Sept. 10, 1968 R. W. REDINGTON 3,401,107

METHOD OF MANUFACTURING SEMICONDUCTOR CAMERA TUBE TARGETS

Filed Aug. 5, 1965 2 Sheets-Sheet 1

Fig. 1.

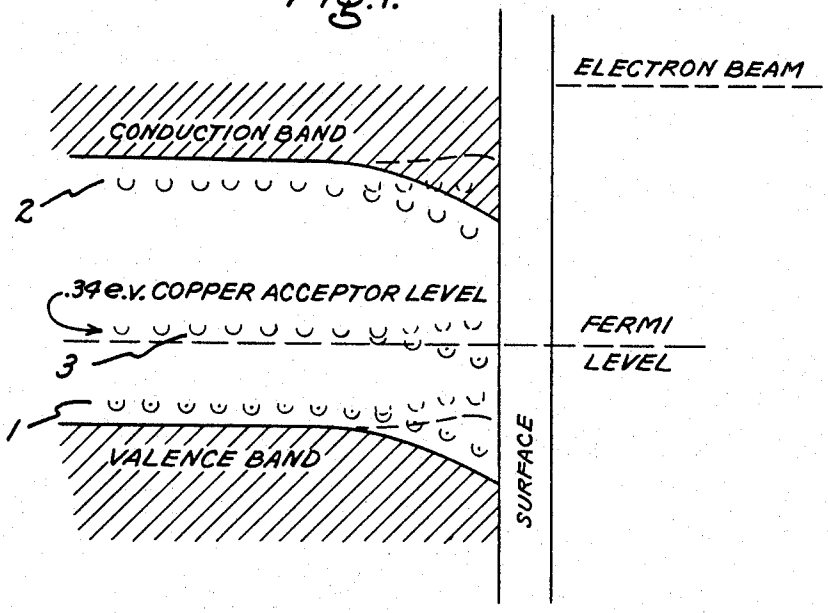


Fig. 2.

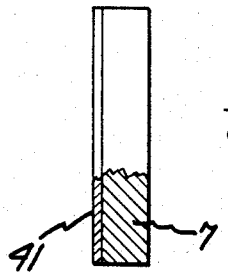
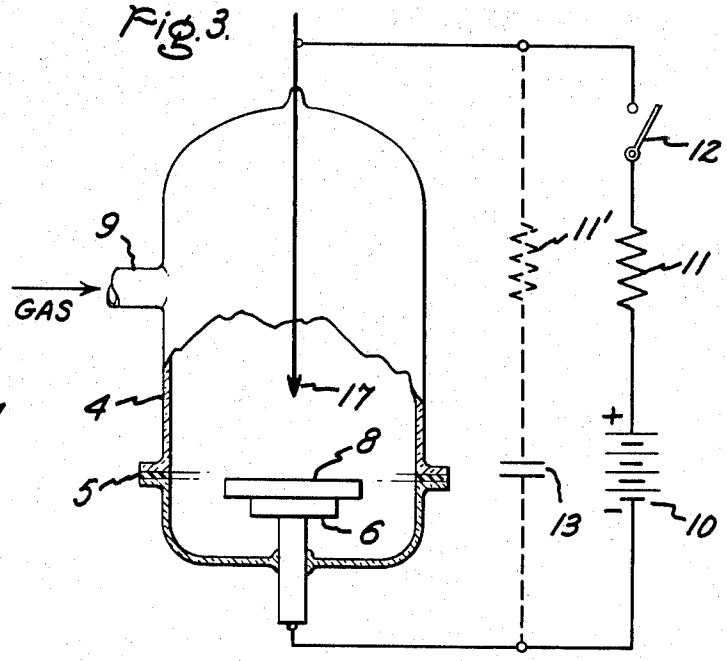


Fig. 3.



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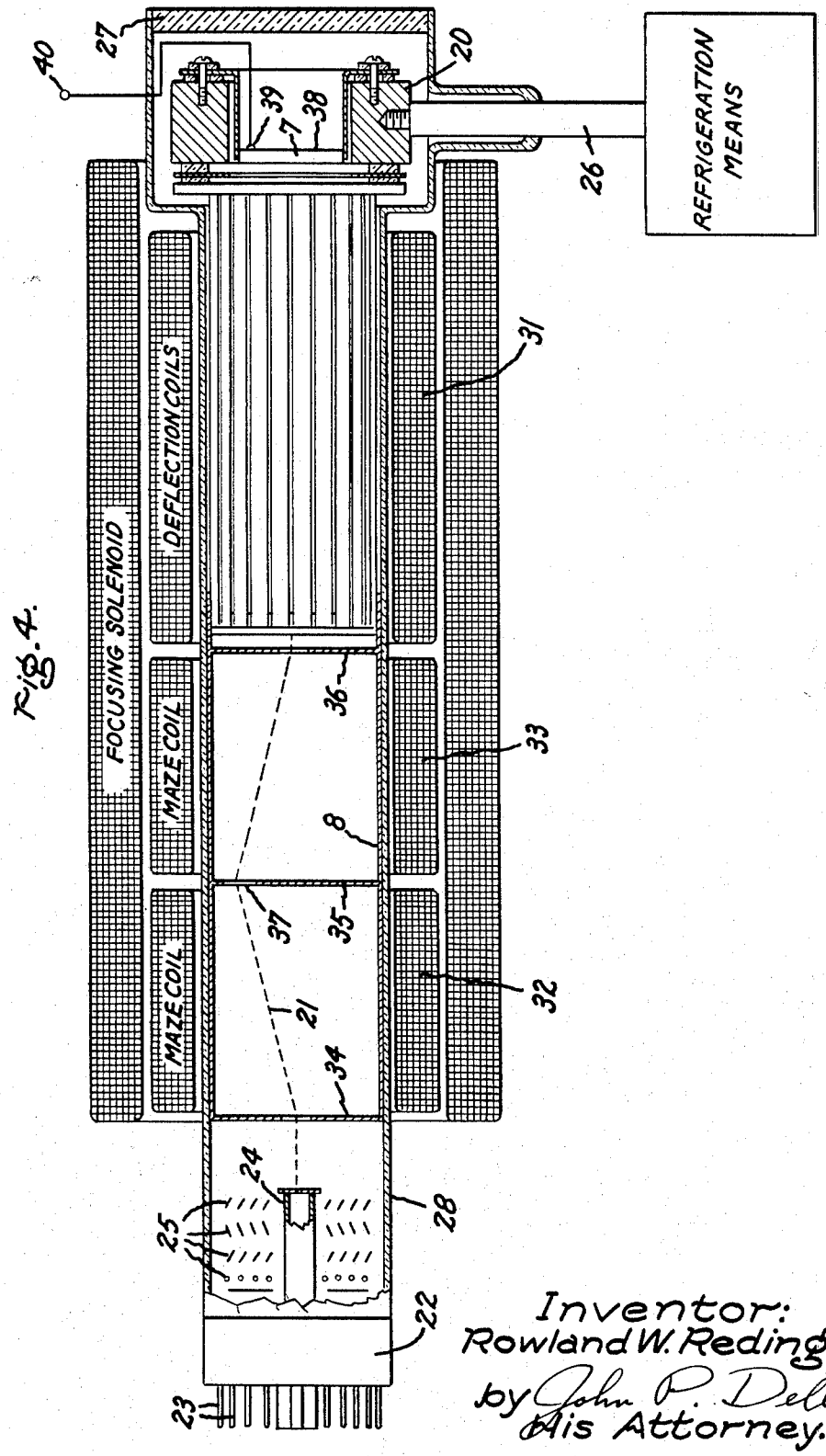


Fig. 4.

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3,401,107

METHOD OF MANUFACTURING SEMICONDUCTOR CAMERA TUBE TARGETS

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Filed Aug. 5, 1965, Ser. No. 477,613
7 Claims. (Cl. 204—164)

ABSTRACT OF THE DISCLOSURE

Camera tube targets are made and depolarized by adding to a donor-doped target blank a quantity of double-acceptor level impurities sufficient to compensate for the original donor concentration and render the target p-type and photoconductive. Non-imaging surface states due to the interaction of the double-acceptor impurities with the scanned surface of the target are removed by bombarding that surface with ions of a Group III metal.

This invention relates to methods of manufacturing semiconductor targets for television type camera tubes and particularly to such methods rendering the targets more stable during the preparation of the tube.

A semiconductor forms a useful photosensitive element and can be rendered sensitive to selected regions of spectral radiation. A relatively thin semiconductor employed as a photoconductive target in a television type camera tube becomes less resistive across its thickness at a point where detected radiation strikes the target. Radiation photons striking the target generate current carriers in the target and these carriers change the target charge as seen by a scanning electron beam with the electron beam providing the output of the device.

With appropriate impurity doping, a semiconductor target can be made sensitive in various portions of the visible and invisible spectrum. For example, copper^{II}-doped germanium is sensitive to the infrared region between 1½ and 4 microns while zinc^{II}-doped germanium is sensitive to the infrared between 8 and 15 microns.

Targets of the semiconductor type are thus manufactured by adding an impurity to the semiconductor rendering it sensitive to the desired portion of the spectrum. However, it has been desirable to alter the polarity characteristics of the target where it will be scanned with an electron beam. For example, in the copending application of Redington and VanHeerden, Ser. No. 56,799, filed Sept. 19, 1960, the target is bombarded with noble gas ions whereby the bombarded surface becomes the same or nearly the same polarity semiconductor as the interior of the target. This treatment renders the target long lived and not subject to a non-imaging state wherein the image tends to blur after a period of operation.

Targets of the semiconductor type have suffered certain disadvantages as employed in a completed camera tube because of the heating required for degassing the tube. Thus, after the target is completed and mounted in a camera tube, the camera tube is usually raised to a high temperature driving gases from the tube parts. Unfortunately this heating tends to alter the effect of ion bombardmnet of the target. Thus, after heating, the non-imaging or blurring conditions of the image sometimes

return. I have discovered an improved method of bombarding the target for preventing the non-imaging state thereof and after which the target is stable at high temperatures, retaining its desired imaging properties despite conventional baking or degassing.

According to the present invention, the side of the target which is to be scanned with an electron beam is first subjected to a glow discharge with ions from Group III metals of the Periodic Table. Specifically, aluminum, boron and gallium are found particularly useful. Glow bombardment with ions of these metals provides a target surface which is not materially changed upon heating.

According to another feature of the present invention, the target surface which is to receive detected radiation, that is the surface opposite the scanning electron beam, is provided with a transparent electrode with ion glow bombardment with Group III metal ions. The ion bombardment is continued for a period longer than employed in the aforementioned altering of the polarity characteristics of the side scanned with the electron beam. An overall electrode surface on the target is formed with the glow discharge which is transparent to detected radiation in the completed tube. A transparent electrode is thus provided in this manner without application of heat to the semiconductor and one which is stable in subsequent degassing of the tube.

It is therefore an object of the present invention to provide a semiconductor camera tube target capable of long lived imaging of detected radiation and a target which is stable at bakeout temperatures used in tube manufacture.

It is another object of the present invention to provide a simple procedure for establishing a transparent electrode on a semiconductor camera tube target.

The subject matter which I regard as my invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. The invention, however, both as to organization and method of operation, together with additional advantages and objects thereof, may best be understood by reference to the following description taken in connection with the accompanying drawings wherein like reference characters refer to like elements and in which:

FIG. 1 is an energy diagram illustrating energy levels for copper ^{II}-doped germanium,

FIG. 2 is a camera tube target, partially in cross-section, coated with acceptor metal during an acceptor metal diffusion step,

FIG. 3 is a cross-section of apparatus employed in ion glow bombardment for removing the non-imaging state of a semiconductor target, and also for providing a transparent electrode thereon, and

FIG. 4 is a completed camera tube including a target prepared in accordance with the present invention.

A camera tube target formed in accordance with the present invention is constituted of extrinsic semiconductor material, that is semiconductor material which contains certain specified impurities in order to render it suitably conductive or photoconductive. In accordance with a specific embodiment, p-type semiconductor material is employed as an infrared detecting target wherein such target is initially formed from semiconductor material which is at first n-type. For example, n-type germanium,

containing arsenic or antimony impurities, then has added thereto a quantity of copper metal which approximately balances the said arsenic or antimony in atomic percentage. Lower "energy states" of the copper impurity act to compensate or "trap" the electrons from the higher energy state of the n-type donor (arsenic or antimony) material. These energy states are depicted in FIG. 1. The resulting compensated material is then effectively of the p-type having a usable acceptor level 3 at approximately .34 electron volt above the germanium "valence band" shown in the energy diagram in FIG. 1. When a quantum of radiation strikes the semiconductor, an electron may be raised thereby from the top of the valence band to the .34 electron volt level, this energy differential corresponding to radiant energy excitation of about 4 microns in wavelength, that is, radiant energy in the usable infrared spectrum. As a result of the radiation, a conducting hole is left in the valence band capable of affecting an electrical output indication. Of course electrons excited from slightly below the top of the valence band will correspond to slightly shorter wavelengths, etc. It therefore follows that a semiconductor target with this impurity acceptor level will be sensitive to and receive energies in the infrared radiation region.

Copper as a p-type impurity, in addition to providing an energy level appropriate to infrared detection, provides sufficient electron mobility and sufficient dark current resistivity, particularly at low temperatures, to function well in a photoconductive target. The dark current resistivity of the copper doped or copper impurity containing germanium employed increases from about one ohm-centimeter at room temperature to greater than 10^{12} ohm centimeters at the boiling temperature of liquid nitrogen. However other p-type impurities, notably zinc, are also efficacious.

The semiconductor target may be constructed in accordance with one feature of the present invention by copper plating a slightly oversized target wafer blank of commercially available n-type germanium, containing an arsenic or antimony impurity. The target **7** blank is illustrated in FIG. 2 including a copper coating **41**, e.g. on the scanned side thereof. The plated blank is heated or roasted for approximately a day or two allowing the metal to diffuse into the semiconductor blank. The temperature at which this heating is carried out is determined by the initial amount of n-type impurities, i.e., the arsenic or antimony, initially included in the semconductor blank, as conveniently determined, for example, by Hall effect measurements. It is desired to balance off the n-type impurity with approximately 95% or so as much copper acceptor metal by atomic percentage. The amount of metal added by the heating process is understood to be a function of the temperature at which the process is carried out and is therefore determined from solid solubility curves of a metal in a semiconductor, e.g., copper in germanium. For such a chart, reference may be had to page 86, vol. 105, Physical Review, Jan. 1, 1957, "Triple Acceptors in Germanium" by H. H. Woodbury and W. W. Tyler. The germanium is saturated with copper at the diffusion temperature.

According to my concurrently filed copending application Ser. No. 477,615, filed Aug. 5, 1965 and entitled "Method of Manufacturing Semiconductor Camera Tube Targets" about one-third to one-half of the amount of copper impurity necessary to balance the n-type impurity is added for the heat diffusion procedure and the effective concentration of the acceptor impurity is increased in a subsequent annealing step whereby substantial balance is achieved. The process including this annealing step has the advantage of rendering the semiconductor target more heat resistant and less subject to alteration of its properties during a subsequent tube degassing or bakeout step.

After the semiconductor is heated for a day or two, long enough to diffuse in the desired concentration of acceptor type material, the copper plating is peeled off or removed by hydrofluoric acid. The copper plating is removed prior to any annealing step.

In accordance with the copending application of Redington and VanHeerden, Ser. No. 56,799, entitled "Method of Manufacturing Semiconductor Camera Tube Targets," the target prior to placement in the camera tube is subjected to an ion glow bombardment with noble gas ions. This treatment is effective in preventing the formation of a non-imaging state of the semiconductor target, wherein the television image obtained becomes somewhat blurred. While bombardment with noble gas ions and particularly with helium ions very adequately prevents this non-imaging state, the target as thus prepared is somewhat sensitive to the high temperatures employed in the subsequent degassing or bakeout procedure. Thus after placement of the target in a finished tube and bakeout of the tube for a time sufficient to remove undesired gases from the tube interior, the non-imaging state frequently tends to return; thus the heating during bakeout has a tendency to undo the effect of this ion bombardment. I have discovered the non-imaging state is prevented by bombardment of the target surface with ions of materials selected from the group consisting of Group III metals in the Periodic Table, these ions being acceptors in the semiconductor material. After ion glow bombardment with these Group III metal ions the non-imaging state is substantially permanently removed and does not return upon raising the finished camera tube, including the tube's target, to customary bakeout or degassing temperatures. The Group III metals preferred in this procedure are boron, aluminum and gallium.

FIG. 3 illustrates an apparatus wherein ion glow bombardment of the semiconductor target with Group III ions is suitably performed. A gas tight enclosure **4** sealed with a rubber gasket at **5** includes an electrode support **6** oriented opposite a point of electrode **17**. The electrode support makes contact with semiconductor target **8**, which may be copper or zinc doped germanium having the surface which is to be scanned with an electron beam in the completed camera tube oriented towards energized electrode **17** with the distance therefrom suitably being on the order of 2½ inches. A gas conduit **9** conducts a gas to the interior of enclosure **4** containing the Group III acceptor metal preferably in chemical combination. A suitable gas is boron trifluoride at a pressure of 5 to 10 mm. of mercury. The boron trifluoride contributes to an ion glow bombardment of boron ions directed towards the semiconductor target **8**. Aluminum ions are similarly produced by substituting aluminum chloride vapor.

A voltage source **10** of from 2 to 10 kilovolts, and preferably between 4 and 8 kilovolts, is coupled between electrode support **6** and electrode **7** through limiting resistor **11** and switch **12**. The resistance of element **11** is suitably about 20,000 ohms. The desired discharge is established by closing switch **12** completing the circuit for a fraction of a second. A suitable alternative is illustrated by dotted lines in FIG. 3. Here a capacitor **13** of a few microfarads is charged to between 2 and 10 kilovolts and then discharged between electrode **6** and **7** via a limiting resistor **11'** having a value similar to resistor **11**. In either case the voltage and electrode spacing are such as to produce a glow discharge between electrode **7** and the surface of target **8** and this glow discharge eliminates the non-imaging state of the target. Apparently the glow discharge effectively introduces shallow acceptor levels near the surface of the semiconductor whereby an offending dipole layer near the surface of the semiconductor is removed and the semiconductor near its surface is caused to have nearly the same polarity characteristics as the semiconductor interior. In the case of copper-doped germanium the semiconductor near the surface thereof is caused to be substantially p-type to substantially as great an extent as

the interior of the semiconductor. It is important to note the discharge employed herein is a glow discharge and not an arc discharge. An arc discharge is not suitable for uniform sensitive semiconductor target surfaces as used in a television type camera tube because of damage caused in an arc.

The theory believed applicable to the present invention will be described with reference to the energy chart illustrated in FIG. 1 showing energy levels for electrons in germanium. The germanium target surface which is to be scanned by an electron beam is indicated at the right of the diagram.

Energy is shown as increasing in a vertical direction for electrons and decreasing for holes, and the horizontal distance from right to left roughly indicates the distance of such energy distribution from the surface of the semiconductor. In this diagram the valence band represents a group of energy levels for stable germanium electrons in the nonexcited semiconductor. The conduction band on the other hand is a group of normally empty levels to which electrons must be excited in an intrinsic (non-doped) semiconductor in order for conduction to take place. The Fermi level is that statistical level below which energy levels are most likely to be filled with electrons and above which most energy levels are likely to be empty of electrons. The gap or forbidden zone between the conduction band and the valence band indicates a usual complete absence of electrons or levels having corresponding energies in the intrinsic semiconductor.

The same diagram applies to extrinsic semiconductors except acceptor levels, e.g. copper levels, are added to which electrons may be excited by light quanta. To review semiconductor physics, extrinsic semiconductors are characterized as to polarity type depending upon the primary current carrier present. In general, two types of conduction occur in extrinsic semiconductors, depending upon the impurity added, i.e. conduction of electrons in n-type semiconductors, and conduction of holes in p-type semiconductors. The polarity type may be ascertained from the energy diagram where the relatively closer proximity of the conduction band to the Fermi level indicates n-type material wherein conduction will take place via electrons moving in the conduction band, while proximity of the valence band to the Fermi level indicates p-type material wherein conduction will take place via positive holes moving in the valence band. In this specific example, an extrinsic copper metal doped germanium is the semiconductor employed, rendering the material effectively p-type, and therefore conduction will take place primarily by movement of holes along energy levels in the valence band from left to right towards the back surface, these holes having been created by quanta of light falling upon the semiconductor's opposite surface exciting electrons to an acceptor level.

Now it is known that in germanium p-n junctions the contact potential difference between the n-type and the p-type material is much smaller than the energy band gap or "forbidden energy zone." This implies that near a semiconductor surface the energy band structure of n-type germanium bends up and that of p-type germanium bends down due to the charge of the surface states. Since the impurity doped semiconductor employed as a target in the specific example is of the p-type, the band structure of this p-type material bends down near the surface thereof; relatively positive surface states exist on the crystal surface due possibly to individual surface atoms introducing energy levels in the vicinity of, but not too far below the normal position of the Fermi level which would be filled in the neutral atom. This type of surface induces a relatively negative space charge layer near the surface in the area where the energy bands bend down, producing a retarding field for holes or barrier in this region. This band distortion is apparently the cause of the non-imaging state encountered with extrinsic semiconductor target tubes. The bending down of the band structure may be thought of as representing a potential hill which is difficult for the positive hole to cross, and further may be thought of as indicating a semiconductor near the surface only weakly of the same polarity type as the semiconductor interior inasmuch as the current-carrier-containing bands bend away from the Fermi level.

In the specific example, positive holes created by radiation quanta tend to pile up at the relatively negative barrier, creating a dipole layer or barrier, and these holes consequently never reach the surface scanned by the electron beam in a camera tube. The non-imaging state of extrinsic semiconductor tubes is then due to the sidewise conduction or diffusion of these holes near the surface which cannot reach the electron beam side of the target and cannot therefore establish the necessary condition for proper imaging, i.e., the condition where the electrons and holes recombine as fast as they arrive.

If there are hole traps in the surface region, the polarization will not at first produce the non-imaging state since the offending holes will at first be trapped, but once these hole traps are all filled, then additional polarization leaves free holes in the valence band near the surface resulting in the surface conductivity that produces the non-imaging state. The non-imaging state is then spread by sidewise diffusion of these holes. In accordance with the present invention, the non-imaging state is prevented or eliminated by rendering the semiconductor near the surface more nearly the same polarity type as the interior employing the described ion glow bombardment.

The bombardment is effective in raising the right hand energy band boundaries as illustrated by the dashed extensions in FIG. 1. It is postulated that bombardment with Group III metal ions penetrates this semiconductor to approximately the area of space change or potential hill, removing semiconductor atoms from their lattice sites and resulting in the addition of shallow energy states in this region. These energy states receive electrons from energy states **3** in FIG. 1 and all energy states rise as indicated by the dashed lines. Thus, the previous potential hill tends to be eliminated. As a consequence no barrier is encountered by holes travelling from left to right in the valence band and thus no layer of holes will be built up near the surface. The area near the surface becomes more nearly the same polarity type as the semiconductor interior and cross-conduction or running or blurring of the image is prevented. The response of the tube is much improved.

In operation of a television camera tube employing a target prepared in accordance with the present invention, the target requires an electrode connection on the side thereof opposite the scanning electron beam. This connection is coupled to a source providing the flow of current through the semiconductor target in response to quanta of detected radiation falling upon the target. This electrode extends across the face of the target opposite that scanned by the electron beam and detected radiation passes through this electrode is reaching the interior of the target. The target electrode must be uniform across its radiation sensitive face and transparent to detected radiation. Target electrodes have heretofore been formed by means of metal heat diffusion. However, a target electrode in accordance with the present invention is suitably established in a similar manner to that used in preventing the non-imaging state, and without additional heating. Thus the apparatus of FIG. 3 is suitable in establishing such electrode on the semiconductor target surface opposite that which is to be scanned with an electron beam. The same specifications with regard to materials and gases and electrical constants apply. Thus the apparatus is operated as previously described in connection with FIG. 3, except the semiconductor target **8** is now turned over and the discharge is established for a longer period of time. Instead of a discharge lasting for about a fraction of a second, the discharge is now established for several seconds, e.g. between 10 and 20 seconds. In one example, an electrode on

a zinc^{II} doped germanium target was prepared with a 15 second glow discharge current of 65 milliamps at a voltage of 4 kilovolts. The gaseous pressure was about 5 torr of boron trifluoride. An electrode prepared under these conditions showed resistance at liquid nitrogen temperature to a soldered contact of less than 2000 ohms.

FIG. 4 illustrates a complete camera tube employing the target prepared in accordance with the present invention and includes a long cylindrical glass envelope **28** closed with a base **22** providing connections **23** for electron gun structure **24** and electron multiplier output device **25**. A mask **34** at the electron gun end of the tube has a central aperture to receive electron beam **21** while partition **36** near the middle of the tube has a similar aperture. An intermediate partition **35** has its aperture **37** radially displaced and the electron beam **21** is caused to pass through that aperture without being accompanied by unwanted heat radiation. Maze coils **32** and **33** deflect the electron beam **11** through the illustrated path. The electron beam is caused to scan photoconductive semiconductor target **7** through the magnetic action of deflection coils **31**.

Annular member **20** acts to support the semiconductor target **7** and conduct heat therefrom. In the infrared detection region it is frequently desirable to operate the target at temperatures near the temperature of liquid nitrogen or below. To this end, cold finger **26** is joined to annular member **20** and passes through a seal in glass envelope **28**. Connection **39** joined to the target electrode **38** is coupled to terminal **40** maintained by means not shown at a positive voltage. Radiation is received through window **27**.

Aspects of the construction and operation of this tube are further described and claimed in the patent of Redington and Van Heerden, 3,185,891, assigned to the assignee of the present invention, Briefly, according to tube operation, the target **7** receives radiation through window **27**, appearing as a pattern upon the target and causing a variable amount of conduction of current carriers (holes) through the target. Electron gun **24** produces a relatively slow stream of electrons **21** focused at the opposite surface of target **7** and caused to deflect in an appropriate television type raster by deflection coils **31**. The deflection field of these coils is arranged such that electron beam scans the back side of target **7** depositing or attempting to deposit electrons thereon, while the other side of the target is maintained at a positive voltage. A quantum of radiant energy excites the free hole which becomes a current at the point where the radiation strikes. The hole passes through the target neutralizing the electron beam charge where it passes through. When the target is again scanned with beam **21**, just enough electrons are deposited to replace a negative charge removed in the preceding frame in the photoconduction process. The signal output from electron multiplier **25** is a function of return beam electrons returning from the target along the length of the tube.

This tube with the target **7** in place must, of course, be baked out or degassed during its manufacture. As previously indicated, targets have heretofore been undesirably sensitive to the bakeout temperatures and were apt to have their characteristics undesirably changed thereby. However, in accordance with the present invention, the target is stable at the bakeout temperatures for periods of time adequate to accomplish the desired degassing function. For example, targets prepared in the manner hereinbefore set out have properties which are substantially constant for periods of up to 8 hours at 300° C. or for longer periods of 250° C.

Although in the present embodiment the target **7** has been described as a p-type semiconductor, e.g., germanium appropriately doped with copper after a prior doping with arsenic or antimony, and although such a composition has particular advantages especially in the infrared region, it should be noted the stable manufacturing method according to the present invention is applicable to other extrinsic semiconductor materials, for example, silicon appropriately doped. Also other dopings suitable for germanium are, in addition to copper: zinc, platinum, gold, silver, and transition metals such as iron, cobalt, nickel and manganese. Zinc, like copper, is particularly useful in the infrared region where it is operative in the manner similar to copper as appropriately compensated in an initially n-type semiconductor. Appropriate dopings for use with silicon semiconductor materials, and whose use also depends on the spectral response desired, are boron, gallium, indium, aluminum, zinc and gold. This list is not to be construed in a limiting sense. The process of the present invention, with respect to eliminating the non-imaging state, has been described as applicable to solid targets but this process is also suitable in preparing thin target layers as described and claimed in my copending application, Ser. No. 418,920, filed Dec. 16, 1964, and assigned to the assignee of the present invention.

In addition to Group III metals boron, aluminum and gallium used to supply glow discharges according to the present invention, other Group III metals may also be utilized, for example indium and thallium.

While I have shown and described embodiments of my invention, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from my invention in its broader aspects; and I therefore intend the appended claims to cover all such changes and modifications as fall within the true spirit and scope of my invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of making a semiconductor camera tube target having a depolarized rear surface wherein information-containing radiant energy is incident upon a front surface thereof and an electric current representative of said information is produced in conjunction with an electron beam scanning said rear surface and the absence of a back-surface dipole charge is necessary for proper operation which method comprises:

(a) providing a target blank having a predetermined donor concentration therein,

(b) adding to said target blank a first acceptor impurity in sufficient quantity to substantially balance the donor impurity and impart p-type conductivity characteristics thereto,

(c) bombarding said rear surface of said target blank which is to be scanned by an electron beam with ions which are second acceptors in the semiconductor material of said blank and are selected from the Group III metals of the Periodic Table until a dipole formed by a negative space charge induced at the surface region of said rear surface by the interaction of said added first acceptor impurity with said rear surface is overcome.

2. The method of claim **1** where said dipole-eliminating second acceptor ions are added to said rear surface by ion glow discharge bombardment.

3. The method of claim **1** wherein the rear surface of said target blank is connected as one electrode of a glow discharge, a second electorde is provided within an hermetically sealable chamber, and said second acceptor is added to said chamber in a gas containing the same.

4. The method of claim **3** wherein the said semiconductor target blank is germanium, said first acceptor impurity is selected from the group consisting of copper and zinc, and the Group III metal is selected from the group consisting of boron, aluminum, and gallium.

5. The method of claim **1** wherein said first added acceptor impurity is a double acceptor having two levels of acceptor states and said first acceptor is added in approximately the same atomic concentration as said donor impurity so that one level of said acceptor states substantially compensates for said donor impurities and the sec-

ond level of said first acceptor states renders said target blank p-type and photoconductive.

6. The method of claim 5 wherein said first added double acceptor impurity is added by diffusion and said second Group III acceptor is added by glow discharge ion bombardment.

7. The method of claim 5 wherein said double acceptor impurity is selected from the group consisting of copper and zinc and said Group III metal is selected from the group consisting of boron, aluminum, and gallium.

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