

# United States Patent [19]

Poleshuk et al.

[11] 3,765,962

[45] Oct. 16, 1973

[54] **METHOD OF MAKING A CHARGE  
STORAGE DEVICE**

3,687,745	8/1972	Chung et al. ....	315/10 X
2,823,148	2/1958	Pankove .....	148/178
3,419,746	12/1968	Crowell et al. ....	148/187 X
3,548,233	12/1970	Cave et al. ....	317/235 NA

[75] Inventors: Michael Poleshuk, Mahopac, N.Y.;  
Alfred E. Milch, Teaneck, N.J.

[73] Assignee: North American Philips  
Corporation, New York, N.Y.

[22] Filed: Nov. 23, 1971

[21] Appl. No.: 201,551

[52] U.S. Cl..... 148/177, 148/178, 148/179,  
148/185, 317/235 R, 313/65 R, 315/10 R

[51] Int. Cl. .... H01I 7/46

[58] Field of Search..... 148/177, 178, 179,  
148/185; 317/235 NA; 313/65 R, 65 T, 65  
AB; 315/10 R

## [56] References Cited

### UNITED STATES PATENTS

3,011,089 11/1961 Reynolds..... 313/65 AB

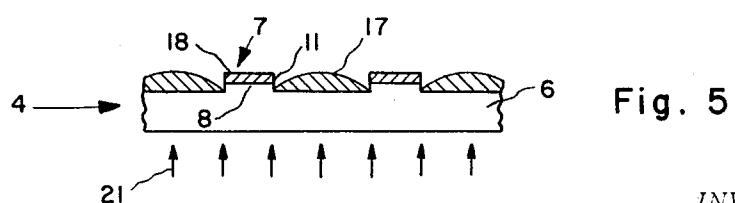
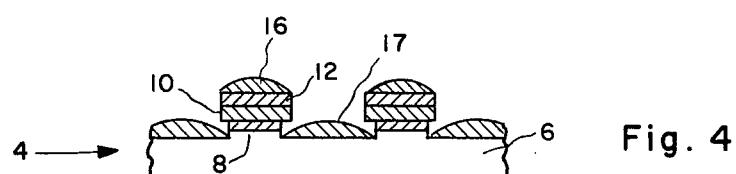
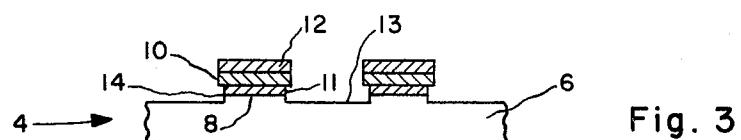
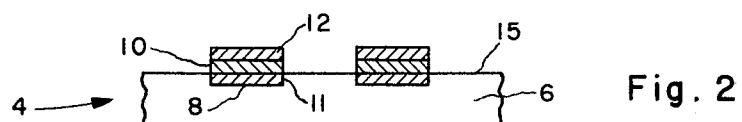
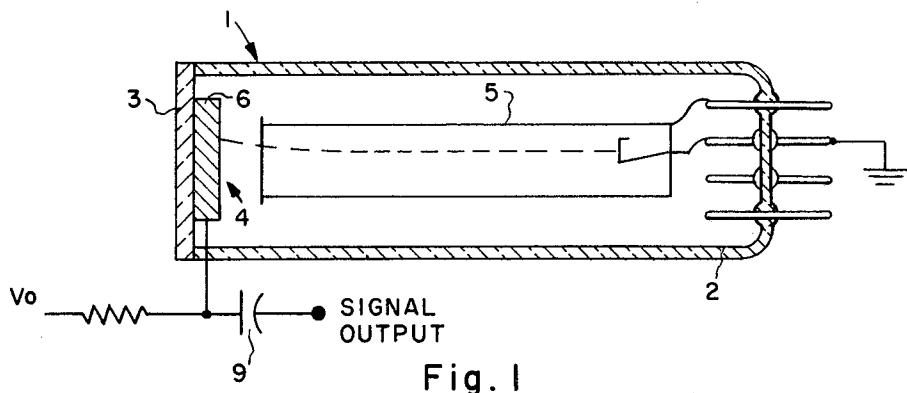
Primary Examiner—G. T. Ozaki  
Attorney—Frank R. Trifari

[57]

## ABSTRACT

An improved method for fabricating a vidicon camera tube having a germanium target comprising an array of p-n junctions is described. Each of the p-n junctions is surrounded by an insulating layer whereas the surface of each of the p-n junctions facing an electron beam source is free of insulating materials. The new method of making the germanium vidicon camera tube target results in improved electrical performance for the vidicon camera tube while being economical.

8 Claims, 5 Drawing Figures



INVENTOR.S

MICHAEL POLESHUK

ALFRED E. MILCH

BY

AGENT

## METHOD OF MAKING A CHARGE STORAGE DEVICE

### BACKGROUND OF THE INVENTION

The invention described herein was made in the performance of work under a government contract and is subject to the provisions of Section 9-107.5(b) of the Armed Services Procurement Regulation of Jan. 1, 1969.

This invention relates to charge storage devices having a charge storage target scanned by a reading means and particularly concerns a target of the type comprising an array of diodes which are scanned by an electron beam.

One such type of charge storage device is a vidicon camera tube having a germanium target comprising a multiplicity of diodes scanned by an electron beam and the invention will be described in connection with its use in such camera tubes. Germanium vidicon camera tubes find application for image forming at long infrared wavelengths at which wavelengths the silicon vidicon camera tubes become ineffective.

A typical germanium vidicon camera tube target comprises a wafer of germanium material having an array of discrete photosensitive diodes comprising p-n junctions on the surface of the target facing the electron gun. It has been found that the most practical means of forming p-n junctions in the germanium wafer with characteristics desirable for vidicon camera tube operation has been by means of the indium alloy process.

In operation, the electron beam sweeps repetitively across the target surface and charges each diode up to cathode potential. Photoconduction and consequent discharge occurs at each of the p-n junctions in accordance with an infrared image projected onto the reverse surface of the target. The recharging current constitutes the electrical signal output of the vidicon camera tube. An insulating layer on the portions of the target between diodes prevents the electron beams from hitting the germanium wafer so that the so-called dark current is minimized. The insulating layer is usually deposited in moats around each of the diodes for best performance.

One of the major problems of the prior art methods of forming the electron beam target surface for the vidicon camera tube is in forming an insulating layer in moats around each of the diodes without leaving insulating material on the diodes therealso and thereby degrade the electrical performance of the target. Another problem of prior art configurations is the possibility of forming an incidental insulating coating, usually an oxide, on the indium metal remaining on top of the indium alloy diodes subsequent to their formation. In such cases, during operation of the vidicon camera tube a charge builds up on the insulating coatings which charge repels the electron beam away from the diode thereby degrading the performance of the camera tube.

One prior art method for making a vidicon camera tube employs a photolithographic process for the deposition of the insulating material into the moats around each of the diodes of the target. In this method a mask is prepared and placed on the beam target surface so that during the deposition of insulating material into the moats around each of the diodes, no insulating material settles on top of the diodes. Considerable care is

necessary for the proper alignment of the mask. The removal of the insulating material which happens to settle on the diodes is accomplished by etching. The oxidation of the indium metal remaining on the diodes is not avoided by this method.

Another prior art method for making a vidicon camera tube involves simply depositing magnesium oxide over the entire beam target surface including all of the diodes and then removing the insulating material from the diodes by abrading the surface. An alternate method used for exposing the diodes is to place pressure sensitive tape on the insulating layer on the target and then to remove the tape. Removal of the tape also carries away the insulating material lying on top of the diodes. Both of the above techniques for exposing the diode surfaces are not only ineffective in removing all of the undesirable insulating material but these procedures also damage many of the p-n junctions and there is nothing to prevent the cleaned indium from re-oxidizing before the final encapsulation of the target in its vacuum envelope.

The present invention is particularly directed on an improved method of making a vidicon camera tube simply and economically with the resulting vidicon camera tube having electrical characteristics greatly improved over prior art vidicon camera tubes.

According to the present invention an array of alloy indium p-n junction diodes and moats around each of the diodes on a germanium wafer are formed by known procedures. Next, mercury is placed on the beam target surface so that the residual indium metal on each of the diodes forms a liquid amalgam therewith which dissolves in and is removed with the liquid mercury. Removal of the amalgam exposes each of the diode surfaces completely since both the deposited insulating material and the incidental insulating coatings are also swept away mechanically with the liquid mercury and dissolved indium amalgam. The exposed diode surface is germanium doped with indium metal and will not oxidize easily under ordinary conditions. The resulting target is then incorporated into a vidicon camera tube by known methods.

Accordingly, an object of the present invention is to provide an improved method for making a charge device having a charge storage target comprising an array of p-n junction diodes.

Another object of the present invention is to provide a method for making vidicon camera tube having an improved target comprising an array of p-n junction diodes.

Another object of the present invention is to provide an improved method for making a germanium vidicon camera tube.

Other objects and features of the present invention will be apparent from the description that follows and the appended claims and will occur to those skilled in the art upon a reading thereof.

The following drawings form a part of the description:

FIG. 1 is a side sectional view of an improved vidicon camera made in accordance with the present invention, and

FIGS. 2 to 5 are fragmentary sectional views of the target of FIG. 1 at various stages of manufacturing; FIG. 5 is the final form.

### DESCRIPTION OF THE PREFERRED EMBODIMENT

The germanium vidicon camera tube 1 shown in FIG. 1 comprises an evacuated envelope 2 having a transparent faceplate 3 at one end with an adjacent germanium target 4. An electron gun 5 inside envelope 2 of conventional construction and shown only diagrammatically, forms an electron beam which is directed to target 4. Means for accelerating, focusing and deflecting the electron beam to cause it to scan target 4 are of well known form and are not shown for the sake of simplification.

The target 4, a portion of which is shown in greater detail in FIG. 5, comprises a plurality of diodes 7 having surfaces 18 and p-n junctions 8 formed, as later to be more fully described, on the surface of bulk germanium region 6. In normal operation, the bulk germanium region 6 is biased by a potential,  $V_o$ , a few volts positive with respect to the cathode potential of electron gun 5. The scanning electron beam impinges on each of the diode surfaces 18 and since each p-n junction 8 is reversed biased, the electrons accumulate on surfaces 18 until surfaces 18 reach cathode potential and repel the electron beam. In the absence of incident radiation, a good p-n junction 8 can retain most of its accumulated charge a considerable time. However, when radiation 21 is absorbed in the bulk germanium region 6, charge carriers are formed therein which migrate to the p-n junctions 8 and result in the leakage of the accumulated charge. The next time the electron beam scans the surface 18, surface 18 is quickly brought to cathode potential. The recharging current is coupled through the bulk germanium region 6 to capacitor 9. The output signal can be coupled to video signal processing equipment not shown.

Turning now to the details of the present invention, reference is made to FIGS. 2 to 5. FIG. 2 shows typical alloy indium p-n junctions 8 formed by a known method in an n-type bulk germanium region 6 having a wafer shape. One method for making p-n junctions 8 comprises the deposition of indium metal onto portion surface 15 through a mechanical mask. An incidental insulating coating 12, generally an oxide, usually forms on the outer surface of the indium metal 10, shortly after exposure to the air. The next steps are depositing a silicon oxide layer on surface 15 and the surface of insulating coating 12, alloying the indium metal into germanium region 6 through heating, and then removing the silicon oxide layer by etching with an HF and  $HNO_3$  solution. The function of silicon oxide layer is to keep the low-melting indium metal at each diode site during the heating process. The indium metal 10 not used up in the doping of the p+ region 11 and insulating coating 12 remain on top of the p+ region 11.

Next, referring to FIG. 3, moats 13 are etched around each of the p+ regions 11 by a known method. For example, the target surface 15 is immersed in a 4 percent KOH solution and used as an anode with a germanium rod used as a cathode; the reverse side of the target 4 is illuminated during the etching process. It is preferable to permit undercutting 14 of indium metal 10 during this step. Referring to FIG. 4, a suitable material is deposited in the moats 13 to form an insulating layer 17 and incidentally on top of insulating coating 12 to form an insulating layer 16. One of the commonly used methods for the deposition of insulating material which

is suitable here employs the evaporation of silicon monoxide from a source at about  $1000^\circ C$  in a low pressure oxygen environment. The insulating layers 16 and 17 comprise silicon dioxide for this case.

The target 4 is then immersed in liquid mercury at, for example, ambient conditions. The mercury amalgamates with indium metal 10 whereupon merely shaking target 4 and lightly brushing the beam target surface is sufficient to remove the amalgam with both the insulating layer 16 and the insulating coating 12, thereby exposing each of the diode surfaces 18. Germanium is insoluble in mercury and at room temperatures mercury does not even wet germanium so that the mercury does not adversely affect the electrical properties of target 4. However, to ensure complete removal of mercury from beam target 4, it is preferable to bake target 4 in a vacuum for about two hours at about  $180^\circ C$ .

Note that under cutting 14 which arises from the umbrella masking effect of indium metal portion 10 contributes to the rapid formation of the amalgam by permitting direct contact between indium metal portion 10 and the applied mercury. It is believed that small defects in insulating layer 16 and insulating coating 12 also allow the applied mercury to contact indium metal portion 10. FIG. 5 illustrates a section view of a finished target 4.

The invention is also useful for the manufacture of targets in which other metals such as tin, lead, bismuth, gold, thallium, silver, zinc, and gallium are used in combination with a germanium target which other metals also amalgamate with mercury. The procedure for these other metals would not vary substantially from the procedure for indium metal. Similarly, the invention is suitable for targets in which silicon is substituted for germanium since silicon is also insoluble in mercury and is also not wet by mercury at room temperature.

Upon completion of the above steps given for the preparation of target 4, the usual steps are followed for the incorporation of target 4 into vidcon camera tube 1.

We claim:

1. A method of making a charge storage device comprising the steps of providing a semiconductor wafer, forming an array of alloy p-n junction diodes on a major surface of said wafer with a metal which amalgamates with mercury, depositing an insulating material on said major surface and said alloy p-n junction diodes, and removing a residual portion of said metal from the top of at least one of said diodes using liquid mercury whereby a portion of the insulating layer on top of the diode is also removed.

2. A method of making a charge storage device according to claim 1, wherein said metal is selected from the group consisting essentially of indium, gallium, thallium, bismuth, silver, gold, and zinc.

3. A method of making a charge storage device according to claim 1, wherein said wafer consists of a semiconductor material selected from the group consisting of germanium and silicon.

4. A method of making a charge storage device according to claim 1, further comprising the step of forming moats around each of said diodes and depositing said insulating material in said moats.

5. A method of making a charge storage device according to claim 4, wherein said moats extend partially beneath respective ones of said diodes, thereby en-

hancing said step of removing said residual metal portion.

6. A method of making a charge storage device according to claim 1, further comprising the step of heating said wafer to remove said mercury.

7. A method of making a charge storage device ac-

cording to claim 1, wherein said metal is indium and said wafer comprises germanium.

8. A method of making a charge storage device according to claim 1, wherein said device is a vidicon camera tube.

\* \* \* \* \*

10

15

20

25

30

35

40

45

50

55

60

65