Jan. 2, 1968 YUJI KIUCHI ETAL 3,361,919
TARGET INCLUDING AT LEAST THREE PHOTOCONDUCTIVE LAYERS OF LEAD OXIDE OF SIMILAR CONDUCTIVITY TYPE
Filed Dec. 10, 1965 2 Sheets-Sheet 1

FIG. 1

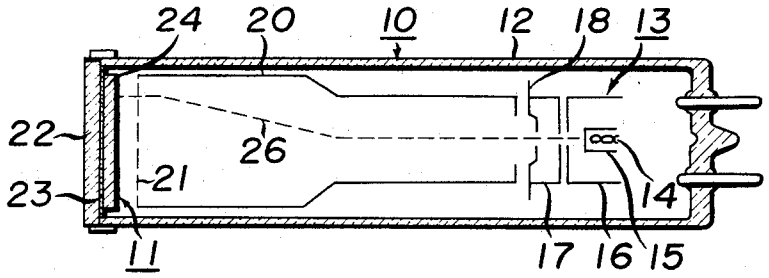


FIG. 2

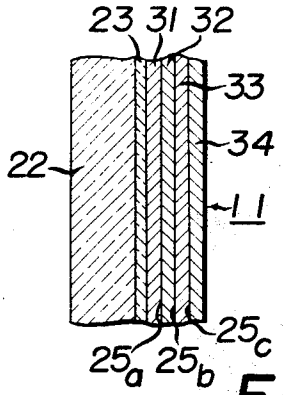


FIG. 3

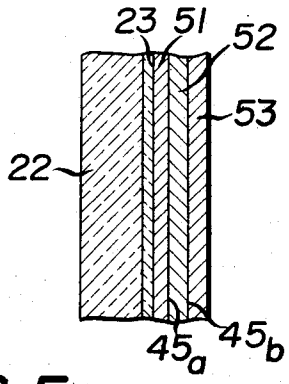


FIG. 4

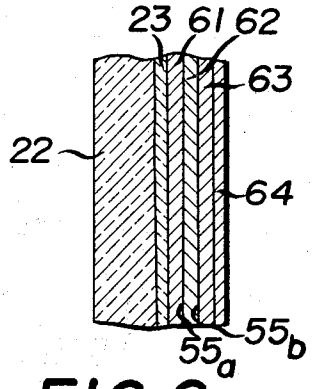


FIG. 5

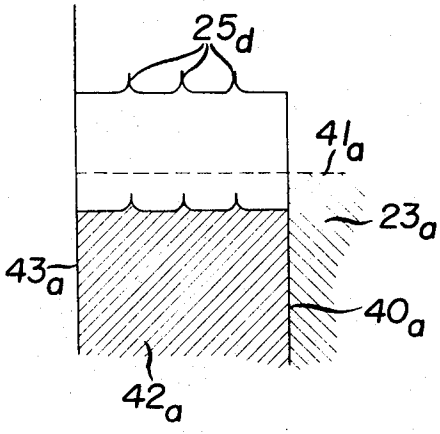
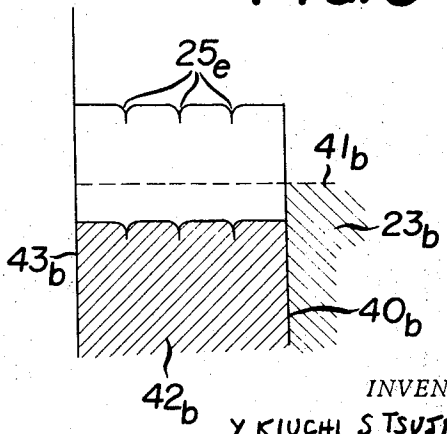


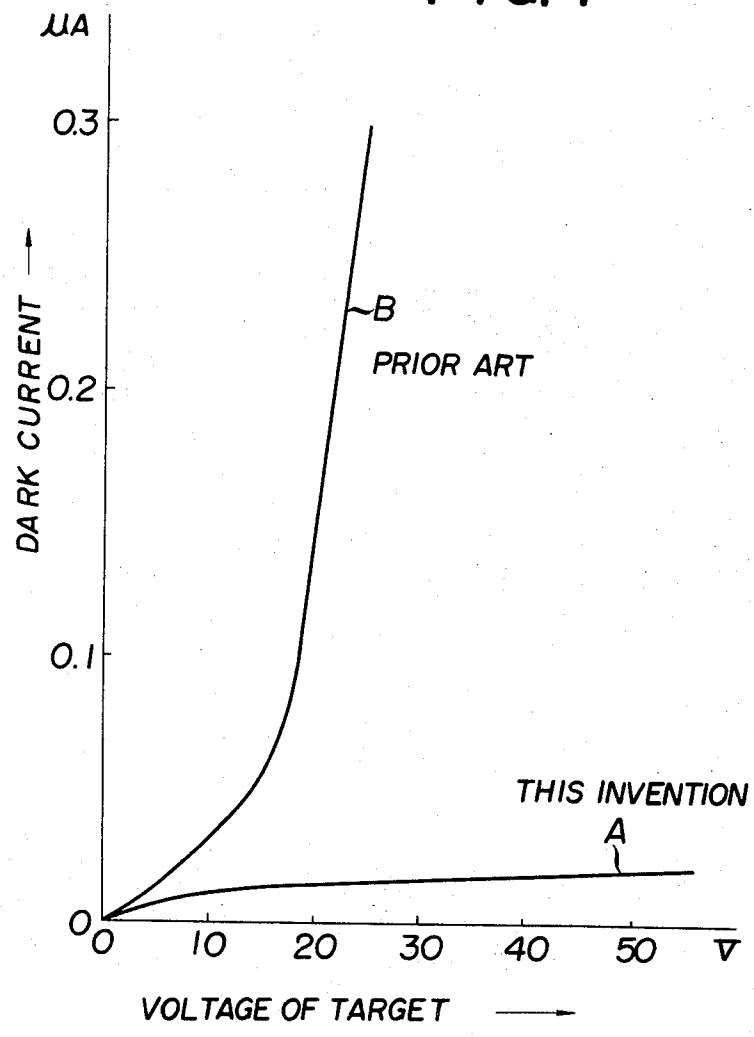
FIG. 6



INVENTORS
Y. KIUCHI, S. TSUJI &
Y. NAKAYAMA
BY
Stephen H. Fleischer ATTY

Jan. 2, 1968 YUJI KIUCHI ETAL 3,361,919
TARGET INCLUDING AT LEAST THREE PHOTOCONDUCTIVE LAYERS OF LEAD OXIDE OF SIMILAR CONDUCTIVITY TYPE
Filed Dec. 10, 1965 2 Sheets-Sheet 2

FIG. 7



Y. KIUCHI, S. TSUJI &
Y. NAKAYAMA
INVENTORS
BY Stephen A. Fredman
Atty

United States Patent Office 3,361,919
Patented Jan. 2, 1968

3,361,919

TARGET INCLUDING AT LEAST THREE PHOTOCONDUCTIVE LAYERS OF LEAD OXIDE OF SIMILAR CONDUCTIVITY TYPE

Yuji Kiuchi, Yokohama-shi, and Shiegeo Tsuji and Yoshiaki Nakayama, Tokyo, Japan, assignors to Tokyo Shibaura Electric Co., Ltd., Kawasaki-shi, Japan, a corporation of Japan

Filed Dec. 10, 1965, Ser. No. 512,967
Claims priority, application Japan, Dec. 15, 1964, 39/96,429
7 Claims. (Cl. 313—96)

ABSTRACT OF THE DISCLOSURE

A photoconductive film provided with a plurality of successive photoconductive layers of lead oxide with a plurality of geometrically well defined interfaces formed therebetween so as to form electric barriers at the point of said interfaces thereby increasing the dark resistance in the direction of the thickness of said photoconductive layers.

This invention relates to improvements in photoconductive targets containing lead oxide especially suitable for use as targets of vidicon type television camera tubes.

The television camera tube of the type above referred to comprises a vacuum envelope, a signal electrode or a transparent film usually termed as the NESA film deposited upon the inner surface of the face plate of the envelope and a layer of photoconductive material serving as the photoconductive target and in contact with the signal electrode.

The surface of the photoconductive target is scanned by an electron beam emitted from an electron gun similarly disposed in the vacuum envelope to bring the potential of the surface to the cathode potential and then the light reflected from the object outside the envelope is caused to impinge upon the surface of the target through the signal electrode while a voltage higher than the cathode electrode is being applied to the signal electrode. Then the resistance of the photoconductive material is varied depending upon the intensity of the light thus forming a positive potential pattern. Thus, when the surface is scanned by the electron beam of next field, the positive potential will be neutralized while at the same time a video signal will be produced from the signal electrode.

The aforementioned material for the photoconductive target is selected by taking into consideration such factors as stability, dark current, sensitivity, spectral distribution, residual image and the like.

More particularly it is essential that the photoconductive material should have high sensitivity, should not deteriorate during use, should have large time constant when dark, i.e. the dark resistivity should be higher than 10^{11} Ω—cm., should especially have high conductivity when irradiated by light, suitable spectral distribution, appropriate capacitance of photoconductive target and small time lag.

Although it is difficult to obtain a photoconductive material which satisfies all of these desirable characteristics, antimony trisulfide having high sensitivity to light is generally used. Recently lead oxide has been developed as a photoconductive material for photoconductive targets having higher sensitivity than antimony trisulfide and desirable dark current and response time characteristics.

However it is very difficult to prepare lead oxide targets. According to one prior method metal lead was vapor-deposited in vacuum upon a glass substrate coated with a transparent conductor and then the layer of the deposited metal lead was oxidized by a heat treatment in oxygen atmosphere or in air. In another method powder of lead oxide was vapor-deposited as a single layer upon a substrate in a low pressure oxygen atmosphere.

However the characteristics of photoconductive layers prepared by these prior methods vary greatly so that it has been impossible to obtain uniform photoconductive targets having usable characteristics and nearly all of them have some defects that render them unsuitable for practical use. Even when targets of high initial sensitivity were produced their sensitivity rapidly degraded in short time during use due to electron beam scanning.

An object of this invention is to provide an improved photoconductive target made of lead oxide having high sensitivity and small dark current as well as small residual image.

Another object of this invention is to provide a novel photoconductive target made of lead oxide and having a simple construction that permits high yields of products of good quality and yet having excellent characteristics.

Still another object of this invention is to provide a novel photoconductive target made of lead oxide, which is stable against scanning electron beam and has a long operating life.

These and further objects together with features of the invention will become apparent from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a longitudinal sectional view of a television camera tube having a target embodying this invention;

FIG. 2 is an enlarged sectional view of the photoconductive target shown in FIG. 1;

FIGS. 3 and 4 are enlarged sectional views of portions of different embodiments of this invention;

FIGS. 5 and 6 are diagrams of energy levels for explaining the operation of this invention; and

FIG. 7 shows graphs comparing the characteristics of the target of this invention and a prior art target.

Referring now to FIG. 1 of the accompanying drawings there is shown a television camera tube **10**, such as a vidicon provided with a photoconductive target **11**, embodying this invention. The tube comprises a cylindrical vacuum envelope **12** which contains an electron gun **13** consisting of a heater **14**, a cathode **15** and grid electrodes **16**, **17** and **18**, a fourth grid electrode **20** coaxial with the electron gun **13** and a circular mesh **21** provided for the grid electrode **20** at one end thereof facing a target. A transparent conductive film **23** is deposited upon the inner surface of a face plate **22** closing the opposite end of the vacuum envelope **12** and a film of a photoconductor **24** containing lead oxide is stacked upon the conductive film **23** to form a photoconductive target thus completing a vidicon type television camera tube. As shown more in detail in FIG. 2, the photoconductive target **11** is constructed such that the transparent conductive film **23** is deposited upon the inner surface of the face plate **22** and the layer **24** of a photoconductor consisting of lead oxide is formed by it on the transparent conductive film by several independent procedures whereby to interpose a number of electric barriers **25***a*, **25***b* and **25***c* between successive layers **31** to **34** of lead oxide. In this manner the photoconductive target **11** is formed by firstly providing the transparent layer **23**, which may be a NESA film, upon a substrate such as the face plate **22** and then providing thereon a plurality of, for example, four layers of photoconductive layers **31** through **34** made of lead oxide.

As the result of experiment we have found that lead oxide can be used with good result as photoconductive

targets when geometrically that is, physically and electrically well defined barriers are provided between layers of lead oxide. According to the embodiment shown in FIG. 2 the first layer **31** is vapor-deposited upon the transparent conductive layer **23** in a low pressure oxygen atmosphere and then the deposited layer is maintained at that condition for a predetermined time interval while the substrate is heated thus thoroughly oxidizing the surface of the layer **31**. Upon vapor depositing the second layer **32** in the same manner as the first layer **31** upon the oxidized surface a well defined interface which acts as an electrical barrier **25***a* is formed between the first and second layers **31** and **32**. Similarly the third and fourth layers **33** and **34** are formed by vapor deposition to interpose well defined electrical barriers **25***b* and **25***c* between successive layers.

The operation of the television camera tube is as follows:

The electron beam **26** emitted from the electron gun **13** is focused and deflected by a focusing coil and a deflection coil (not shown) and then passes through the mesh **21** to scan the surface of the photoconductive target **11** at a low velocity.

In the absence of light impinging upon the photoconductive target **11** the resistance of the target in the direction of its thickness is high because it comprises the sum of the resistances of the first to fourth layers **31**, **32**, **33** and **34** and also due to the presence of electrical barriers **25***a*, **25***b* and **25***c*. This means that target **11** which is scanned by the electron beam **26** emitted from the electron gun **13** becomes balanced at nearly the same potential as the cathode. However when an optical image is precisely focused upon the surface of the target by means of an optical lens (not shown), the electric resistance of the target will vary depending upon the intensity of light as if these electrical barriers were not effectively provided thus increasing the conductivity. Since the transparent conductor **23** is supplied with a positive DC voltage the surface of the target facing to the electron gun **13** is charged with a positive voltage having values corresponding to locally reduced resistance values. This charge is caused to discharge by the scanning of the electron beam; the discharge current through the transparent conductor **23** thus corresponds to the light and shade and a representation of the image is transformed into electrical signals.

Referring to FIG. 5 which shows the energy level diagram with regard to electrons of the target embodying this invention a portion **23***a* shaded with dotted lines represents the transparent conductor **23**, a solid line **40***a* indicates the interface between the transparent conductor **23** and the photoconductive layer **31** and spikes **25***d* barriers between successive photoconductive layers. Since the barriers are definitely defined, the spikes are sharply pointed. A horizontal dotted line **41***a* extending through the photoconductive layers represents the Fermi level whereas a portion **42***a* shaded with broken lines of the photoconductive layer represents a valence band. A solid line **43***a* at the open end of the photoconductive layer represents the surface which is scanned by the electron beam, thus completing an energy level diagram of the target with respect to electron blocking.

In the absence of any incident light upon the photoconductive layer electric barriers **25***d* exhibit blocking function against electrons, thus increasing electric resistance. Hence the dark current is very small. On the other hand when the light impinges upon the photoconductive layer, its resistance is reduced to increase conductivity because the electric barrier is effectively reduced.

FIG. 6 shows an energy diagram of the target which is different from that shown in FIG. 5 and exhibits blocking function against holes. Similar to the case of electrons a portion **23***b* shaded with dotted lines represents the transparent conductor, a solid line **40***b* the interface between the transparent conductor **23** and the photoconductive layers **31**, and sharp depressions **25***e* in the photoconductive layers electric barriers between successive photoconductive layers. A broken line **41***b* extending through said photoconductive layers represents the Fermi level, a shaded portion **42***b* of the photoconductive layers the valence band and a solid line **43***b* at the open end of the photoconductive layers the surface scanned by electron beam, thus forming an energy level diagram of the target.

It will be seen that the electric barriers exhibit blocking function against holes. Since other functions are identical with those of the target with regard to electrons, it may be unnecessary to describe them again.

FIG. 7 shows dark current characteristics of a vidicon employing a target constructed in accordance with this invention and of a vidicon employing a conventional single layered lead oxide target, from which it will be clearly noted that the dark current-target voltage characteristic A of this invention is far more excellent than that B of prior construction. Thus, the merit of providing a plurality of barriers is significant.

Moreover, it is possible to make large the dark time constant without sacrificing the characteristics at the time of light irradiation, thus satisfying the requirements of the target of television camera tubes. Further, the provision of a plurality of barriers greatly increases reproducibility in electrical characteristics which are caused by foreign gasses, especially air, at the time of assembling the target in the image pickup tubes, whereby such tubes can be readily fabricated.

FIG. 3 shows another embodiment of this invention wherein a transparent conductive layer **23** is deposited upon a substrate **22** made of glass and the like, a first layer **51** of lead oxide containing an oxide or sulfide of a monovalent or trivalent metal is vapor-deposited on the layer **23** and a second layer **52** of lead oxide and a third layer **53** of lead oxide containing an oxide or sulfide of a monovalent or trivalent metal (which is selected to correspond to the metal of the first layer) are successively vapor-deposited. The purpose of the oxide or sulfide of a monovalent or trivalent metal contained in the first and third layers is to improve the sensitivity and spectral distribution of the target and again well defined electric barriers **45***a* and **45***b* are formed between the layers.

Where oxide or sulfide of a trivalent metal is included in the first layer **51** it is advisable to include an oxide or sulfide of a monovalent metal in the third layer **53**.

The content of the oxide or sulfide is preferably to be in a range of 0.01% to 10%.

One example of preparing the target shown in FIG. 1 is as follows:

A transparent conductive layer **23**, for example, a layer of tin oxide serving as the signal electrode was deposited upon a flat glass plate **22** of excellent light transmitting property. Then the coated substrate **22** was put in a vacuum vessel, for instance, a transparent bell-jar and heated to a temperature of about 150° C. A low pressure oxygen atmosphere, for example, of a pressure of 5×10^{-2} mm. Hg was filled in the vacuum vessel and in said vessel lead oxide containing 0.5% of oxide or sulfide of a trivalent metal, for example, antimony trioxide was vapor-deposited upon the layer of tin oxide **23** coated on the substrate **22** to form the first layer **51**. It is desirable that the first layer has a thickness of less than 1 micron. Then, in the same oxygen atmosphere, lead oxide was vapor-deposited upon the first layer **51** to form a second or intermediate layer **52** of a thickness of about 5 to 10 microns. Thereafter also in the same oxygen atmosphere lead oxide containing 0.5% of oxide or sulfide of a monovalent metal for example, cuprous oxide was vapor-deposited to form the third layer **53**. The third layer is desirable having a thickness of less than 1 micron.

In every process the distance of 50 mm. was kept between the source heater and the substrate. Thus the film of photoconductive lead oxide **7** was constituted from the

first layer **51**, second layer **52** and the third layer **53**. Depending upon the particular application the first layer **51** and the third layer **53** may be interchanged and certain layers may not contain impurity. As the impurity to be included in lead oxide comprising the first layer **51** oxides or sulfides of such trivalent metals as antimony, arsenic, bismuth, indium and the like are suitable while as the impurity to be included in lead oxide comprising the third layer **53**, oxides or sulfides of such monovalent metals as copper, silver, thallium and the like are suitable. As a result of experiments the following conditions were found suitable for vapor-deposition of the photoconductive layer. Thus, the quantity of the impurity contained in the lead oxide has an influence upon the electric resistance and the sensitivity of the film so that a quantity of about 0.01% to 10% gives the best result since an excessive quantity results in the decrease in sensitivity.

Further the temperature of the substrate **22** has an influence upon the size of polycrystallines of lead oxide and upon the light response characteristic so that the most suitable temperature lies in a range of from 100° to 300° C. It is also necessary to maintain the pressure of the oxygen atmosphere utilized in the vapor deposition processes at a value more than 10^{-4} mm. Hg in order to prevent decomposition of lead oxide. However various conditions of vapor deposition, i.e. the pressure of oxygen, the temperature of the substrate and the distance between the source of vapor and the substrate are related each other and the most suitable conditions are determined by experiments.

As has been described in detail hereinabove the target **15** embodying this invention is formed by a process comprising the steps of forming a layer of lead oxide containing an oxide or sulfide of a trivalent metal as the impurity upon a substrate heated in a low pressure oxygen atmosphere, depositing a layer of lead oxide thereon and further depositing on the second layer a layer of lead oxide containing an oxide or sulfide of a monovalent metal as the impurity whereby to form a film of photoconductive lead oxide. This target has well defined interfaces between successive layers which serve as electric barriers so that the target is furnished with a high electric resistance and a rapid light response characteristic. Moreover its electric characteristics are stable against the atmosphere. Moreover, the target should be fabricated in a very short time, for example, in about 10 minutes so that it is suitable for mass production because it does not need heat treatment of long time after vapor deposition. Further, since it is possible to always and readily produce films of photoconductive lead oxide of uniform characteristics the process is very effective to improve the yield of the products of good quality. Further, this invention enables the production of practical films of photoconductive lead oxide of good photoelectric sensitivity. While in the above embodiment the respective photoconductive layers have been vapor-deposited in the same oxygen atmosphere, if a very thin excessively oxidized layer of the order of several tens angstroms were formed at the interface of the layer at each time the layer is vapor-deposited, a photoconductor having more excellent photoelectric sensitivity, dark resistance and response characteristics would be obtained.

When a photoconductive layer prepared by the method this invention is applied to a target of a well known vidicon type television camera tube the dark current characteristic of the target is greatly improved over the conventional target having a single layered lead oxide.

FIG. 4 shows still another modification of this invention wherein a target comprising three layers of lead oxide is shown. More particularly a transparent conductive layer **23** serving as the signal electrode is deposited upon a substrate **22**, and a first layer **61** of lead oxide is vapor-deposited upon the layer **23** in an oxygen atmosphere. Thereafter said oxygen atmosphere is evacuated, much more quantity of oxygen than the oxygen pressure at the time of vapor deposition of the first layer **61** is introduced prior to the vapor deposition of a second layer **62** and then the pressure of the atmosphere is reduced to the previous pressure, and vapor-deposition of the second layer **62** is made. By the identical procedure a third layer **63** is vapor-deposited and finally a layer **64** made of electron bombardment proof substance, such as silicon monoxide, is vapor-deposited to have a suitable thickness. In the target of this invention prepared by the method described above well defined interfaces are presenting between the successive lead oxide layers thus forming electric barriers **55***a* and **55***b*. As stated above these barriers exhibit blocking function against movement of charge carriers not only to increase the dark electric resistance but also to increase the conductivity when irradiated by light rays. The layer **64** of electron bombardment proof substance fuctions to prevent deterioration of target by electron bombardment thus effectively prolongs the life of target. It is preferred to make the thickness of the silicon monoxide layer relatively thin since it is an electric insulator.

In addition to silicon monoxide SiO, antimony trisulfide Sb_2S_3, silicon dioxide SiO_2, calcium fluoride CaF_2, magnesium fluoride MgF, arsenic trisulfide As_2S_3, antimony oxy sulfide and the like may be used as said layer.

As pointed out hereinabove since the target of this embodiment is provided with a protective layer it is possible to successfully utilize the photoconductive material consisting of lead oxide which has high sensitivity but is liable to deteriorate under bombardment of the electron beam. This material immediately deteriorates when taken out into the atmosphere after vapor deposition so that it has been impossible to utilize the material for targets but when it is taken out after being deposited with the protective film in the same vacuum vessel it becomes stable for a considerably long time in the air whereby manufacture of television camera tubes becomes very easy. Also while it is well known that the targets utilizing lead oxide are sensitive to X-rays they deteriorate by gradual decomposition accompanying loss of oxygen. However, by providing the protective layer as in the above modification it is possible to prevent loss of oxygen, thus providing photoconductive targets useful for X-ray radiation.

Thus the invention provides a novel photoconductive target wherein at least three layers of lead oxide are vapor-deposited on a transparent conductive layer which is formed on a transparent substrate whereby to form a plurality of electric barriers interposed between successive layers. Thus the construction of this invention eliminates the disadvantage of lead oxide which is recognized to have excellent characteristics as the photoconductive material but could not be used for mass production of targets for television camera tubes because of its instability.

In this manner this invention provides targets which can improve such characteristics desired for photoconductive targets as stability, dark current, sensitivity, spectral characteristics, response time and the like and also can be manufactured very easily.

While the invention has been described in detail with reference to some preferred embodiments thereof it should be understood that there may be may modifications and alterations within the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A photoconductive target comprising a transparent conductive film formed on a transparent substrate, at least three photoconductive layers of lead oxide of the same conductivity type formed on the transparent conductive film, said layers being superimposed above each other with physically defined interfaces interposed therebetween the energy level diagram having pronounced spikes at said interfaces so as to form physically and electrically sharply defined barriers between successive photoconductive layers thereby increasing the dark resistance in the direction of the thickness of said photoconductive layers.

2. A photoconductive target according to claim 1 wherein, three photoconductive layers of lead oxide are provided, said layers consisting of a first layer deposited upon said transparent conductive film, and second and third layers superposed upon said first layer; at least one of said first and third layers containing an oxide or sulfide of a monovalent or trivalent metal.

3. A target according to claim 2 wherein said first layer contains oxide or sulfide of a trivalent metal and wherein said third layer contains oxide or sulfide of a monovalent metal.

4. A target according to claim 2 wherein said first layer contains an oxide or sulfide of a monovalent metal and wherein said third layer contains an oxide or sulfide of a trivalent metal.

5. A target according to claim 1 wherein interfaces between said successive layers of lead oxide are formed with portions of excessively oxidized lead oxide.

6. A target according to claim 1 wherein a layer of

electron bombardment proof substance is stacked upon the photoconductive layer of lead oxide on the side remote from the transparent conductive layer.

7. A target according to claim 6 wherein the layer of electron bombardment proof substance is made of a member selected from the group consisting of silicon monoxide SiO, antimony trisulfide Sb_2S_3, silicon dioxide SiO_2, calcium fluoride CaF_2, magnesium fluoride MgF_2, arsenic trisulfide As_2S_3, arsenic triselenide As_2Se_3, antimony triselenide Sb_2Se_3, and antimony oxy sulfide.

References Cited

UNITED STATES PATENTS

2,875,359	2/1959	Cope	313—94 X
2,888,372	5/1959	Feibelman et al.	313—94 X
2,890,359	6/1959	Heijne et al.	313—94 X
3,289,024	11/1966	De Haan et al.	313—94 X

ROBERT SEGAL, *Primary Examiner.*