

[54] **PHOTOCONDUCTIVE CAMERA TUBE AND METHODS OF MANUFACTURE**

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[52] U.S. Cl. **315/10, 250/353, 250/370, 313/65 T**

[51] Int. Cl. **H01j 29/70**

[58] Field of Search 307/88.5; 250/83.1 TR, 250/211, 213, 238, 347, 353, 370; 313/65, 68, 65 T, 68 R; 338/18; 315/10-12

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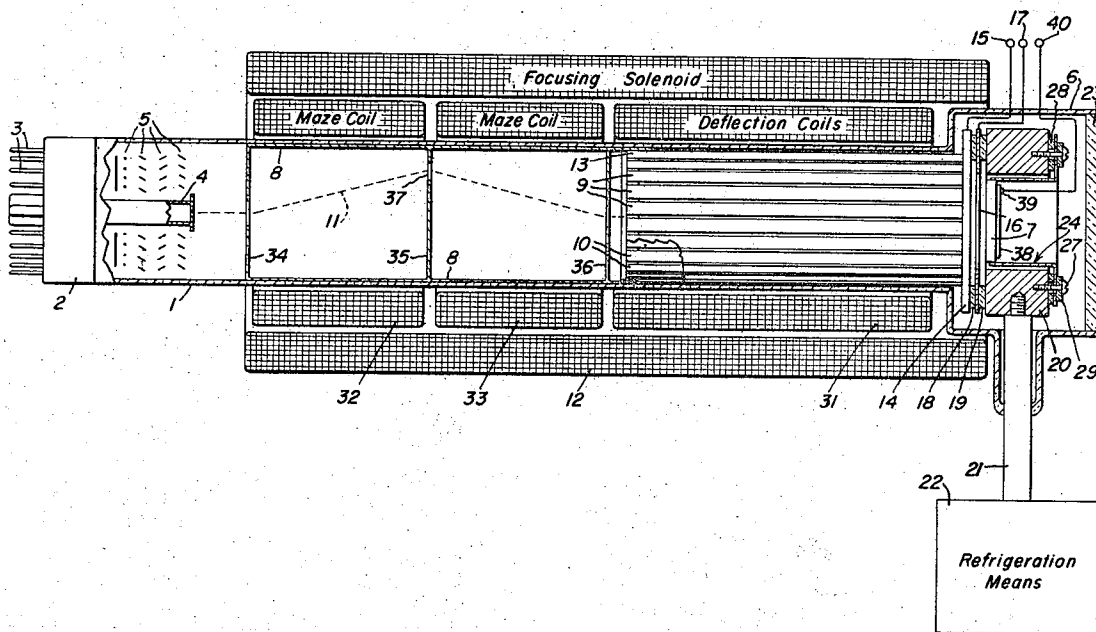
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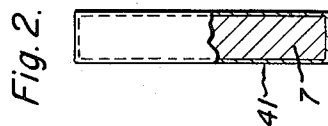
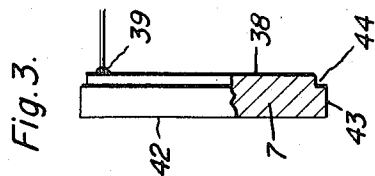
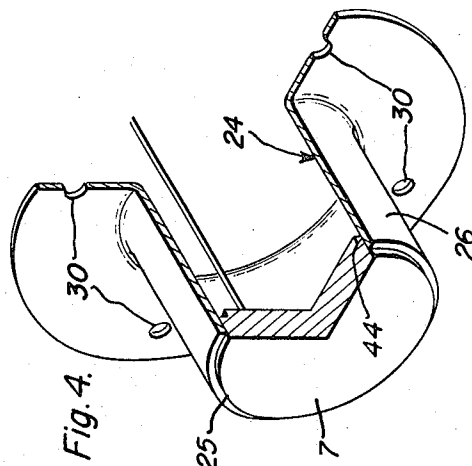
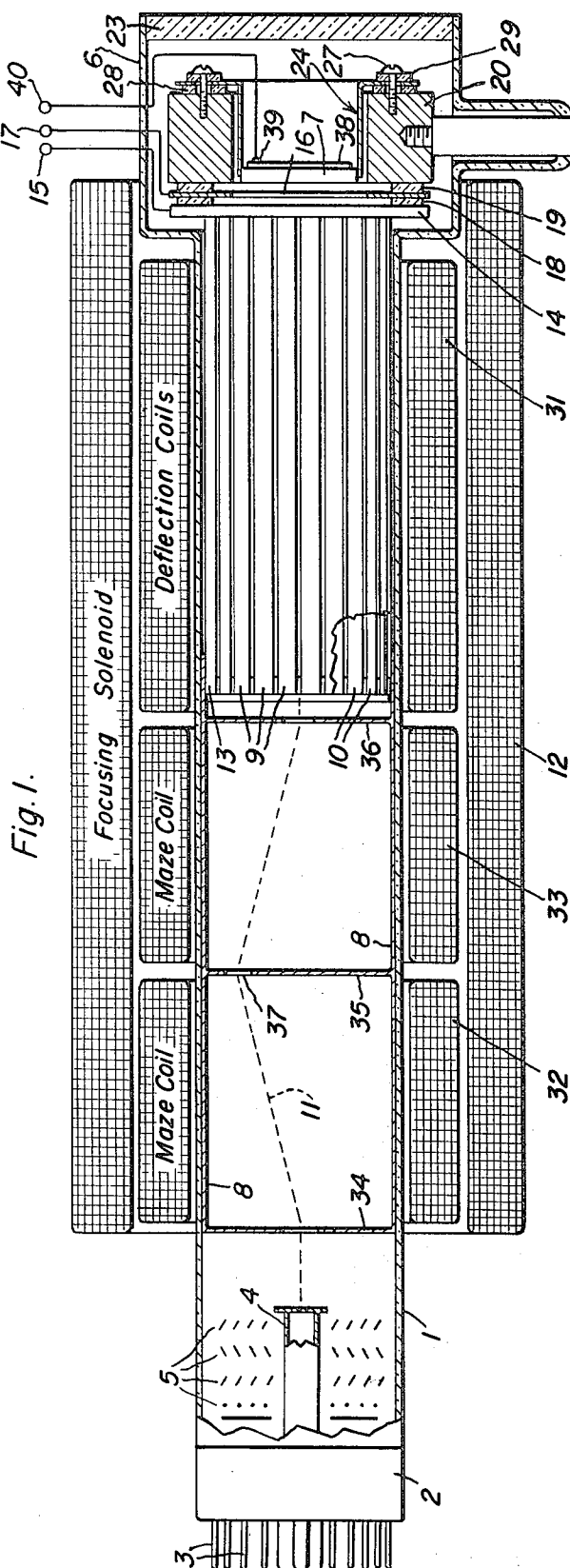
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ABSTRACT

The object of this invention is to provide an improved photoconductive camera tube target of increased extended sensitivity utilizing a target composed of arsenic or antimony doped germanium semiconductor with the addition of copper to the semiconductor.

14 Claims, 10 Drawing Figures





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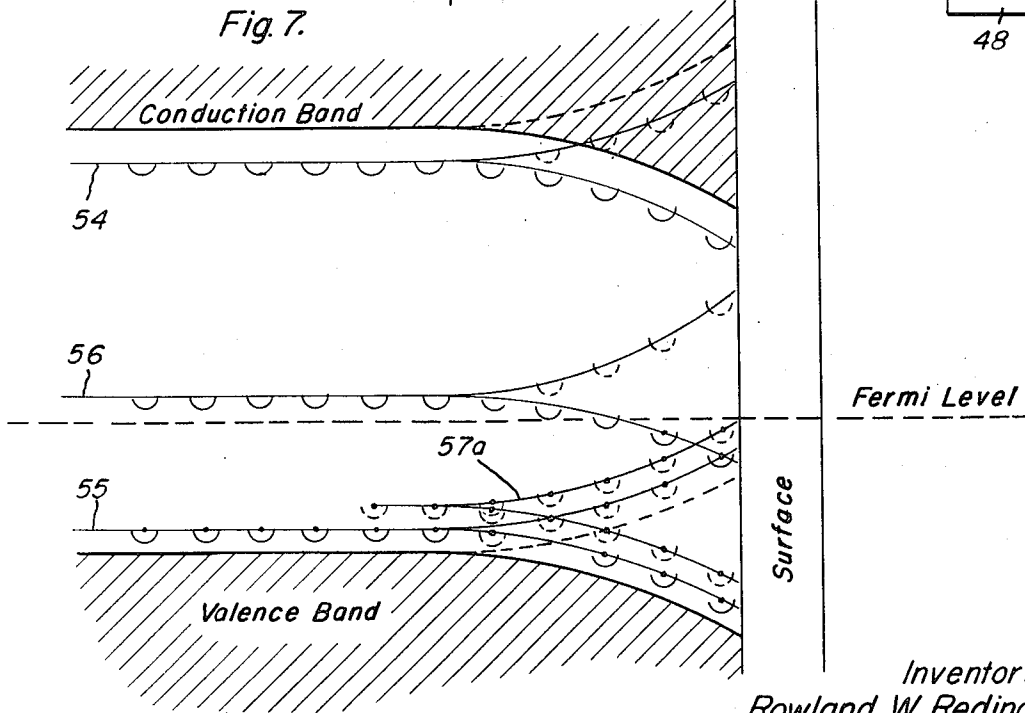
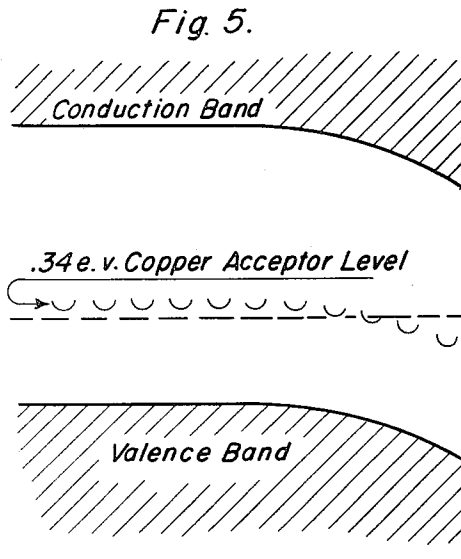
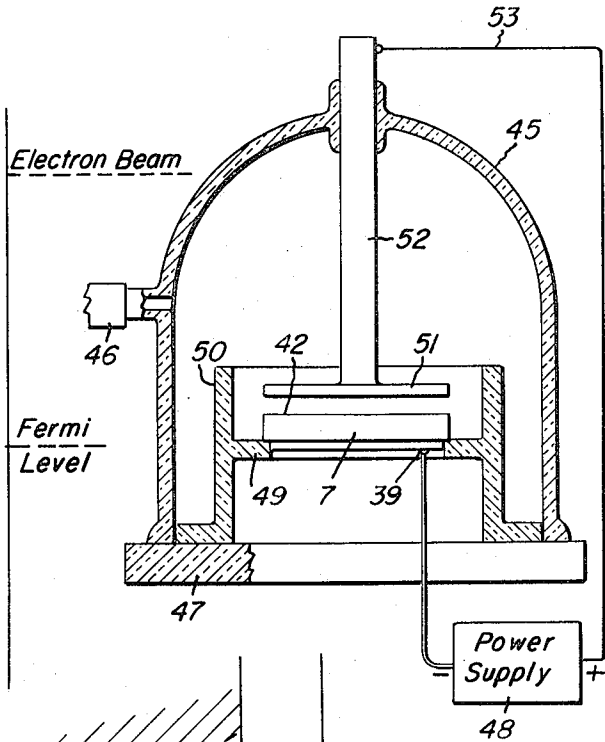
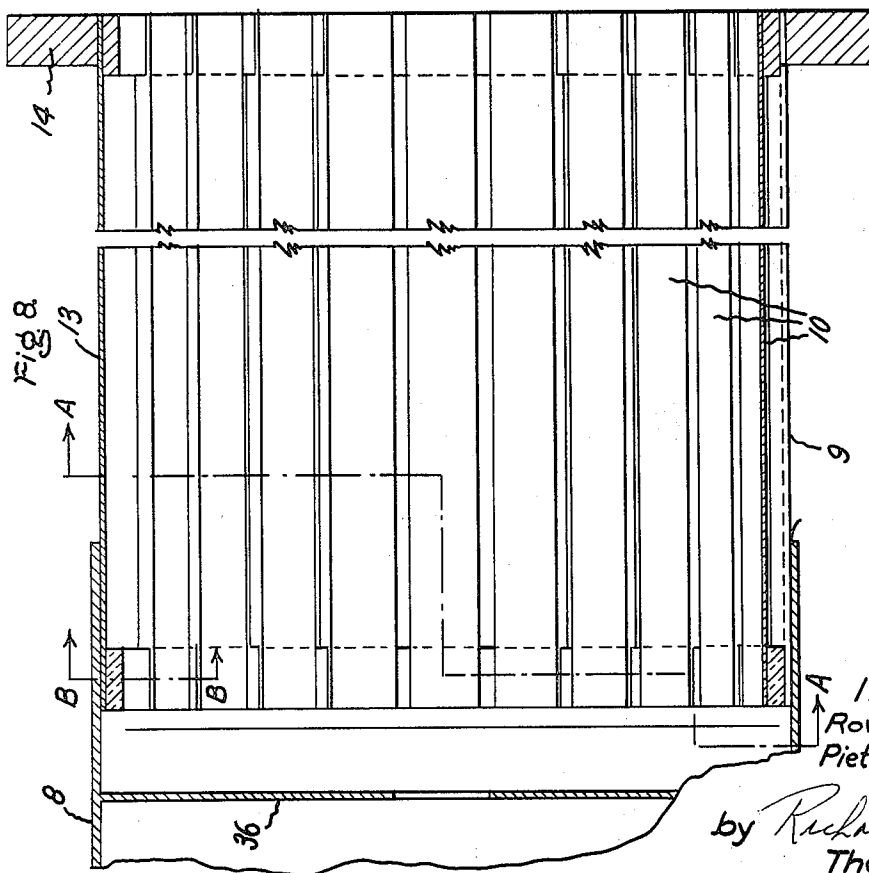
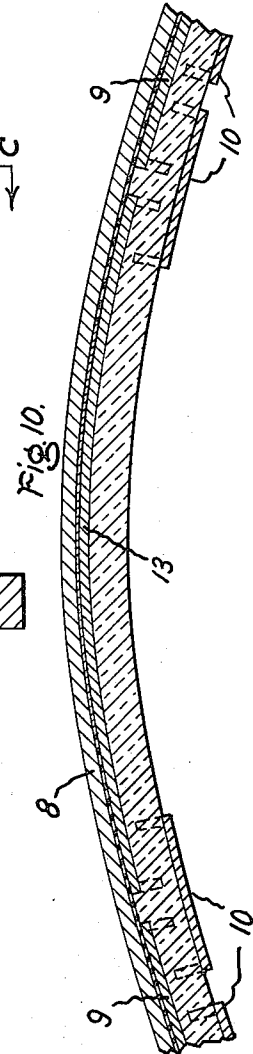
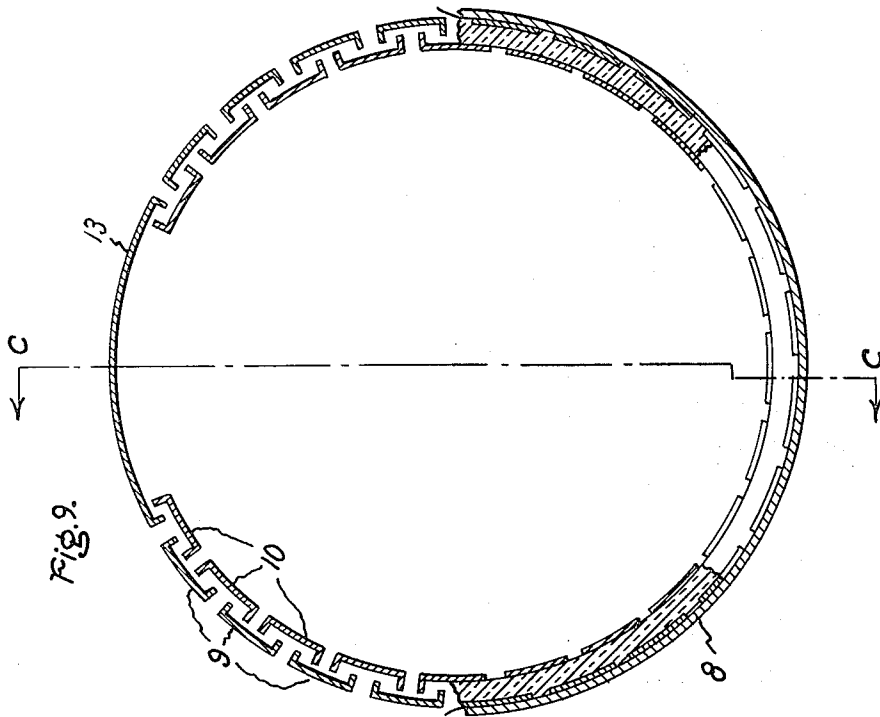


Fig. 6.



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PHOTOCONDUCTIVE CAMERA TUBE AND METHODS OF MANUFACTURE

This application is a division of our application Ser. No. 56,799, filed Sept. 19, 1960, now U.S. Pat. No. 3,781,955 entitled "Photoconductive Camera Tube and Methods of Manufacture."

This invention relates to photoconductive tubes employing semiconductor targets and to means, methods and materials for increasing the effectiveness thereof.

Certain semiconductor materials exhibit photoconductive properties, and therefore may be suitably employed for targets in television-type camera tubes. In a vidicon-type tube, for example, illumination is received on one side of a semiconductor target through a relatively positive transparent electrode contacting the semiconductor surface. The reception of illumination creates free charge carriers in the semiconductor at the points illuminated. Either an electron or hole may constitute a carrier which may pass through or part way through the target to establish a photocurrent. The photocurrent reduces the voltage drop across the photoconductive layer in the illuminated area to make the opposite target surface, exposed to a scanning electron beam, more positive. At the instant when the illuminated picture element is scanned by an electron beam, just enough electrons are deposited by the scanning beam to replace the negative charge removed in the preceding frame period by photoconduction. The instantaneous charge build-up, capacitively coupled to the transparent electrode, constitutes the picture signal output in the ordinary vidicon.

Semiconductor materials of both the intrinsic or extrinsic type may be utilized as a photoconductive material in a camera tube target, a main consideration being the illumination wave length which is to be detected. The "extrinsic" materials are so named because certain impurities are added to the semiconductor. Semiconductors of this type are frequently more useful for detecting illumination or radiation at longer wavelengths, for example, in the infrared region.

Infrared detectors of the camera tube type with extrinsic semiconductor targets are superior to the infrared detection schemes heretofore proposed. Prior systems of the point detector type utilize radiation from different points in the detected scene which are consecutively directed on to a single detector. In such a system radiation from each point of the observed scene is used only during optical passage over the detector cell. If 10,000 picture elements are to be imaged in this manner only one ten-thousandth of the radiation from the observed scene would be used. Alternatively, a number of point detectors may be employed in a linear array but the arrangement becomes mechanically and electrically complicated and the resultant picture signal lacks fidelity, while sensitivity is decreased since each point detector still consecutively covers a number of elements in the scene under observation. A television-type picture tube, on the other hand, is well suited to radiation imaging since an image is continuously received and stored at the target while the target representation is scanned at conventional television scanning rates.

The use of extrinsic semiconductor targets is convenient to detection in the infrared region because such impurities may be added which create energy levels in

the semiconductor which lie in close proximity to "energy bands" associated with the semiconductor. Thus an electron may be excited by infrared radiation from the semiconductor stable energy state or "valence band" to a shallow acceptor level provided by added impurity material, the acceptor energy level corresponding in its "energy" distance above the valence band to the energy of radiation in the infrared region. A conducting "hole" may thereby be freed in the semiconductor valence band, acting as the current carrier for the photoconductive target.

Unfortunately extrinsic semiconductor materials heretofore employed for photoconductive targets have exhibited a very severe defect due to an unexplained "non-imaging" stage wherein the detected scene blurs or "runs", resulting in an enormous decrease in resolution after a short period of operation. This non-imaging state is more or less permanent in that it reoccurs each time the apparatus is used to detect an image.

It is therefore an object of the present invention to provide a photoconductive camera tube employing extrinsic semiconductor target material which has an extended and practical operating life.

It is another object of this invention to provide an improved photoconductive camera tube target of increased extended sensitivity.

It is another object of this invention to provide a manufacturing method for photoconductive camera tube targets which will prevent the non-imaging state thereof.

It is another object of this invention to provide an improved photoconductive camera tube target sensitive to infrared radiation and an improved method of manufacturing the same.

We have discovered that the non-imaging state in extrinsic semiconductor target camera tube targets is due to lateral electric conduction along the scanned target surface. We believe this sidewise conduction is fostered by a potential barrier near this surface of the semiconductor and have likewise discovered that the potential barrier and the attendant sidewise conduction may be eliminated by providing a semiconductor surface layer which is at least as strongly the same polarity type as the interior of the semiconductor. For example, when the semiconductor is p-type, a surface layer is provided which is nearly, or preferably at least, as p-type as the rest of the semiconductor body.

In accordance with the process aspect of our invention, the surface layer polarity is altered by bombarding the semiconductor surface, intended to be oriented towards the tube's electron beam, with relatively high momentum submolecular particles. After such bombardment the non-imaging surface condition is substantially permanently eliminated and the target can be freely handled or even cleaned with appropriate solutions without harming its desirable polarity properties.

In accordance with another aspect of the present invention the extrinsic semiconductor target is manufactured by selecting an arsenic or antimony doped germanium semiconductor and then adding copper to the semiconductor, to the extent that the latter material nearly balances the initial n-type impurity in atomic percentage. Manufacturing is accomplished by coating a body of this n-type germanium with copper, heating the coated body so that this metal diffuses into the semiconductor while the arsenic or antimony diffuse

out at the edges, and removing the metal coating by appropriate means. The diffused semiconductor is then cut down in size except for one surface thereof, which will form a good electrical contact. The latter surface is used for both a reference electrode when bombarding the target with high momentum particles and also as the relatively transparent target connection on the side of the semiconductor target opposite the electron beam in a vidicon-type arrangement.

The subject matter which we regard as our 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 further objects and advantages 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 elevational view, partially in cross-section, of an infrared camera tube and target constructed in accordance with the present invention;

FIG. 2 is an enlarged elevational view, partially in cross-section, of the semiconductor target coated with metal, specifically copper;

FIG. 3 is an enlarged elevational view, partially broken away, of the target with the metal coating removed and with portions of the semiconductor material removed;

FIG. 4 is an isometric drawing of the semiconductor target placed in its retaining member;

FIG. 5 is an energy diagram for the untreated semiconductor target surface;

FIG. 6 is a cross-sectional view of apparatus for bombarding the semiconductor target with charged particles;

FIG. 7 is an energy diagram for the semiconductor target material including the various impurity levels both before and after surface treatment;

FIG. 8 is an enlarged cross-sectional view of the drift space electrode walls in the FIG. 1 apparatus taken along section C—C in FIG. 9;

FIG. 9 is a lateral cross-section of the aforementioned drift space and walls taken along section A—A in FIG. 8 and showing the interlocking drift space wall construction; and

FIG. 10 is an enlarged cross-section taken along section B—B in FIG. 8.

Referring to FIG. 1, showing by way of example an infrared sensitive camera tube embodying features of the present invention, a long cylindrical glass envelope 1 is closed at one end by means of a tube base 2 providing connections 3 for electron gun structure 4 and electron multiplier output device 5. The electron gun is a source of relatively low velocity electrons directed towards the opposite end of the glass envelope, the latter being enlarged in diameter at 6 to accommodate structure for a target 7. The glass envelope 1 houses conducting cylindrical drift space defining walls 8, 9 and 10, maintained at a potential to aid in focusing an electron beam 11 which is produced by the electron gun 4 and focused generally along the axis of said drift space defining walls 8, 9 and 10 by a focusing solenoid 12. Cylindrical drift space wall 8, conveniently formed of copper or copper-plated stainless steel and extending approximately one-half of the length of the focusing solenoid from the electron gun, is joined at the middle of the tube to a double walled drift space section com-

prising walls 9 and 10. Walls 9 and 10, which accomplish a heat limiting function, extend for approximately the remainder of the focusing solenoid length to enlarged envelope portion 6. Termed a "bird cage", this latter section is employed primarily in connection with infrared pickup and is illustrated in greater detail in FIGS. 8, 9 and 10.

Included in the bird cage are an outer cylindrical wall 9 and an inner cylindrical wall 10, both of which are longitudinally slotted in the direction of the tube axis to suppress heat generating eddy currents induced by the magnetic circuits surrounding the tube. The slots in inner wall 10 are displaced from juxtaposition with the slots in wall 9 and the edges defining the slots in each wall are bent towards an inter-slot portion of the other cylindrical wall thereby providing a circuitous and therefore effectively shielded path between outside radiation and the drift space. Moreover, the outside of the inside wall and the inside of the outside wall are blackened, for example, with copper oxide material for further absorbing any possible radiation passing therethrough.

Outer wall 9 is matingly received by wall 8, the latter being arranged to overlap wall 9 for a short distance to insure outside radiation masking at their junction. All sections of walls 9 and 10, however, are electrically insulated from wall 8 at the junction, except for a single electric connecting section 13 of wall 9, conveniently located at the top of the tube. The electrical connection can be formed by soldering walls 8 and 9 together at this point.

The various sections forming walls 9 and 10 are all insulated from each other except at the target end of the tube where they are joined electrically and mechanically to a copper flange 14 to which further electric connection is made by means of terminal 15 in FIG. 1, maintained at the tube's drift space potential. Features of the bird cage are described and claimed in our application entitled "Electron Optics for Infrared Camera Tubes", Ser. No. 56,798, filed Sept. 9, 1960, now U.S. Pat. No. 3,185,891, issued May 25, 1965 and assigned to the assignee of the present invention.

Annular decelerating ring 16 in FIG. 1, connected to the appropriate decelerating voltage by means of terminal 17, is joined to flange 14 with sapphire spacing members 18, while additional sapphire members 19 joined to the remaining side of ring electrode 16 are further secured to annular member 20, conveniently formed of copper. Annular member 20 acts to support the target 7 and to conduct heat away from the forward or target end of the tube including especially target 7. In the infrared radiation region it is frequently desirable to operate the tube target at temperatures near the temperature of liquid nitrogen or below in order to increase the target's dark current resistivity and therefore sensitivity. To this end, cold finger 21, which may also be formed of copper, is joined to annular member 20 and passes through a seal in the glass envelope 1 to refrigeration means 22. The refrigeration means 22 may be any convenient apparatus for securing to tube target 7, an appropriate operating temperature, e.g., the temperature of nitrogen at its boiling point. Refrigeration means 22 may consist of a double Dewar flask containing liquid nitrogen or some other low temperature liquid which may be readily replenished during operation by means not shown. Alternatively, any convenient refrigeration device reaching these temperatures may be

utilized, and if desired, a refrigerant can be pumped inside cold finger 21 and around inside member 20.

The tube is directed so that detected radiation falls upon the front of target 7 through window 23, conveniently formed of sapphire for targets which are not sensitive at wavelengths longer than 6 microns, and an optical system (not shown) in front of the tube. The radiation then passes through substantially transparent electrode 38 on the front surface of target 7.

Target 7, formed of an extrinsic semiconductor material, is positioned within annular member 20 by means of a flanged retaining member 24, shown in greater detail in FIG. 4. The semiconductor target 7 may take the form of relatively thin and desirably monocrystalline wafer of appropriately doped germanium or silicon, soldered around its edge 25 to retaining member 24 with indium solder. Retaining member 24 has a cylindrical section 26 with a smaller outside diameter than the inside diameter of member 20 and is secured to member 20 by a radial flange at the end of the cylinder remote from target 7. The radial flange extends over the forward side of annular member 20 so that it may be joined thereto with machine screws 27. These machine screws are tapped into annular member 20 but are electrically insulated from retaining member 24 by sapphire spacers 28 positioned between annular member 20 and retaining member 24, as well as by insulating washers 29, which may be formed of the material known as teflon, disposed between the screw heads and member 24. Holes 30 in the retaining member flange, which receive the screws 27, are large enough in diameter so that no electrical connection is made between the flange and the screws.

Conventional deflection coils 31 surround drift space walls 9 and 10, on the inside of focusing solenoid 12 while maze coils 32 and 33 are arranged in that order from the electron gun end of the tube to the deflection coils and also inside focusing solenoid 12. Apertured masks or partitions 34, 35 and 36 are joined to the inside surface of the drift space defining wall 8 at selected intervals therealong, these apertures providing a path for electron beam 11. These maze coils and masks, like the aforementioned bird cage are employed primarily when the tube is operated in the infrared detection region.

A first mask 34, at the electron gun end of the tube has an aperture desirably centrally spaced to receive easily the undeflected electron beam, while partition 36, near the middle of the tube, also has an aperture conveniently centrally located so that the electron beam will exit near the center of the envelope where it is influenced in orthogonal directions by deflection coils 31. However, an intermediate apertured partition 35 has its aperture 37 radially displaced with respect to the central axis of the tube. Maze coil 32 is arranged to laterally deflect the relatively slow electron beam through aperture 37. Maze coil 33 is then reversed in electrical polarity to deflect the electron beam back to its central location for passage through the aperture in partition 36. The inside surface of drift space wall 8 is conveniently blackened with copper oxide material as are both sides of the partitions. In the above manner direct heat radiation caused by a heated cathode in electron gun 4, being substantially straight line, is prevented from reaching the forward or target end of the tube 6. The maze consisting of partitions 33, 34 and 35 blocks the heat radiation although the electron beam is

conducted through the maze with maze coils 32 and 33. The heat shielding of the target and the forward end of the tube contributed by the maze and slotted walls 9 and 10 considerably reduces its ambient heat and therefore increases the quality of the picture produced by the target. It is desirable to locate the aperture centrally in outside partitions 34 and 36 while offsetting aperture 37 in partition 35, the electron beam being therefore most easily received from the electron gun and transmitted on to the deflection region for substantially perpendicular presentation to the target. Maze coils 32 and 33 are similar to one another and are connected to relatively constant but equal and opposite sources of voltage (not shown) to provide the constant deflection pattern through the maze of partitions. The return electron beam, passing from target 7 back to electron multiplier 5, will be similarly conducted through the maze in a reverse direction by the maze coils. Features of the maze are also described and claimed in our aforementioned U.S. Pat. No. 3,185,891, filed concurrently herewith.

The front end of target 7, or the side oriented toward window 23, is provided in a manner to be described with a relatively conducting although substantially transparent, "coating" or "electrode" 38, this coating being analagous to the transparent electrode in the vidicon-type tube. A soldered connection 39 may be made conveniently to this coating and is coupled to terminal 40, maintained by means not shown at a voltage between approximately zero and 60 volts positive. The voltages at terminals 15, 17 and 40 are arranged, inter alia, in combined effect for causing electron beam 11 to normally return to electron multiplier 5 in the absence of photoconduction through target 7 of the specific embodiment.

The tube together with its focusing solenoid may have a construction similar to but having an overall length approximately twice that of a conventional image orthicon tube, the target being placed at an electron beam focal point twice the usual distance from the electron gun. The deflection coils in the tube may then be the same as in such conventional image orthicon, but with added maze coils of similar construction occupying an approximately equal length between such deflection coils and the electron gun.

In general operation, the camera tube of FIG. 1 functions to receive radiation on target 7 through sapphire window 23 after passing through an optical system (not shown), this radiation pattern appearing as the variations in the scanned output signal of electron multiplier 5. Electron gun 4 produces a relatively slow stream of electrons deflected into a somewhat spiral pattern and focused at the target 7 back surface by focusing solenoid 12 cooperating with drift space defining walls 8, 9 and 10, the latter being maintained at substantially the same voltage as the electron beam. Maze coils 32 and 33 deflect the electron beam through the apertures in partitions 34, 35 and 36 and thence to the area of the drift space circumscribed by drift space walls 9 and 10 wherein the electron beam is deflected into an appropriate television-type raster by deflection coils 31. The deflection field of these coils is arranged such that the electron beam scans the "back" side of target 7 depositing or attempting to deposit electrons thereon, while the transparent electrode 38 is maintained at positive voltage relatively to the electron beam, being on the order of a plus 50 volts.

A quantum of radiant energy, for example infrared energy, passing through transparent electrode 38 into a p-type target 7 excites a free hole which becomes a current carrier at the point where the radiation strikes. The hole theoretically passes directly through the target 7 to the electron beam side neutralizing an electron charge where it passes through. When the picture element is scanned, just enough electrons are deposited by the scanning beams to replace the negative charge removed in the preceding frame by the said hole neutralizing an electron, that is by the photoconduction.

If no substantial amount of charge is replaced by the scanning beam at the instant it is directed to the point under consideration, it will substantially fully return by essentially the same path through the tube to the electron multiplier 5. The signal output is then a function of reduction in returned beam electrons caused by illuminated target elements.

This electron multiplier output arrangement is desirably included for increasing the sensitivity of the tube although it will be apparent to those skilled in the art that the output signal could be coupled alternatively from the transparent electrode 38, utilizing an appropriate power supply dropping impedance.

The target 7 employed in the FIG. 1 embodiment may be conveniently approximately one inch in diameter and from 10 to 40 mils in thickness. The 40 mil thickness will result in an infrared resolution of approximately 100 lines per centimeter while the 10 mil thickness will result in resolution giving approximately 400 lines per centimeter.

In accordance with a feature of the invention the target 7 is formed 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 to it 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. This action is more fully described subsequently.

The resulting compensated material is then effectively of the p-type having a usable acceptor level at approximately 0.34 electron volts above the germanium "valence band" shown in the FIG. 4 energy diagram, and described in connection therewith. Then when a quantum of radiation strikes the semiconductor, an electron may be raised thereby from the top of the valence band to the 0.34 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. A conducting hole is then left in the valence band. 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, pro-

vides 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.

The extrinsic type, that is the doped or impurity containing type, semiconductor has further advantages as a target material; targets of such material may be made thicker than would an intrinsic or non-doped semiconductor material. The thickness of any photoconductive camera tube target is normally limited either by the requirement that the radiation be approximately homogeneously absorbed or that the thickness be less than the range of the photogenerated charge carriers. The limits are very short for many materials and thus the thickness is often limited in the case of conventional intrinsic semiconductors to thicknesses on the order of one radiation length. However, with an extrinsic semiconductor, quanta of radiation absorbed as they pass through the target may be regulated by the effective amount of impurity added in the material. Therefore an extrinsic photoconductor target may be thicker than an intrinsic photoconductor. The added thickness decreases the target's capacitance from one surface to the other making its response quicker, and increases the allowable overall size and effective sensitivity of the target by as much as 10 times over what an intrinsic target sensitivity would be for the same allowable amount of capacitance lag or "stickiness".

The semiconductor target 7 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 blank is illustrated in FIG. 2 including a copper coating 41. 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 semiconductor blank, as conveniently determined for example by Hall effect measurements. It is desired to add enough copper impurity by the heat-diffusion process to balance off the n-type impurity with approximately 95 percent 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. While the copper diffuses into the semiconductor, the n-type impurity diffuses out somewhat at the surface. Since arsenic and antimony have appreciably smaller diffusion constants than copper, only a thin layer near the surface is depleted of the n-type impurity.

After the coated semiconductor blank is heated for a day or two, the copper plating is peeled off or removed by hydrofluoric acid and the back side of the wafer or side which is to be oriented towards the electron beam is surface-etched or undercut in some other

manner to remove a layer where the n-type impurity has diffused out somewhat. Such undercut area is numbered 42 in FIG. 3. The undercutting may be conveniently accomplished with a solution known as CP-4 consisting of hydrofluoric acid and nitric acid. The edges 43 are similarly undercut and an edge portion of the back side of the semiconductor blank which is to be oriented toward the front of the tube is similarly removed as at 44, leaving only area 38 remaining where the arsenic or antimony has diffused out somewhat, leaving a copper heavy contact area. This area serves as the target's transparent electrode. A lead may be soldered to the electrode as at 39.

Unfortunately, a tube and extrinsic semiconductor target even constructed in the above manner ordinarily operates successfully for short periods of time only, after which a blurring effect occurs. We attribute this short period of satisfactory operation to the presence of surface currents on the back side of the target or side oriented towards the electron beam. It is further postulated that the surface conduction is in turn caused by a barrier potential near the surface of the semiconductor.

The theory connected with the present invention will be described with reference to the energy chart illustrated in FIG. 5, showing energy levels for electrons in a germanium semiconductor and including its back surface layer at the right. 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 non-excited semiconductor. The conduction band on the other hand is a group of normally empty levels to which electrons must be excited in an intrinsic 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 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 the 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 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. 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 at the surface thereof; and it is possible that 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. We have discovered that this surface band distortion is the cause of the non-imaging state encountered with extrinsic semiconductor target tubes.

The bending down of the valence bands 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 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, and these holes consequently never reach the surface scanned by the electron beam. 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 we have further discovered that this non-imaging state is prevented or eliminated by providing a target back surface layer near to being the same polarity type as the interior of the semiconductor, as distinguished from the surface band distortion of the usual semiconductor which may be characterized as indicating a surface layer quite a bit weaker in polarity than the interior. When the semiconductor is made more nearly the same polarity, the energy bands tend to straighten out or bend the other way, reducing or eliminating the potential hill. We have additionally discovered that such surface layer may be provided by subjecting the target surface to bombardment with relatively high momentum particles e.g., by bombarding the surface layer of a p-type

semiconductor target with relatively high momentum submolecular particles such as noble gas ions.

An apparatus for accomplishing this bombardment is illustrated in FIG. 6 wherein a glass bell 45 is supplied with noble gas, for example, helium gas at a pressure of a few mm. Hg., through tube 46. Bell 45 is supported upon a glass base 47. The target blank 7 having a contact 39 soldered onto the copper diffused side thereof is electrically connected to the negative side of d-c power supply 48, the semiconductor target blank 7 being supported in the bell 45 on an annular quartz ledge 49, and surrounded by a quartz supporting cylinder 50 extending upwardly beyond ledge 49. A flat horizontal electrode 51 is aligned in spaced relation to target blank 7 and is secured to an electrode post 52 passing through the top of the bell and connected by means of lead 53 to the positive end of power supply 48. The power supply is adjusted to deliver voltage between 250 and 600 volts d-c, which will cause a discharge of helium ions in the bell, away from electrode 51 towards surface 52 of target blank 7. The device is spaced and adjusted to produce a current density in the range of 1-5 milliamps per square centimeter. The discharge is maintained for approximately 15 minutes.

The resulting semiconductor surface layer is rendered at least as p-type as the semiconductor interior by this treatment and the surface layer is quite stable despite handling, exposure to oxygen for short periods, rinsing in common solvents such as water, acetone, coating with polystyrene coatings, etc. The treatment is effective in permanently preventing the non-imaging state in targets thus treated. Tubes with such targets have been operated for extended periods of time without ill effects.

The bombardment is effective in raising the right hand energy band boundaries as illustrated by the dashed extensions in FIG. 7, indicating an upward bending of the energy bands. It is understood that some improvement would be experienced in raising the bands to a lesser degree, for example in producing a level or nearly level condition. The latter may be accomplished by bombarding for a much shorter period of time. In the present example the bands are raised to bend upwardly and the surface layer in the vicinity of the former space charge or potential hill is rendered at least as p-type as the interior of the semiconductor. Thus the highly desirable condition of no barrier is produced.

The energy distribution mechanism for establishing a surface layer polarity so that the non-imaging state does not occur is more fully illustrated in FIG. 7 showing an energy diagram similar to the one shown in FIG. 5 and specific to copper doping, for illustrative purposes. Energy states indicated generally at 54 in this figure illustrate the donor energy states of an n-type impurity, i.e., the arsenic or antimony originally found in the semiconductor of the specific embodiment. In the original n-type semiconductor these energy states 54 would contain electrons, easily excitable the short distance to energy levels in the conduction band for supporting n-type conduction therein. However, in accordance with one aspect of the present invention, the semiconductor material has been changed to effectively p-type, by the addition of copper. The energy states then produced by the copper, which is added in quantity sufficient to obtain an atomic percentage of copper approximately equal to the original n-type im-

purity, produces energy states at 55 and 56 in FIG. 7. These energy states are at 0.04 volt and 0.34 volt levels, respectively, above the valence band. Electrons formerly contained in energy states 54 drop, for the most part, to energy states 55 of the acceptor metal, filling those states at points interior to the semiconductor. However, the additional energy states 56 of the copper metal are left vacant, for the most part, and represent a level above the valence band to which electrons may be conveniently raised by the energy of approximately 4 micron infrared radiation. Electrons deeper in valence band, raised to energy states 56, will correspond in energy change to infrared radiation striking the semiconductor at slightly shorter infrared radiation wavelengths. A good response is therefore secured by such a semiconductor target in the range between 1½ and 4½ microns, a range which is not highly absorbed by the atmosphere and which may be therefore used conveniently for infrared detection, i.e., in viewing of objects giving off heat.

The presence of the differential combination of donor and acceptor levels described above tends to produce the general energy level configuration relative to the Fermi level shown in the FIG. 7 chart; that is, the valence band will be closer to the Fermi level than the conduction band, particularly at points interior to the semiconductor, indicating an effectively p-type material with energy states 56 acting as an empty acceptor level slightly above the Fermi level. However, in the surface layer at the right where the various levels bend downward, the level of states 56 falls below the Fermi level and states 56 will be filled in this region. Conducting positive holes travelling towards the right surface in the valence band will be prevented from reaching the surface due to the retarding field indicated by this downward curvature of the valence band and will pile up immediately to the left thereof, forming a dipole layer near the surface. This will result in near surface conduction of holes producing the undesirable non-imaging state.

The dashed energy band and energy state levels in the FIG. 7 chart on the other hand represent the energy picture after the bombardment with relatively high momentum submolecular particles. It is positioned that such a bombardment penetrates the semiconductor to approximately the area of the aforementioned space charge or potential hill, knocking semiconductor atoms out of their proper lattice sites and resulting in the addition to this region of shallow energy states numbered 57 in the diagram. These energy states receive electrons from the right hand portion of energy states 56 and all energy states rise as indicated by the dashed lines whereby again empty energy states occur above the Fermi level and filled ones below. Induced shallow energy states 57, caused by the bombardment, rise to position 57a. It is seen that in this area of induced states 57a, the semiconductor has become at least as strongly the same polarity, e.g., as strongly p-type, as the interior of the semiconductor since the valence band is in fact closer to the Fermi level near the surface. 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. It has been found that creating this surface layer, more nearly the same polarity type as the semiconductor interior, eliminates cross-conduction and therefore prevents

running or blurring of the image. The response of the tube is therefore drastically improved.

While the FIG. 7 diagrams show the energy bands and levels bent upwardly as a result of the bombardment, it is again understood the levels need only be relatively straightened to secure a surface layer as strongly the same polarity type as the interior. Moreover, some improvement may be had by merely raising the levels somewhat above what they would be in the untreated state, i.e., by making the surface more strongly of the same polarity to some degree, but weaker than the interior. The bombardment time may be shortened to produce these somewhat less advantageous results.

The semiconductor surface adapted for orientation in the direction of the tube's electron beam has been described in the specific example as being bombarded with noble gas ions for altering its surface polarity strength. However, other submolecular particles may alternatively be employed such as protons, neutrons or even electrons if the latter are accelerated sufficiently to reach momentums similar to the ions.

Although in the illustrative embodiment the target 7 has been described as a p-type semiconductor, e.g., germanium appropriately doped with copper, and although such a construction has particular advantages especially in the infrared region, it is apparent that other extrinsic semiconductor materials may be utilized. For example, silicon may be similarly employed as the semiconductor. In the specific example a copper acceptor metal dope is added to the germanium, but other dopings resulting in appropriate conductivity characteristics may be used, depending upon the frequency spectrum responses desired and the basic semiconductor involved. Other dopings suitable for germanium are certain elements in addition to copper, such as zinc, platinum, gold and silver and also the transition metal elements, iron, cobalt, nickel and manganese. Appropriate dopings for use with a silicon semiconductor material, 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. With the target surface layer provided in accordance with the present invention nearly all known dopings of silicon and germanium, for example, become potential camera tube materials.

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

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

1. In a camera tube having a photoconductive target, means for providing an electron beam for scanning over said target, and coupling means to said target for providing a target current, the target comprising an extrinsic semiconductor of predetermined effective polarity type at regions internal thereto and having a surface adjacent region on the side toward said electron scanning beam which is at least as strongly the same polarity type as the interior of said semiconductor.

2. The apparatus as recited in claim 1 wherein the said polarity type is p-type.

3. The apparatus as recited in claim 1 wherein said semiconductor is copper-doped germanium.

4. The apparatus as recited in claim 1 further including means for refrigerating said semiconductor to a temperature at least near the temperature of liquid nitrogen.

5. In a camera tube having a photoconductive target, means for generating an electron beam for scanning said target, and means for coupling a source of voltage to said target, the target comprising an extrinsic semiconductor wafer of a predetermined effective polarity type at regions internal to said wafer, said wafer being provided with a surface which is at least as strongly the same polarity type as the interior of said wafer, said tube providing a drift space between said means for generating an electron beam and said target, and an electron multiplier for receiving electrons returning through said drift space from the direction of said target and for driving an output signal therefrom.

6. An infrared photoconductive camera tube comprising a photoconductive target, means for providing an electron beam for scanning said target, means for coupling a voltage to said target, said target comprising an extrinsic semiconductor wafer effectively of p-type formed from copper-doped germanium, said wafer being provided with a surface in the direction of said electron beam which is at least as strongly p-type as the interior of said wafer, and means for refrigerating said wafer to a temperature at least near the temperature of liquid nitrogen to raise the dark current resistivity of said target, whereby said camera tube is responsive to infrared radiation.

7. In a camera tube having a photoconductive target, means for generating an electron beam for scanning said target, and means for coupling a voltage to said target, said target comprising an extrinsic semiconductor wafer of a predetermined effective polarity type at regions internal to said wafer, said wafer having a surface potential in a surface-adjacent region at the electron beam side characterized by a minimized dipole barrier such that the passage of currents through said barrier between said electron beam side and said means for coupling a voltage to said target is not prevented.

8. An electron discharge device target comprising a relatively thin flat body of semiconductor material exposed on one side thereof to the discharge of electrons in said device, said semiconductor characterized as being a predetermined effective polarity type and provided with a surface adjacent region on the said side toward said discharge of electrons which is at least nearly as strongly of the same polarity type as the interior of said semiconductor, for decreasing cross currents near the surface thereof.

9. A radiant energy discharge device target electrode including a wafer of copper-doped germanium semiconductor which also includes donor doping material wherein the atomic percentage of copper present is near the atomic percentage of donor material present so that the said semiconductor is effectively characterized as p-type, a given energy level of added copper energy states accepting electrons from a similar number of said donor states leaving at least a second copper energy level to which electrons may be excited, said donor material doping being selected from the group consisting of arsenic and antimony a surface-adjacent

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region of said wafer on one side of said target being at least as strongly p-type as said wafer.

10. The apparatus as recited in claim 9 further including means to refrigerate said wafer to at least near the temperature of liquid nitrogen.

11. A radiant energy discharge device target comprising a thin body of semiconductor material which is characterized as being effectively p-type semiconductor, said body of semiconductor being provided with a surface adjacent region which is p-type to at least the same degree and having a surface potential which presents a reduced barrier to p-type carriers, whereby electrical conduction transversely through said body is not impeded by a barrier potential, but conduction along said surface is impeded.

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12. A camera tube target comprising a semiconductor body characterized as being a predetermined polarity type having a first side for positioning towards a tube electron beam and a second side for receiving the radiation to be detected, a surface-adjacent region of said first side being at least as strongly the same polarity type as the interior of said body, and a diffused metal contact area on said second side through which detected radiation passes.

13. The target as recited in claim 12 wherein said metal is copper.

14. The target of claim 13 wherein said semiconductor contains copper impurity.

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