leave one surface uncoated.

In the single figure of the drawing by way of example, is shown a vidicon tube **10** that is conventional except for the target **12**. The tube comprises an elongated glass envelope **14** closed at one end thereof by a transparent glass faceplate **16**. The faceplate is sealed across the end by means of an indium ring **18** and 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 **24**. In the other end portion of the envelope **14** is positioned an electron gun (not shown) for providing an electron beam. The electron beam is scanned across the target **12** by suitable means such as electromagnetic coils (not shown) disposed outside of the envelope **14**.

The target **12** is a multilayer structure. It includes a relatively thin layer or film **26** of an electrically-conducting material such as tin oxide, in contact with the faceplate **16**. The conducting layer **26** is light-transparent and serves as a signal electrode. A first stabilization film **28** is deposited on the inner surface of the signal electrode film **26**. A vitreous layer **30** including selenium is supported on and contacts the first stabilization film **28**. A second stabilization film **32** may be deposited over the surface of the vitreous selenium layer **30** facing the gun. The film **32** should be electrically insulated, as by a relatively small spacing, from the indium ring **18**.

The stabilizing layers **28**, **32** are made of materials that not only effect the desired crystal stabilization of the two opposite surfaces of the selenium layer **30**, but the layer **32** nearest the gun, in addition, should have no major adverse effect upon the operation of the tube. A major adverse effect that has to be avoided is the loss of resolution in the target due to excessive lateral electrical conductivity of the nearer the gun layer **32** of the target. Such lateral conductivity is not objectionable in the bottom stabilizing layer. However, it is important that the stabilizing layer 28 remote from the gun have sufficient electrical conductivity in a normal direction, to permit the transfer therethrough of a signal charge to the signal plate 26. This is also true in the case of the layer 32.

Materials that are suitable for use to form the underlying stabilizing layer 28 are gold, silver, copper, rhodium, palladium, germanium and germanium oxide, antimony tri-sulfide, gallium, gallium oxide, iridium and antimony. In our novel target we have found no evidence of chemical combination of these materials with the photoconductor. However, any other materials that satisfy the mechanical, electrical and optical requirements set forth in the foregoing, can be used in forming the underlayer 28.

The stabilizing layer 32 on the gun side can be formed of one of the following materials: germanium, germanium oxide, antimony tri-sulfide and antimony tri-oxide. It will be noted that some of the materials suitable for the glass-side layer 28 do not serve well as the material for the gun-side layer 32. One reason for this is that some of the layer materials, particularly the metals, cause excessive lateral conductivity even in the relatively thin film forms to be described. Other materials than those specified herein for use in forming the gun-side stabilizing layer 32, can readily be determined by persons skilled in the art from the foregoing description of mechanical, electrical and optical properties they should have.

Electron diffraction studies have shown that the action of the stabilizing films in stabilizing the selenium layers is physical rather than chemical. For example, when a gold film is used to stabilize the selenium there is no formation of a gold selenide. The diffraction studies show only evidence of separate phases of gold and selenium.

The material found best for the layer 28 on the faceplate side, from the standpoints of mechanically stabilizing crystal activity in the adjacent surface of the selenium layer 30, light transparency, and electrical conductivity, is gold. For the gun-side layer 32, the best materials are germanium and germanium oxide. These materials possess the required low lateral conductivity coupled with adequate normal conductivity for charge transfer.

It should be pointed out that the mechanical bond between the selenium layer 30 and the stabilizing layer 28, is improved by the smoothness and cleanliness of the substrate 16. However, satisfactory results have been obtained even when the substrate 16 and/or the signal plate 26 are rough.

The several layers or films 26, 28, 30 and 32 of the target may be formed by conventional evaporation techniques including the determination of thickness by suitable monitoring plates positioned to receive the evaporant and indicating thickness by the magnitude of light absorbed by the evaporated coating or by other standard techniques.

The overall thickness of the combined layers 26, 28, 30 and 32 of the target should be about five microns in order to achieve suitable sensitivity and speed of response for the tube.

With respect to the thickness of each individual layer or film 26, 28, 30 and 32, the most care should be taken with the two stabilizing films 28, 32. The layer 28 may at one extreme consist of only one or a few molecular layers. Films which are effective in stabilizing crystal growth have been estimated to be as thin as six Angstroms. The optimum thickness of the stabilizing film 28 is estimated to be from about 10 to about 30 Angstroms.

The gun-side layer 32 has a thickness within limits determined by its effects on the electrical properties of the tube. Thus, the gun-side layer 32 should be sufficiently thin so that its lateral conductance is small enough to preserve lateral resolution in the image. Its bulk conductivity should be sufficiently high to maintain electrical contact between the electron beam and the selenium photo-

conductor. We have found that a thickness of from about 10 to about 60 Angstroms is satisfactory.

The signal plate or film 26 should be thin enough to be light transparent and yet sufficiently thick to have the required lateral conductance for service as the signal electrode of the tube.

The composition of the photoconductive layer 30 is determined by the spectral response desired. If only response to blue and ultraviolet light is required, vitreous selenium alone may be used. However, if it is desired to improve the red response, up to about 25% by weight of tellurium may be alloyed with the selenium. Furthermore, the addition of arsenic or antimony in amounts up to about 3% by weight improves the sensitivity and speed of response of the tube. We have found that the stabilization layers 28, 32, described above, are also effective for the restraint of crystal growth when used in association with the alloys described above.

It is apparent from the foregoing that we have provided an improved photoconductive device in which selenium is employed to appreciably greater advantage than heretofore.

We claim:

1. A photoconductive device comprising:
(a) a substrate,
(b) a signal electrode on said substrate,
(c) a vitreous layer containing selenium and having two flat surfaces, and
(d) means between said signal electrode and vitreous layer mechanically engaging one of said two flat surfaces for restraining crystal growth therein.

2. A photoconductive device comprising:
(a) a substrate,
(b) a signal electrode on said substrate,
(c) a vitreous layer containing selenium and having a surface, and
(d) stabilizing means mechanically engaging said surface and said signal electrode for restraining crystal growth in said surface,
(e) said stabilizing means comprising a substantially transparent and extremely thin coating of a material different from the material of said signal electrode intimately engaging said surface.

3. A photoconductive device comprising:
(a) a substrate,
(b) a signal electrode on said substrate,
(c) a vitreous layer containing selenium and having a flat surface, and
(d) light transparent stabilizing means mechanically engaging said signal electrode and said flat surface for restraining crystal growth in said surface,
(e) said stabilizing means comprising a coating made of a material different from the material of said signal electrode and having a thickness within the range of from one molecular layer to about 30 Angstroms.

4. A photoconductive device comprising:
(a) a relatively smooth substrate,
(b) a signal electrode comprising tin oxide on said substrate,
(c) an extremely thin stabilizing film comprising gold over said signal electrode, and
(d) a layer of vitreous selenium over said stabilizing film.

5. A photoconductive device comprising:
(a) a substrate,
(b) a signal electrode on said substrate,
(c) a vitreous layer containing selenium over said signal electrode, and
(d) means between said signal electrode and layer of amorphous selenium for restraining crystal growth in said selenium,
(e) said means comprising an extremely thin stabilizing film made of a material selected from the group consisting of gold, silver, copper, rhodium, palladium, germanium and germanium oxide, antimony tri-sul-

fide, gallium, gallium oxide, iridium and antimony.

6. A photoconductive device comprising:
(a) a substrate,
(b) a signal electrode over said supstrate,
(c) a vitreous layer containing selenium over said signal electrode, and
(d) a stabilizing film between said signal electrode and layer and mechanically engaging said layer for restraining crystal growth therein, and
(e) said stabilizing film having a thickness of from about 6 to 30 Angstroms.

7. A target for a photoconductive pickup tube comprising:
(a) a light permeable substrate having a flat surface,
(b) a light permeable conducting film on and substantially coextensive with said flat surface,
(c) a vitreous layer containing selenium substantially coextensive with said conducting film, and
(d) means comprising an extremely thin coating mechanically engaging adjacent one surface of said conducting film and said amorphous selenium layer for mechanically restraining crystal growth in said layer, whereby the amorphous character of said selenium layer is temperature stabilized.

8. A target for a photoconductive pickup tube comprising:
(a) a substantially light transparent substrate having a flat surface,
(b) a substantially light transparent signal electrode on and substantially coextensive with said flat surface,
(c) a vitreous layer containing selenium substantially coextensive with said conducting film, and
(d) means between said signal electrode and layer and mechanically engaging said layer for mechanically restraining crystal growth in said vitreous layer,
(e) said means comprising an extremely thin electrically conductive stabilizing film.

9. A target for a photoconductive pickup tube comprising:
(a) a substantially light transparent substrate having a flat surface,
(b) a substantially light transparent signal electrode on and substantially coextensive with said flat surface,

(c) a vitreous layer containing selenium substantially coextensive with said conducting film, and
(d) means between said signal electrode and said layer mechanically engaging said layer for mechanically restraining crystal growth therein,
(e) said means comprising a substantially light-transparent and electrically conductive stabilizing film,
(f) said film being made of a material selected from the group consisting of gold, silver, copper, rhodium, palladium, germanium and germanium oxide, antimony tri-sulfide, gallium, gallium oxide, iridium and antimony,
(g) said film having a thickness from about 6 to about 30 Angstroms.

10. A target for a photoconductive pickup tube comprising:
(a) a light transparent substrate,
(b) a flat light transparent signal electrode on said substrate,
(c) a first light transparent stabilizing film on said signal electrode having a thinness of from about 6 to about 30 Angstroms,
(d) a vitreous layer containing selenium and having one flat surface mechanically engaging said first stabilizing film, and
(e) a second stabilizing film mechanically engaging the opposite flat surface of said layer,
(f) said second stabilizing film having a relatively low order of lateral conductance to prevent any substantially lateral transmission of an electrical charge thereon, and
(g) said second stabilizing film being made of a material selected from the group consisting of germanium and germanium oxide, antimony tri-sulfide and antimony tri-oxide.

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