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A. Z. CZIPOTT ET AL

2,884,508

THIN METAL FILMS AND METHOD OF MAKING SAME

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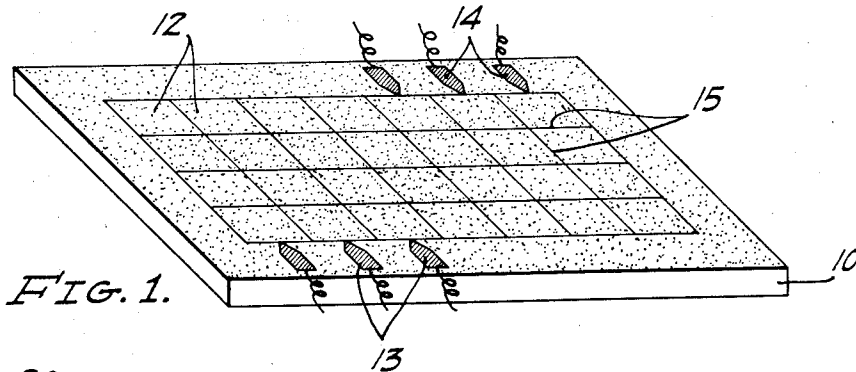


FIG. 1.

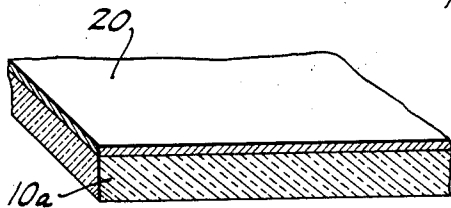


FIG. 2.

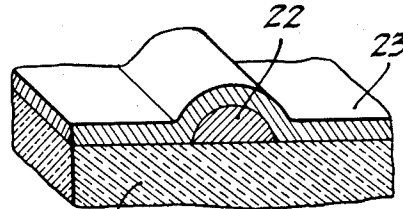


FIG. 6.

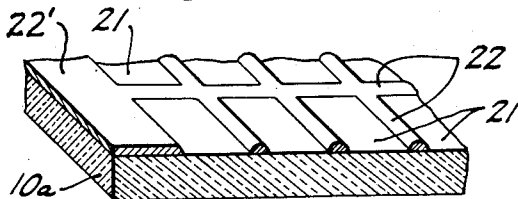


FIG. 3.

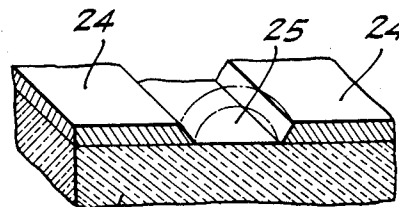


FIG. 7.

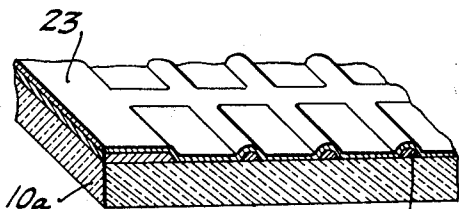


FIG. 4.

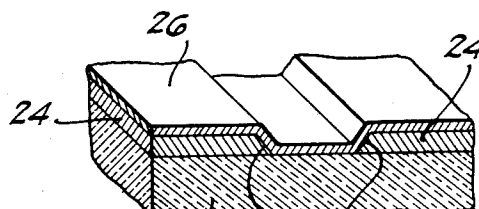


FIG. 8.

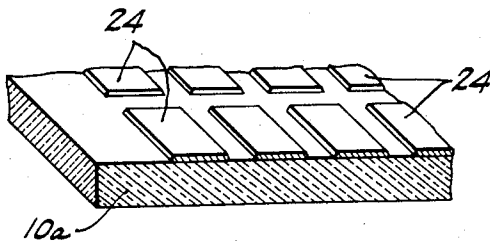
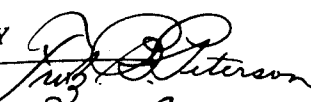


FIG. 5.

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THIN METAL FILMS AND METHOD OF MAKING SAME

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Application October 1, 1956, Serial No. 613,172

7 Claims. (Cl. 201—63)

This invention relates to photoconductive cells, and more particularly to a photoconductive cell having a layer or coating of a photosensitive substance, and electrical conductor means, such as electrodes or terminals, making ohmic contact with the photosensitive material. The term "ohmic contact" as herein used means an electrical contact or boundary having substantially the same resistance to current flow in either direction.

It has heretofore been known to produce photosensitive cells using a layer or film of cadmium sulphide deposited from sublimated powder as the photosensitive element. In such cells the cadmium sulphide is deposited as a layer between and in contact with conductor means, such as thin conductive films of chromium, which serve as electrodes. A procedure illustrative of this mode of cell construction is set forth in copending patent application Serial No. 489,397, filed February 21, 1955, for example. It has been found that the electrical contact between the conductive films of chromium and the photoconductor layer are not always ohmic, and that the difference in resistance to current flow in opposite directions may be of the order of 10^3 , due, apparently, to the rectifying nature of the metal-to-semiconductor contact. The lack of uniformity of the contact resistivity from cell to cell is an undesirable characteristic attending the previously employed thin conductive films or electrodes.

Since in a photoconductive cell of the powder layer or film type, current must flow from a conductor into a thin layer or film of powder or polycrystalline semiconductor and from the latter into a second conductor, the importance of ohmic contact between the conductors and semiconductor film is apparent. Without substantially low resistance ohmic contact, cell sensitivity of only a low order is obtainable, since current can only with difficulty be forced across one of the zones of contact. Further, with non-ohmic contact between conductor and semiconductor, the voltage versus current characteristic of such a cell is non-linear. Linearity of this characteristic would be highly desirable and valuable.

It has been determined that by employing as a conductor in the contact zone, indium, or gallium, or any alloy of the two, or other metal having a low electronic work function, ohmic contact is attained. Hence by employing either of these metals or an alloy of the two, a highly sensitive photoconductive reticle-type cell having linear voltage versus current characteristics may be produced.

An advantage of indium, gallium, and alloys of the two, over hard metals such as chromium, in the production of reticle-type cells, is that thicker coatings of indium or the like can be used, whereby conductivity of electrodes or terminals can be greatly increased. When chromium, for example, is employed in forming the conductive films on

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a base and the films are to be separated by only small distances, as in reticle-type cells, the metal is deposited as a continuous layer over the base and over thin lines of hardened photoengravers glue. When the glue is subsequently removed the overlying chromium or other hard metal falls away leaving a metal-free area in the form of a fine line-like area on the base. If, however, a substantial layer of chromium or other hard metal is deposited, the metal layer has sufficient strength to maintain itself intact in parts after removal of the underlying glue, and thus forms an effective electrical connection between the conductive films on the base. Since the films are required to be electrically isolated, a cell having such bridges or "shorts" is of little or no value. Another advantage of gallium and indium as a conductor material in such cells is that these conductors can endure without deterioration much higher temperatures than, for example, chromium. Cells of the type under consideration are during manufacture subjected to high baking temperatures.

Stages in the production of an exemplary cell in accord with the concept of the invention are illustrated in the drawings, in which:

Figure 1 is a pictorial representation of the exemplary reticle-type photoconductive cell, with certain areal dimensions exaggerated in the interest of clear representation;

Figures 2 through 5 are fragmentary views illustrating a photoconductive cell at certain different stages of its construction, and with certain dimensions exaggerated;

Figures 6, 7, and 8 are fragmentary views on a larger scale illustrating features of cell construction at several stages of manufacture, the dimensional scale being exaggerated to facilitate clear illustration.

Referring to the drawings, Figure 1 shows somewhat pictorially one exemplary photoconductive cell of the reticle type constructed in accord with the principles of the present invention. Therein a suitable base 10 of electrically non-conductive material, such as glass or quartz, carries on a surface thereof an arrangement of discrete electrically-conductive thin films 12 of indium, gallium, or other metal or alloy having a low electronic work function. Terminals such as 13 and 14 are applied to selected individual films 12; and the terminals may similarly be of indium or the like, and applied in any suitable manner or as portions of the appropriate discrete films 12. The discrete films 12 are separated each from adjacent films by narrow line-like areas 15 which are free of metal. Deposited over at least the line-like areas 15 and contacting the edges of the metallic films, is a coating or layer of photoconductive material, such as cadmium sulphide, which may also overlie and completely cover the films 12. The coating or layer of photosensitive material is very thin, and is indicated in Figure 1 by the scattered dots on the metal films and upper surface of base 10. The photoconductive layer need not cover the entire surface of the base, but should be substantially continuous over at least the line-like areas 15 between the metal films. The metal films 12 may be applied to the base according to any desired procedure, but preferably are applied following a procedure such as is outlined in the aforementioned application Serial No. 489,397, modified in respects hereinafter set out in detail.

Successive stages in the production of a finished reticle type cell are illustrated in Figures 2 through 5, in which the relative dimensions of the films or coatings are exaggerated to facilitate illustration. In Figure 2, a fragment of a non-conductor base 10a, of glass for example, has

applied thereto a coating 20 of photoengravers glue. In Figure 3, the same base 10a is illustrated as it appears following exposure of the glue layer to illumination masked by a photonegative, and development. At this stage, areas 21 of the surface of the base 10a have been uncovered by removal of glue, leaving a network of connected lines 22 of glue, and a marginal portion 22' of the glue layer, intact. A film or layer of indium, gallium, or alloy thereof, is deposited over the remaining glue and the exposed areas 21 of the surface of the base. This is accomplished, for example, by vacuum sublimation of the metal, during which operation the sublimation product is deposited on the base surface. Thus there is deposited on the cell surface and over the network of glue a substantially continuous electrically-conductive sheet or film 23 of the metal (see Figure 4). The film 23 bridges the lines 22 of glue in a fashion illustrated on exaggerated scale in the fragmentary view in Figure 6.

Following deposition of film 23 of the sublimed metal, the remaining glue is carefully removed by soaking the entire cell structure in NaOH solution for approximately thirty minutes, without rubbing or other abrasion. The glue softens and "dissolves" from beneath the overlying porous film of metal 23; and that part of the metal film thus left unsupported by removal of the glue breaks into small fragments which are washed away in a washing operation which preferably includes a sodium hypochlorite rinse followed by a distilled water rinse. Removal of the glue and those portions of the metallic film which were supported by the glue leaves discrete metal films 24 adhering to the base 10a, as indicated in Figure 5; the films being surrounded and separated by metal-free surface areas of the base. The distances of separation of the discrete films or areas of metal are governed by the widths of the opaque lines or areas in the photonegative used in exposing the glue layer, and may be such as is desired. The separation of any two such metallic films is preferably uniform and of a very small dimension. For example, the line-like metal-free areas separating next-adjacent indium films may be of the order of .003 inch wide. A section, to an exaggerated dimensional scale, through two of the indium films 24 and intervening metal-free space is illustrated in Figure 7, the line-like area separating the two films being therein indicated by numeral 25 and the previously removed bridge of indium or metal overlying area 25 being indicated by dotted lines.

Following the steps hereinbefore outlined, the cell with its separate metal films is preferably suitably heated to render the metal more firmly adherent to the glass. This heat treatment may consist, for example, in heating the cell at about 400° C. for approximately thirty minutes. If during the heat treatment an oxide layer is formed, it may be later removed by lightly washing the film with dilute HCl acid. While the heat treatment may under some circumstances be omitted, preferably it is included for the reason and purpose stated. An additional advantage of employing indium rather than chromium or other hard metal is that the former is capable of withstanding longer heating at high temperatures than is a hard metal.

The cell at this stage of manufacture is ready for application of the potentially or actively photoconductive material, which may be applied in accord with the procedure outlined in the aforementioned copending application. The photosensitive material, which may be principally cadmium sulphide, or zinc sulphide or other photoconductor, may if desired be applied to only the areas between the metal films 24 and so as to substantially uniformly contact the edges of the metal films. However, as a matter of convenience and in the interest of uniform contact with the metal films, the photoconductive material may be applied as a layer or film overlying the entire upper surface of the cell, as indicated by the dots in Figure 1 and as indicated in exaggerated form as layer 26

in Figure 8. The layer 26, as indicated in Figure 8, contacts the exposed edges 24a of films 24; and, as hereinbefore indicated, provides an ohmic contact with the electrically conductive films 24.

While a photoconductive reticle-type cell produced in the manner hereinbefore described may be used without further treatment, the cell may be subjected to other treatments, such as those indicated and described in copending patent applications hereinafter identified; and further, the cell may be given a protective coat of a translucent material such as a clear resin such as glyptol.

In certain respects this application is related to the copending patent applications of Akos Z. Czipott, Serial No. 613,177 filed contemporaneously; and Acey L. Floyd, Serial No. 489,397, filed February 21, 1955, to which applications reference is made in respect to details of procedures and materials therein disclosed.

It being evident that with the preceding disclosure, of an exemplary cell and its construction in view, modifications of the procedure, materials and constructions within the scope of the invention will occur to those skilled in the art, it is not desired to be limited to the particular exemplary details set forth, but what is claimed is:

1. A photoconductive cell comprising electrically conductive films with marginal portions having ohmic union with a photoconductive material contacting such marginal portions, comprising, in combination: an electrically non-conductive base; at least two separated discrete films of substantial areal extent of metallic material selected from the class consisting of indium and gallium, firmly adherent to said glass base and each film providing a marginal portion and each film insulated from another film; and a layer of photoconductive material on the cell base and at least bridging an area between and overlapping said marginal portions to provide a photoconductive electric current path therebetween.

2. A photoconductive reticle-type cell comprising, in combination: a glass base, a plurality of electrically conductive discrete films of a material selected from the group consisting of indium, gallium, and alloys thereof, firmly adherent on said base; and a layer composed principally of photoconductive polycrystalline cadmium sulphide overlying an area of said base situated between at least two of said films of said material and at least a marginal area of each of the two films adjacent said area of said base, whereby ohmic electrical contact between the electrically conductive films and the contacting layer of cadmium sulphide is effected.

3. An ohmic photoconductive cell, comprising an electrically insulative base, at least two discrete films of indium on said base, and a deposit of polycrystalline photoconductive material on said base and electrically interconnecting said films of indium.

4. A photoconductive cell comprising, in combination: an insulating base member; at least one body of a material selected from the group consisting of indium, gallium and alloys thereof, firmly adhered on said base member; and a layer composed principally of photoconductive cadmium sulphide overlying an area of said base member and situated in electrical contact with said body, whereby ohmic electrical contact between said layer and said body is effected.

5. An ohmic photoconductive cell comprising: an electrically insulative base; at least two discrete bodies composed of a material comprising principally indium; and a deposit composed principally of photoconductive cadmium sulphate on said base and electrically interconnecting said bodies.

6. An ohmic photoconductive cell comprising: an electrically insulative base; at least two discrete bodies of a material comprising principally gallium; and a deposit composed principally of photoconductive cadmium sulphate on said base and electrically interconnecting said bodies.

7. An ohmic photoconductive cell comprising: an

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electrically insulative base; at least two discrete bodies of a material selected from the group consisting of indium, gallium and alloys thereof; and a deposit composed principally of photoconductive cadmium sulphate on said base and electrically interconnecting said bodies. 5

References Cited in the file of this patent

UNITED STATES PATENTS

2,435,889	Kerridge	Feb. 10, 1948	10
2,482,547	Kerridge	Sept. 20, 1949	
2,644,852	Dunlap	July 7, 1953	

2,654,819
2,662,957
2,747,104
2,765,385

633,848

6

McIlvaine	Oct. 6, 1953
Eisler	Dec. 15, 1953
Jacobs	May 22, 1956
Thomsen	Oct. 2, 1956

FOREIGN PATENTS

Great Britain	Dec. 30, 1949
---------------	---------------

OTHER REFERENCES

Ludwick: "Indium" from Steel Magazine of November 9, 1942, pages 80, 81, 122-124, Indium Digest.