

[54] METHOD OF MAKING A III-V COMPOUND ELECTRON-EMISSIVE CATHODE
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 3,712,700 1/1973 Sommer..... 316/19
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[57] ABSTRACT

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 316/6, 316/8, 316/10, 316/12

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 316/10, 12, 15, 19; 313/94, 103, 104;
 117/219, 223, 225, 211, 217

A III-V compound cathode is produced by exposing the cathode to cesium or cesium and oxygen, then exposing it to an increasing concentration of cesium while heating to about 150°C. The cathode is maintained at about 150°C, then exposed to a decreasing concentration of cesium while cooling.

[56] References Cited

UNITED STATES PATENTS

2,401,734 6/1946 Janes 316/5 X
 2,877,078 3/1959 Gauthier 316/9
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Also disclosed is an electron-emissive tube containing a cesium buffer source of a material incompletely reacted with cesium. The buffer source provides the increasing and decreasing concentrations of cesium for the above heating step.

7 Claims, 3 Drawing Figures

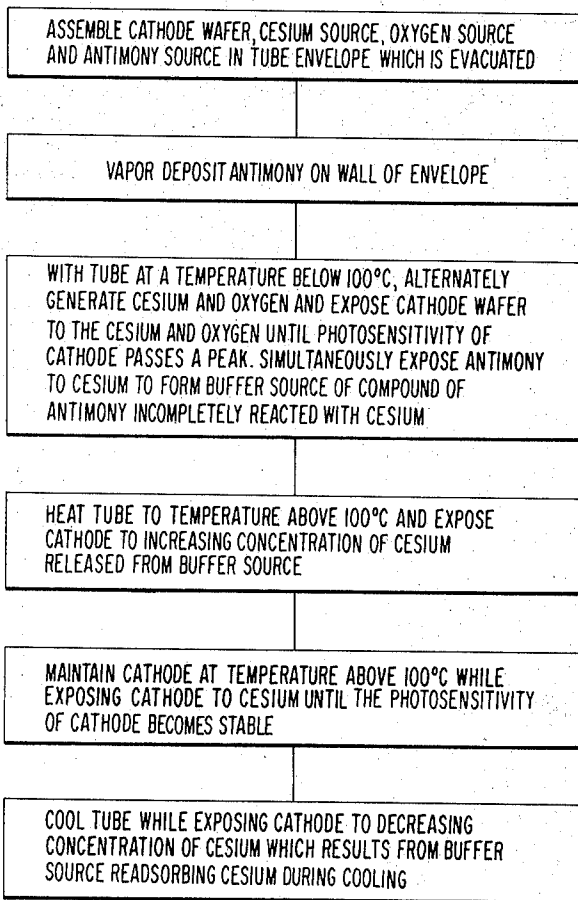


Fig. 1.

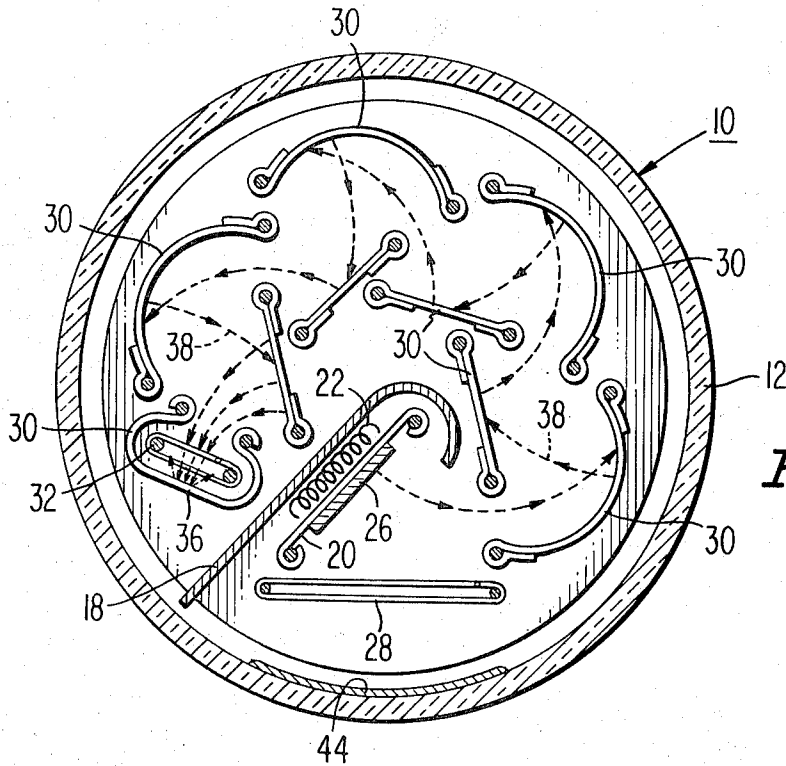
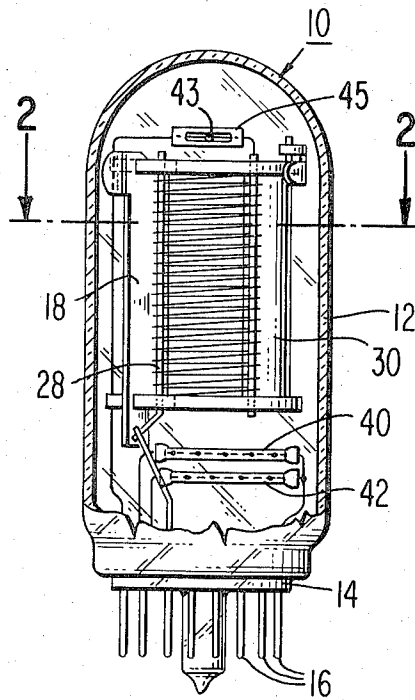
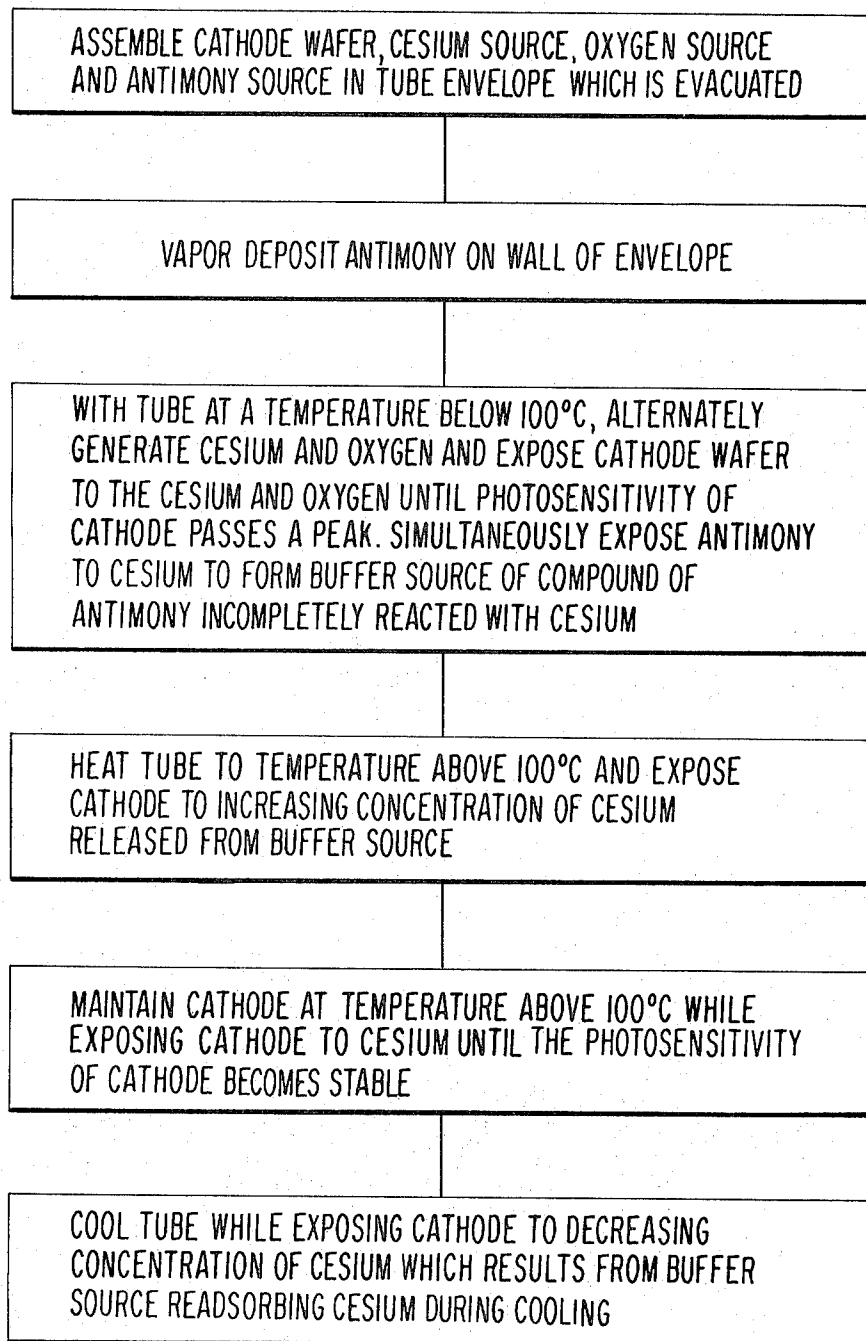


Fig. 2.

*Fig. 3*

METHOD OF MAKING A III-V COMPOUND ELECTRON-EMISSIVE CATHODE

The invention disclosed herein was made in the course of, or under, a contract or subcontract thereunder with the Department of the Army.

BACKGROUND OF THE INVENTION

The present invention relates to processing of electron-emissive tubes, particularly those in which the electron-emissive cathode is a III-V compound coated with a work-function-reducing layer comprising cesium.

The term "cathode," as used herein, refers to any structure which emits electrons into vacuum. Cathodes are used for example as photocathodes, dynodes, and electron gun cathodes in various electron-emissive tubes. Semiconductor compounds of the elements aluminum, gallium, indium, phosphorus, arsenic, and antimony, chosen from Groups III and V of the Periodic Chart of the Elements, are known to be particularly efficient cathodes for both primary and secondary electron emission. They are generally activated by being coated with a layer of cesium in combination with a strongly electronegative element, such as oxygen or fluorine. Examples of such III-V compound cathodes, as well as activation techniques therefor, are described for instance, in the following U.S. Pat. Nos.:

3,387,161 issued 4 Jun. 1968 to J. Van Laar et al.;
3,487,213 issued 11 Nov. 1969 to R. E. Simon et al.;
3,644,770 issued 22 Feb. 1972 to R. L. Bell;
3,669,735 issued 13 Jun. 1972 to D. G. Fisher;
3,696,292 issued 30 Oct. 1972 to G. A. Antypas.

One problem with III-V compound cathodes is their instability in operation. The bonding of cesium to the surface of the III-V compound crystal is relatively weak, as compared to the bonding of cesium to other, more conventional, photocathode base materials such as antimony. Whereas conventional photocathode base material, such as antimony, is activated with cesium at temperatures of 150°C (Celsius) or more, III-V compounds are presently activated with cesium at temperatures below 100°C. When a III-V photocathode activated by present techniques of activating III-V compound cathodes is subjected to temperatures above 100°C, the work-function-reducing coating formed on the surface does not form as desired for a practical device. Cathodes of III-V compounds activated at the lower temperatures according to prior art practices, on the other hand, perform well initially, but become somewhat unstable, even when operated with relatively low current. After a time, their emission is seriously degraded by loss of cesium from the work-function-reducing layer.

SUMMARY OF THE INVENTION

The novel method of making a III-V compound cathode comprises exposing the cathode to cesium vapor at a temperature below 100°C. Then the cathode temperature is raised to above about 100°C, while the cathode is exposed to cesium vapor, until the emission is substantially constant. The cesium concentration to which the cathode is exposed is increased during the raising of the temperature to above about 100°C and decreased during the lowering of the temperature therefrom.

The novel tube comprises a cesium buffer source inside the envelope. The buffer source is a material incompletely reacted with cesium, and provides a small amount of cesium vapor in the interior of the tube envelope during the processing above 100°C, to buffer the loss of cesium from the cathode at that temperature.

A III-V compound cathode activated by the novel method has an increased lifetime over one activated by prior processes. The novel tube with the cesium buffer source, conveniently provides the appropriate low cesium pressure itself from the buffer source during the processing above 100°C. The buffer source releases cesium at an increasing rate with a rising temperature to increase the concentration and absorbs cesium at an increasing rate with a lowering temperature to decrease the concentration.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a novel photomultiplier tube in accordance with the preferred embodiment having a III-V compound photocathode activated by the preferred embodiment of the novel process.

FIG. 2 is a sectional view of the tube of FIG. 1 taken at the section line 2-2.

FIG. 3 is a flow chart outlining the steps of a preferred embodiment of the novel method.

PREFERRED EMBODIMENT OF THE INVENTION

A preferred embodiment of the novel tube is processed in accordance with a preferred embodiment of the novel method. The novel tube is particularly suited for processing in accordance with the novel method. For convenience, the tube structure is described first.

TUBE STRUCTURE - The tube 10, shown in FIG. 1, is a photomultiplier tube having a glass envelope 12 and a base 14 provided with a number of metal pins 16 for making electrical contact to internal components.

Referring now to FIG. 2, inside the envelope is a metal shield 18. Spaced from the shield 18 is a metal substrate 20, on one face of which is mounted a rectangular photocathode wafer 26 of monocrystalline $In_{1-x}Ga_xAs$ ($x = 0.72$) about 2 cm (centimeters) long, 0.5 cm wide, and 0.5 mm (millimeters) thick. Between the shield 18 and the metal substrate 20 is a resistance heating filament 22 for heating the substrate 20 and the photocathode 26.

Proceeding now counterclockwise around the tube 10 as shown in FIG. 2, there is first a grid electrode 28 angularly spaced from the photocathode 26, and generally perpendicular to the direction of light input to the photocathode 26. Following the grid 28 are a series of eight copper-beryllium alloy dynodes 30, and an anode 32. The general direction of average electron trajectories from the photocathode 26 to the anode 32 are indicated by the dashed lines 38. A resistance-heated cesium vapor-generating channel 40 and an oxygen-generating channel 42 for processing of the photocathode 26 are mounted inside the tube 10 near the base 14, as shown in FIG. 1. A platinumantimony alloy bead 43 with a ceramic shield 45 is mounted in the upper part of the tube 10, facing an upper portion of the wall of the envelope 12. A layer 44 of antimony incompletely reacted with cesium, about 10 μm (micrometers) thick, is disposed opposite the bead 43 on the inside upper portion of the wall of the envelope 12. The

layer 44 serves as a cesium buffer source during the processing described below.

THE PROCESSING - In the preferred embodiment of the novel method, the photocathode 26 of the tube 10 of FIG. 1 is activated as follows: After the internal elements of the tube 10 have been assembled inside the envelope 12, the tube 10 is heated to a bakeout temperature of about 350°C for several hours while being simultaneously evacuated through the exhaust tubulation in the base 14 to clean the internal components. The evacuating is continued throughout the processing thereafter. Then the tube is allowed to cool enough to permit handling. Current is passed through the heating filament 22 to heat the cathode 26 along to near decomposition temperature for a short time to prepare the surface of the cathode 26 for activation.

Next, antimony is vapor-deposited to a thickness of about 10 μm on a small area of the upper side wall portion of the glass envelope 12 by resistance heating of the alloy bead 43. The antimony layer reacts with cesium during later cesium processing steps to form the cesium buffer layer 44.

Cesium vapor is now generated in the interior by resistance heating of the cesium channel 40, while the photosensitivity of the photocathode 26 is monitored. The photocathode is exposed to the cesium vapor until its photosensitivity has passed a peak, after which the cesium generation is terminated. Oxygen is now generated from the oxygen channel 42 by resistance heating until the photosensitivity of the photocathode 26 again passes a peak, after which the oxygen generation is terminated. These steps of exposing alternately to cesium and to oxygen are repeated at room temperature a number of times until a maximum photosensitivity is reached. Thereafter, excess cesium is released from the channel 40. Following the release of excess cesium, the tube 10 is heated to about 150°C, until the photosensitivity of the photocathode 26 becomes substantially constant, then allowed to cool to room temperature. The photocathode 26 is now stable. The tube 10 is then sealed off under vacuum at the exhaust tubulation 14.

When the cesium vapor is first generated in the tube 10, a portion of the cesium combines with the antimony of the buffer source layer 44 on the wall of the envelope 12 to form a compound of antimony incompletely reacted with cesium. Cesium also is adsorbed on the crystal surface of the photocathode 26 to form a work-function-reducing layer. As the tube 10 is heated from below 100°C to the higher temperature of 150°C, cesium is released at an increasing rate into the interior of the tube 10 from the buffer source layer 44 by decomposition, thus simultaneously increasing the cesium concentration to which the photocathode 26 is exposed. A dynamic balance condition is established at the surface of the photocathode 26, which prevents a substantial loss of cesium from the work-function-reducing layer. As the tube is then cooled, excess cesium in the interior is absorbed again, at an increasing rate, by the buffer source layer 44 by recombination, thus simultaneously decreasing the cesium concentration to which the photocathode 26 is exposed. Because the photocathode 26 can thus be activated with cesium at a higher temperature of 150°C, rather than only at a temperature below 100°C, the stability of the photocathode 26 is greatly improved.

General Considerations

The novel invention is applicable to activation of any III-V semiconductor compound cathode coated with a cesium-containing work-function-reducing layer. While the higher temperature activation of the preferred embodiment was 150°C, a cathode heated to any temperature above 100°C in the presence of a small amount of cesium vapor, as provided by a cesium compound buffer source, can be expected to have improved stability. For certain III-V compounds it is desirable to include exposure to oxygen, as in the preferred embodiment, or fluorine. Other III-V compounds, such as gallium phosphide for example, are generally not exposed to oxygen or fluorine during the processing.

The cesium buffer source may be provided anywhere in the envelope where its electron emissive properties do not interfere with the normal operation of the tube. For example, since cesium antimonide is photoemissive, it would be undesirable to place the buffer source layer where light incident on it may result in spuriously emitted electrons entering the multiplier. The buffer source should be electrically passive, since neither its primary nor secondary emission characteristics are particularly useful.

It is believed that the cesium-antimony compound of the cesium buffer source of the preferred embodiment tends to produce an optimum cesium equilibrium in the tube at high temperatures because, as a result of slight decomposition, sufficient cesium vapor is generated from it to prevent excessive loss of cesium from the III-V compound cathode. At the same time, the cesium is sufficiently bound in the cesium-antimony at lower temperatures to prevent the remaining of excess cesium which might be deleterious to the cathode. Other cesium compounds which decompose at elevated temperatures above 100°C may be used for the buffer source instead of a cesium-antimony compound. Examples of such compounds are cesium-bismuth, cesium-gold, or cesium-graphite. However, the decomposition should begin at a low enough temperature to provide some cesium at about 150°C.

I claim:

1. A method of making a III-V semiconductor compound cathode, comprising the steps of:

mounting a III-V semiconductor compound cathode wafer in an envelope which is evacuated; then exposing the cathode at a first temperature, below 100°C, to cesium until the photosensitivity of the cathode has passed a peak; then

raising the temperature of the cathode to a second temperature, above 100°C, while simultaneously exposing the cathode to an increasing concentration of cesium; then

maintaining the cathode at said second temperature while exposing the cathode to cesium, until the photosensitivity of the cathode becomes stable; then

lowering the temperatures of the cathode while simultaneously exposing the cathode to a decreasing concentration of cesium.

2. The method defined in claim 1, wherein said second temperature is about 150°C.

3. The method defined in claim 1 wherein, between said exposing at a first temperature and said raising to

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a second temperature, the cathode is exposed to oxygen.

4. The method defined in claim 1 wherein, between said exposing at a first temperature and said raising to a second temperature the cathode is exposed to fluorine.

5. The method defined in claim 1 wherein prior to exposing the cathode at the first temperature to cesium the step of providing in said envelope an electrically passive buffer source of a material which adsorbs cesium at said first temperature and releases cesium at said second temperature, and exposing said buffer

source to cesium when the cathode is exposed to the cesium at the first temperature, said buffer source providing the increasing concentration of cesium when the temperature of the cathode is raised to the second temperature and the decreasing concentration of cesium when the temperature of the cathode is lowered.

6. The method defined in claim 5 wherein the buffer source is a material selected from the group consisting of antimony, bismuth, gold, and graphite.

7. The method defined in claim 5 in which the buffer source is coated on the surface of the envelope.

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