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PROCESS FOR PRODUCING A CESIUM COATED GALLIUM
ARSENIDE PHOTOCATHODE
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3,673,011

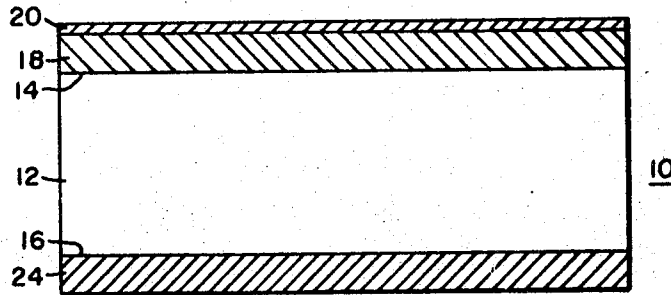


FIG. 1.

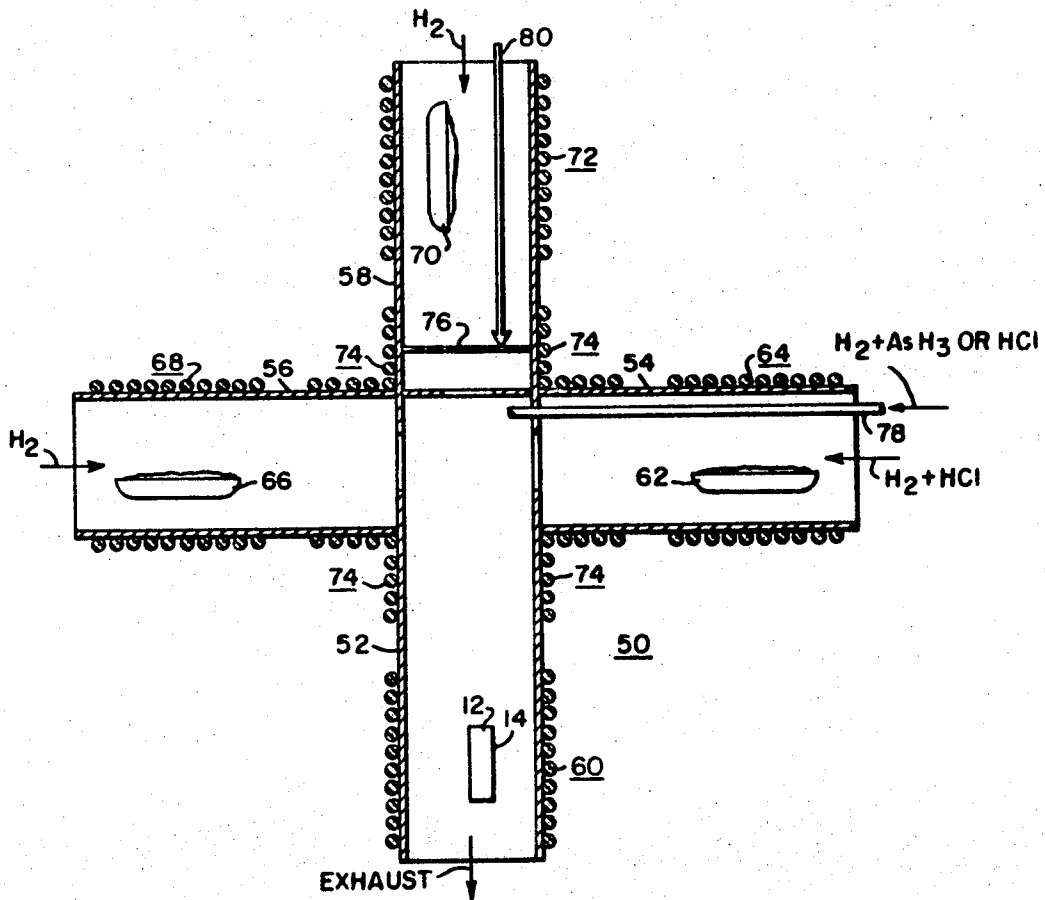


FIG. 2.

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PROCESS FOR PRODUCING A CESIUM COATED GALLIUM ARSENIDE PHOTOCATHODE

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Original application Mar. 7, 1969, Ser. No. 805,130.

Divided and this application Nov. 2, 1970, Ser. No. 86,202

Int. Cl. H011 7/34, 15/06

U.S. Cl. 148-175

4 Claims

DRAWINGS

In order to more fully understand the teachings of this invention, reference should be had to the drawings in which:

FIG. 1 is a cross-sectional view of a photocathode made in accordance with the teachings of this invention; and

FIG. 2 is a view, partly in cross-section, of apparatus suitable for making the photocathode of FIG. 1.

DESCRIPTION OF THE INVENTION

With reference to FIG. 1 there is shown a photocathode 10 comprised of a body 12 of semiconductor material prepared by suitable means, such for example, as by polishing and lapping to parallelism two major opposed surfaces 14 and 16.

Since gallium arsenide is to be grown on the body 12, and since it is desirable that it be monocrystalline, the body 12 must have a crystalline structure the same as, or varying only slightly from, the crystalline structure of gallium arsenide. Therefore, the material comprising the body 12 is preferably gallium arsenide or germanium and has p-type semiconductivity.

The body 12 has a thickness, after preparation, of from 8 to 20 mils, the preferred thickness being 10 mils. The resistivity of the body is from 0.001 to 0.5 ohm-centimeter.

A monocrystalline layer 18 of gallium arsenide is disposed on the surface 14 by any suitable means known to those skilled in the art such, for example, as by the vapor phase epitaxial deposition process. The layer 18 is from 1 micron to 5 microns in thickness and has a resistivity of from 0.001 to 0.5 ohm-centimeter. Preferably the layer 18 is 1 micron in thickness and has p-type semiconductivity.

A monatomic layer 20 of cesium is deposited by a vapor phase deposition technique on the layer 18 of gallium arsenide. In order to obtain the most efficient photocathode 10, the surface of the layer 18 upon which the cesium is deposited must be clean.

To collect the electrons released by the impingement of a radiant energy source on the layer 20 of cesium, a layer 24 of an electrical contact metal selected from the group of metals consisting of indium, gallium, zinc and base alloys thereof, is deposited preferably on the entire surface 16 of the body 12. It is preferred that the metal of the layer 24 be indium. The thickness of the layer 24 is from 200 to 20,000 angstrom units with 5000 angstrom units being preferred.

Referring now to FIG. 2, there is shown apparatus 50 suitable for making the photocathode 10. The apparatus 50 comprises four tubular furnace portions 52, 54, 56 and 58 which are joined together to form a cruciform configuration for the apparatus 50.

The prepared body 12 is disposed on the tubular furnace portion 52. The body 12 is heated to an elevated temperature by resistance heating coil 60 disposed about the furnace portion.

A source 62 of gallium metal is disposed within the tubular furnace portion 54 and is heated by resistance heating coil 64 disposed about the outer periphery of the furnace portion 54.

A source 66 of a suitable impurity such, for example as zinc, manganese, and the like, which will impart the desirable electrical resistivity properties into the gallium arsenide to be grown, is disposed in the tubular furnace portion 56. The source 66 is heated by a resistance heating coil 68 disposed about the outer peripheral portion of the furnace portion 56. A diaphragm 76 seals the source 70 of cesium within the tubular furnace portion 58.

ABSTRACT OF THE DISCLOSURE

A photocathode is comprised of a monocrystalline layer of gallium arsenide grown on either a germanium or a gallium arsenide substrate. A monatomic layer of cesium is disposed on the monocrystalline layer. An electric contact affixed to the photocathode provides a means for connecting it electrically into electrical circuits. The gallium arsenide and the cesium are deposited on the substrate in essentially one continuous growth process.

CROSS REFERENCE TO RELATED APPLICATIONS

This patent application is a division of my copending patent application, Ser. No. 805,130, filed on Mar. 7, 1969, now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a method of producing gallium arsenide-cesium photocathodes.

(2) Description of the prior art

To provide a photocathode of gallium arsenide-cesium construction which will have a high efficiency, it is necessary that the surface of the gallium arsenide, upon which the cesium is to be deposited, be extraordinarily clean.

Heretofore, there are two conventional techniques employed to prepare a surface of gallium arsenide for deposition of cesium thereon. One method is to cleave a body of gallium arsenide in half in a vacuum and, without exposing it to the atmosphere, deposit cesium on the cleaved surface. Another method of obtaining the extraordinarily clean surface of the gallium arsenide requires the utilization of extremely involved cleaning techniques of etching, rinsing, drying and maintaining the surface in an inert atmosphere.

An object of this invention is to provide an improved structure for a gallium arsenide-cesium photocathode.

Another object of this invention is to provide a process for making a gallium arsenide-cesium photocathode having an improved structure.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

SUMMARY OF THE INVENTION

In accordance with the teachings of this invention there is provided a process for manufacturing a photocathode comprising a body of semiconductor material, the semiconductor material being a material selected from the group consisting of gallium arsenide and germanium, the body having at least two major opposed surfaces substantially parallel to each other; a layer of monocrystalline gallium arsenide disposed on one of the at least two major opposed surfaces; a monatomic layer of cesium disposed on the layer of monocrystalline gallium arsenide; and a layer of electrically conductive metal disposed on the other of the at least two opposed major surfaces.

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A source 70 of cesium is disposed within the tubular furnace portion 58 and is heated by a resistance heating coil 72 disposed about the outer peripheral portion of the furnace portion 58.

The center portion of the cruciform shaped apparatus 50 is heated by a separate resistance coil 74 disposed about the ends of the furnace portions 52, 54, 56 and 58 where they are joined together.

Preferably, the surface 14 of the body 12 is cleaned in situ in the tubular furnace portion 52. The body 12 is heated to a temperature of from 650° C. to 950° C. by the coil 60. A stream of hydrogen chloride, diluted in hydrogen, is caused to flow through a bypass tube 78 in the furnace portion 54, through the center portion of the apparatus 50, into the furnace portion 52 and caused to flow over, and about the surface 14 of the body 12. The hydrogen chloride cleans the surface 14 by chemical etching.

To prevent the hydrogen chloride from entering the tubular furnace portion 56, enough hydrogen is caused to flow through the portion 56 into the center portion of the apparatus 50 where it mixes with the hydrogen chloride and its diluent gas hydrogen and then flows in a gaseous mixture with them into the portion 52.

Alternately, the source 62 may be withdrawn from the furnace portion 54 and the stream of hydrogen chloride, diluted by the hydrogen, is passed directly through the portion 54. After cleaning the surface 14 is completed and the flow of hydrogen chloride is stopped, the source 62 is replaced in the portion 54.

Upon completion of the cleaning of the surface 14, the flow of hydrogen chloride is stopped. The temperature of the body 12 is adjusted to a range of from 650° C. to 850° C. with 750° C.±2° C. being preferred. The source 62 of gallium is heated to a temperature of 825° C.±1° C. The source 66 of the impurity material to dope the epitaxial growth of gallium arsenide is heated to its predetermined temperature range at the same time. When the source 66 is elemental zinc, a temperature of 450° C.±5° C. is preferred. The center portion of the apparatus 50 is heated to 825° C.±2° C. by the coil 74.

When the sources 62 and 66, the body 12, and the center portion of the apparatus 50 have reached the preferred respective temperature ranges, simultaneous gas flows are caused to occur in the tubular furnace portions 54 and 56 as well as through the bypass tube 78. Arsine diluted in hydrogen, flows through the bypass tube 78 into the center portion of the apparatus 50. Hydrogen chloride gas, diluted in hydrogen, is caused to flow over the source 62. The gallium is vaporized into the stream of hydrogen chloride where they react with each other chemically to produce gallium chloride, which is caused to flow into the center portion of the apparatus 50 by the hydrogen acting as a carrier gas. The gallium chloride chemically reacts with the arsine in the center portion to produce at least the gallium arsenide in vapor form to be transported over, and about, the surface 14 of the body 12. Zinc is vaporized into the hydrogen passing over the source 66 and acting as a carrier gas carries the vaporized zinc into the center portion where it is mixed with the vaporized gallium arsenide.

The mixture of vaporized gallium arsenide and vaporized zinc is transported by the carrier gas over, and about the surface 14 of the body 12 where zinc doped gallium arsenide of a predetermined resistivity is grown on the surface 14. When the predetermined thickness of layer 18 has been grown, the flow of arsine and hydrogen chloride is stopped, the sources 62 and 66 are cooled, and the flows of hydrogen gas are continued.

The temperature of the body 12 is adjusted to a range of from 100° C. to 300° C. The source 70 of cesium is heated to a temperature by the coil 72 sufficient to vaporize cesium into a carrier gas hydrogen caused to flow over the source 70. When the source 70 has reached

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temperature a plunger 80 is activated to burst the diaphragm 76. Cesium is then transported in the vapor phase over, and about, the heated surface of the newly grown epitaxial layer 18 on the body 12 and deposited as the monatomic layer 20 of cesium on the zinc doped gallium arsenide layer 18. Upon completion of the deposition of the monatomic layer 20 of cesium, the source 70 is cooled, the body 12 and its grown layers 18 and 20 are cooled, and the flows of hydrogen are stopped.

An alternate source of cesium for the monatomic layer 20 is a paste of cesium zeolite heated to a temperature of 700° C. in the source 70.

Upon cooling, the body 12 with the layers 18 and 20 grown therein is placed in a metal vacuum deposition chamber. Employing known masking techniques, such, for example, as a metal mask, the layer 24 of electrical contact metal is deposited on the surface opposite to that which had the layers 18 and 20 grown on. The completed photocathode is shown in FIG. 1.

The employment of this process provides an easy means for the growth of cesium on an extraordinarily clean surface of gallium arsenide. This is accomplished, as shown heretofore, by employing a continuous vapor phase deposition process which grows a monocrystalline layer of gallium arsenide on a gallium arsenide or germanium substrate exposing the new surface on the gallium arsenide to any undesirable ambient, cesium is deposited on the gallium arsenide monocrystalline layer. This process enables one to achieve a high efficiency photocathode much more easily than by any of the prior art techniques described heretofore.

Additionally the process of this invention enables one to employ a body 12 of semiconductor material having any physical shape. Therefore, one can choose the desired shape of his photocathode beforehand and process it accordingly in a relatively very simple manner.

I claim as my invention:

1. A process for making a photocathode, comprising the steps of:

- (1) heating a body of semiconductor material selected from the group of materials consisting of gallium arsenide and germanium having two major opposed surfaces to an elevated temperature in a furnace;
- (2) vaporizing gallium into a stream of hydrogen chloride flowing over a source of gallium whereby the hydrogen chloride and gallium vapor chemically react to produce gallium chloride in the vapor phase;
- (3) introducing arsine gas into the gallium chloride vapors so that said gallium chloride reacts with the arsine gas to produce gallium arsenide in the vapor phase;
- (4) vaporizing a dopant material into a carrier gas;
- (5) mixing the vaporized dopant material in the carrier gas with the gallium arsenide in the vapor phase;
- (6) transporting the vaporized dopant material mixed with the gallium arsenide vapor over and about one of the major surfaces of the heated body whereby a layer of doped gallium arsenide is epitaxially grown on the major surface of said heated body;
- (7) depositing an essentially monatomic layer of cesium on the epitaxially grown layer of doped gallium arsenide, the deposition of the doped gallium arsenide and the cesium layer constituting one continuous vapor phase deposition process; and
- (8) affixing an electrical contact to the other major surface of the body.

2. The process of claim 1 in which the carrier gas is hydrogen.

3. The process of claim 1 in which the dopant material is zinc.

4. The process as defined in claim 1, and including the step of

chemically etching in situ the major surface of the heated body upon which the layer of monocrystalline gallium arsenide is to be grown prior to depositing

the monocrystalline layer of gallium arsenide there-
on.

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