United States Patent [19]

Sommer

[11] **3,712,700**

[45] **Jan. 23, 1973**

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[54] **METHOD OF MAKING AN ELECTRON EMITTER DEVICE**

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[73] Assignee: **RCA Corporation**, New York, N.Y.

[22] Filed: **Jan. 18, 1971**

[21] Appl. No.: **107,372**

[52] **U.S. Cl.** **316/19**, 29/25.11, 117/6, 316/18, 316/24

[51] **Int. Cl.** **H01j 9/18**

[58] **Field of Search** 316/17, 18, 19, 24; 117/6; 29/25.11, 25.17

[56] **References Cited**

UNITED STATES PATENTS

2,184,323	12/1939	Spanner	316/19
2,441,810	5/1948	Glover et al.	316/20
2,505,909	5/1950	Patai	117/6 X
3,353,890	11/1967	Legoux	316/19
3,390,012	6/1968	Haberecht	117/6 X

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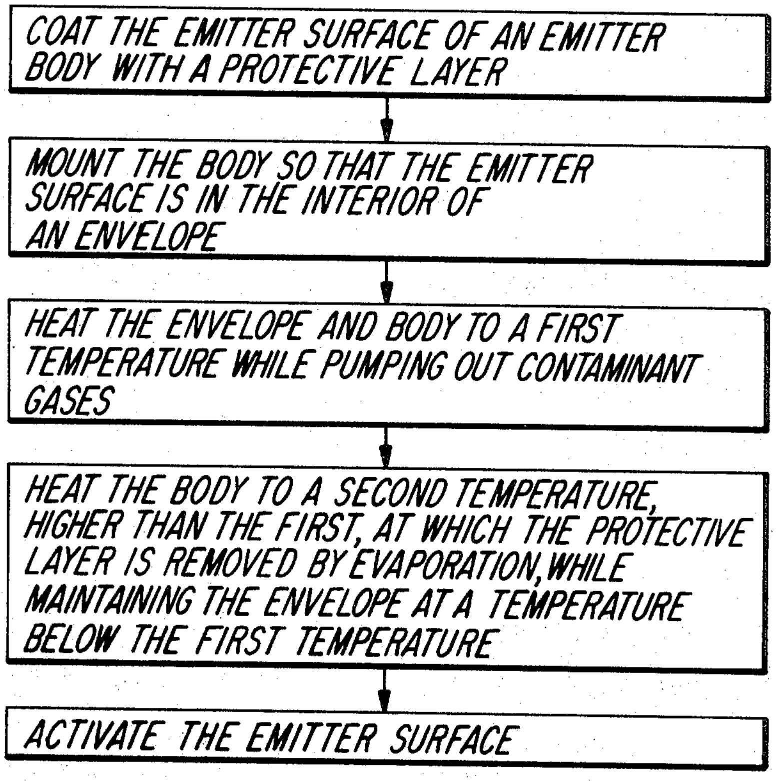
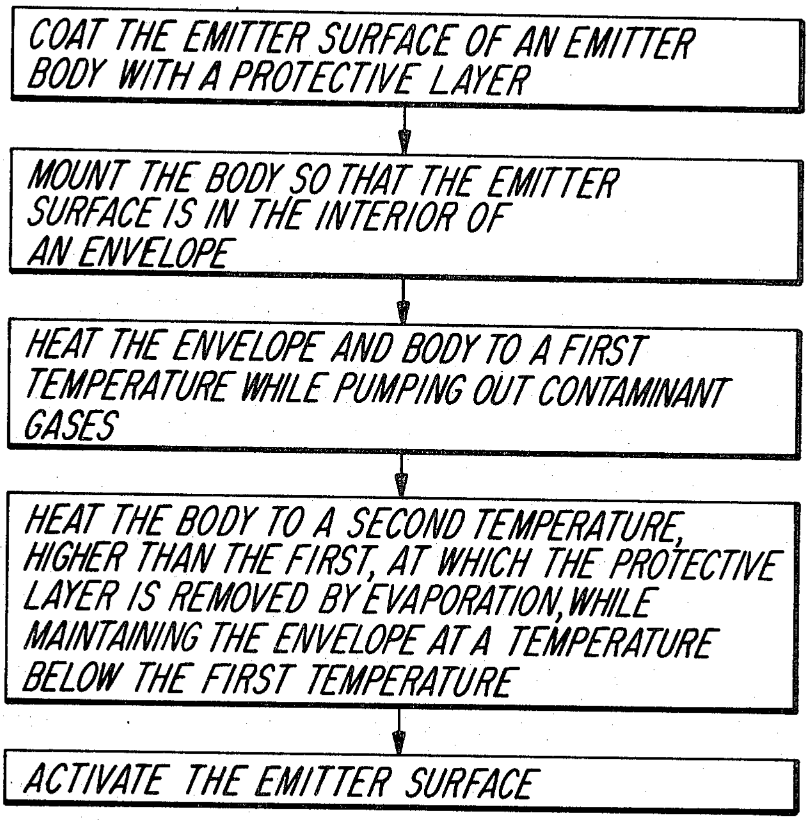
Assistant Examiner—Richard Bernard Lazarus
Attorney—Glenn H. Bruestle

[57] **ABSTRACT**

A method comprising coating an uncontaminated emitter surface of an emitter body with a non-contaminating protective layer and then mounting the body so that the coated surface is in the interior of an envelope. The envelope and body are then heated to a first temperature to drive contaminant gases from surfaces of the envelope interior while these gases are simultaneously pumped out. The first temperature is low enough that the protective layer remains. Then the body is heated to a second temperature, higher than the first, and the protective layer evaporated off the surface while the envelope is maintained at a temperature below the first temperature. Thereafter the emitter surface is activated by the application thereto of a material which lowers the work function.

4 Claims, 2 Drawing Figures





COAT THE EMITTER SURFACE OF AN EMITTER BODY WITH A PROTECTIVE LAYER

MOUNT THE BODY SO THAT THE EMITTER SURFACE IS IN THE INTERIOR OF AN ENVELOPE

HEAT THE ENVELOPE AND BODY TO A FIRST TEMPERATURE WHILE PUMPING OUT CONTAMINANT GASES

HEAT THE BODY TO A SECOND TEMPERATURE, HIGHER THAN THE FIRST, AT WHICH THE PROTECTIVE LAYER IS REMOVED BY EVAPORATION, WHILE MAINTAINING THE ENVELOPE AT A TEMPERATURE BELOW THE FIRST TEMPERATURE

ACTIVATE THE EMITTER SURFACE

FIG. 1

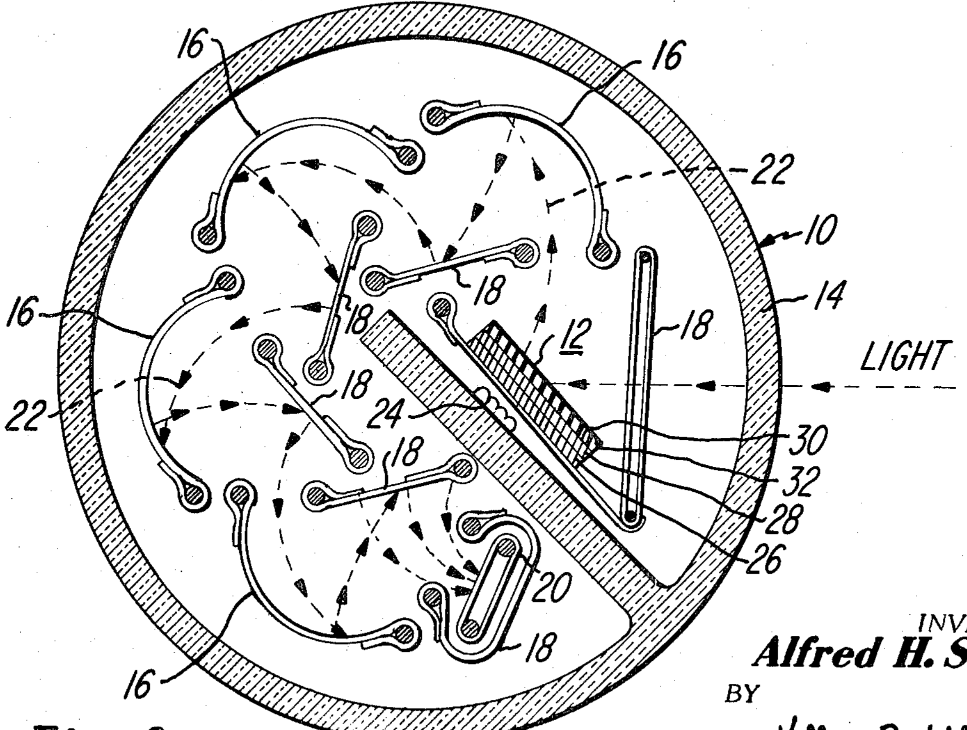


FIG. 2

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METHOD OF MAKING AN ELECTRON EMITTER DEVICE

BACKGROUND OF THE INVENTION

This invention relates generally to a method for making an electron emitter device in which electrons are emitted into vacuum from a surface of an electron emitter body and relates particularly to, but is not limited to, a method for making such a device wherein the emitter body is a semiconductor.

Electron emitters are used, for example, as photocathodes and as secondary emitting dynodes in electron tubes such as image tubes and photomultipliers. Generally, an electron emitter consists of an emitter body having a surface which has been activated to increase its electron emission. Activation is achieved by the application of an electropositive substance such as cesium, either alone or with an electronegative substance such as oxygen, to lower the work function. Examples of photomultipliers, of both thin film and thicker electron emitter structures, of techniques for growing semiconductor emitter material, and of techniques for activation are found in the following references:

U.S. Pat. No. 3,387,161
Title: PHOTOCATHODE FOR ELECTRON TUBES
Issued: June 4, 1968
Inventor: J. Van Laar et al.
U.S. Cl.: 313–94

U.S. Pat. No. 3,478,213
Title: PHOTOMULTIPLIER OR IMAGE AMPLIFIER WITH SECONDARY EMISSION TRANSMISSION TYPE DYNODES MADE OF SEMICONDUCTOR MATERIAL WITH LOW WORK FUNCTION MATERIAL DISPOSED THEREON
Issued: Nov. 11, 1969
Inventor: R. E. Simon et al.
U.S. Cl.: 250–207

Syms, C. H. A. "Gallium Arsenide Thin-Film Photocathodes." In Advances in Electronics and Electron Physics, N. Y., Academic Press, 1969, Vol. 28A; pp. 399–407 **Edited by: J. D. McGee et al.**

In order that an acceptable initial emission and operation lifetime be obtained from the emitter, it is important that the emitter surface be free of contaminants at the time of activation. The emitter bulk of some emitters, such as antimony, may be evaporated from a bead in an electron tube envelope after contaminants have been removed from the interior of the envelope by a bakeout, a heating of the envelope and simultaneously evacuation of contaminant gases evolved from the envelope walls and from internal elements. Other emitters, however, which cannot readily be evaporated from a bead are considerably more difficult to incorporate into an electron tube. For instance, binary and ternary semiconductor compounds such as GaAs, GaP, and $InGa_{1-x}As_x$, as well as the elementary semiconductor silicon, are highly suitable materials for electron emitters but cannot be readily evaporated from a bead. In the case of silicon, evaporation is difficult because of the high evaporation temperature of silicon. In the case of the compounds, evaporation is difficult because the unequal rates of evaporation of the elements of the compounds at a given temperature result in decomposition of the compound. For these other emitters it is not presently feasible to form by evaporation emitter bodies having the characteristics needed for a sufficiently effective emitter surface. These other emitters are generally incorporated in an electron tube envelope by mounting the already-formed emitter body in the envelope prior to the envelope bakeout. For effective removal of contaminants from the tube, the bakeout should be at a temperature of at least about 350°C, preferably 400°C. The higher the bakeout temperature, the more rapid and complete is the removal of contaminants. It is found, however, that heating the tube to about 350°C even for a short time, on the order of several minutes or less, results in contamination of the emitter surface by chemical reaction of the released gases with the emitter body material. The emitter surface may then be permanently contaminated or must be recleaned inside the envelope by separate heating or sputtering prior to activation. Such recleaning is difficult to perform in the complex geometry of photomultiplier or image tubes. While some III–V semiconductor compounds can be cleaned by heating for about 1 minute to about 25°C below their decomposition temperature, some other semiconductors require more intense cleaning processes. Silicon, for example, is generally cleaned by bombardment with high energy electrons with subsequent annealing at about 1,000°C for about 1 hour or more. Since in practice it is extremely difficult to perform such a cleaning process on a silicon emitter after it has been assembled inside an envelope, the use of silicon as an electron emissive surface in electron tubes has been severely restricted, despite the fact that silicon is otherwise highly desirable for such an application.

SUMMARY OF THE INVENTION

The novel method for making an electron emitter device comprises coating an uncontaminated electron emitter surface of an emitter body with a non-contaminating protective layer to protect it from contamination during further device fabrication. At a later stage of device fabrication, when ambient contaminants have been substantially removed, the layer is removed by evaporation from the emitter surface. Thereafter, the emitter surface is activated by the application thereto of a material which lowers the work function.

When the uncontaminated emitter surface is covered with a protective layer until just prior to activation, the emitter body may be exposed to contaminants during bakeout of a tube envelope in which it is mounted without degradation. After removal of the protective layer, the emitter surface need not be recleaned prior to activation. Furthermore, semiconductors such as silicon which require cleaning processes which previously restricted them from commercial applications as electron emitters in electron tubes may now be so utilized with the novel method.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart outlining the steps of a preferred embodiment of the novel method.

FIG. 2 is a sectional view of a photomultiplier tube provided with a photocathode by the method of FIG. 1 and shown at a stage of processing between the third and the fourth steps of FIG. 1.

PREFERRED EMBODIMENTS OF THE INVENTION

EXAMPLE I

In a first embodiment of the novel method, generally outlined in the flow chart of FIG. 1, a circular cage photomultiplier tube **10** shown in FIG. 2 is provided with an opaque semiconductor compound photocathode **12** emitter body. The tube **10** is shown in FIG. 2 during a stage of processing prior to the activation of the photocathode **12**. The tube **10** includes a glass envelope **14**, a number of electron multiplying dynodes **16**, field electrodes **18**, and an anode **20** for collecting multiplied electrons which travel from one dynode **16** to another generally along the path indicated by the dashed lines **22**. Behind the photocathode **12** is a heating filament **24**. Also included in the envelope **14**, but not shown in the drawings, are sources of cesium and oxygen for activating the photocathode **12**. The envelope **14** is connected by a short length of exhaust tubulation to a high-speed vacuum pump, also not shown.

The photocathode **12** comprises a ½-inch square gallium arsenide substrate **26** about 50 microns thick having on one face an epitaxial layer **28** of gallium arsenide emitter bulk about 10 microns thick with an emitter surface **30**. The emitter surface **30** is coated with a protective layer **32** of potassium chloride (KCl) about 0.05 microns thick.

Prior to the incorporation of the photocathode **12** in the envelope **14**, the protective layer **32** is evaporated on the emitter surface **30** as follows: First the emitter surface **30** is cleaned of contaminants in a continuously evacuated chamber, in which it is baked for at least 1 hour at a pressure of about 10^{-6} torr or lower and a temperature of about 200°C and cooled back to room temperature. Then, the substrate **26** and emitter bulk **28** are heated for about **1** minute to about 650°C, a temperature which is near but somewhat below the decomposition temperature of gallium arsenide, by heat radiated from a nearby resistance heated filament and again cooled to room temperature. Now the protective layer **32** is applied to the emitter surface **30** by evaporation from a potassium chloride bead on a second resistance heated wire.

Installation of the photocathode **12** in the photomultiplier tube **10** is as follows: The coated photocathode **12** is mounted in the interior of the envelope **14**. The envelope **14** is continuously evacuated by the vacuum pump through the exhaust tubulation to a pressure of about 10^{-6} torr or less while the envelope **14** is baked out at about 350°C for at least 1 hour before being cooled back to room temperature. The interior of the envelope **14** is thus cleaned of contaminating gases while the emitter surface **30** is shielded from these contaminating gases by the protective layer **32**. Now the photocathode **12** is heated from the side opposite the protective layer **32** by radiation from the filament **24** to about 500°C with the remainder of the tube **10** at room temperature until the potassium chloride is evaporated off the emitter surface **30**, from where it is either deposited elsewhere in the interior of the tube **10** or is pumped away by the vacuum pump. Finally, the emitter surface **30** is activated with cesium and oxygen and the exhaust tubulation sealed off under vacuum between the tube **10** and the pump.

EXAMPLE II

In a second embodiment of the novel method a photomultiplier tube is provided with an opaque photocathode as in EXAMPLE I, but by use of a protective layer **32** of cesium iodide (CsI) instead of potassium chloride. Processing is generally the same as described for EXAMPLE I, except that since cesium iodide evaporates at a lower temperature than potassium chloride, the bakeout temperature is about 300°C and the temperature to which the photocathode **12** is heated for removal of the protective layer is about 400°C. Because of the relatively low temperature at which a cesium iodide protective layer evaporates off the emitter surface **30**, cesium iodide is useful primarily for emitter bodies which themselves have relatively low evaporation (or decomposition) temperatures such as, for example, indium antimonide semiconductor alloy, some compositions of which decompose at about 450°C.

GENERAL CONSIDERATIONS

The novel method may be used for protecting different emitter materials, whether metal, semiconductor or insulator, provided that the evaporation temperature (or decomposition temperature in the case of an alloy or compound) of the emitter bulk is higher than that of the protective layer, so that the protective layer may be removed therefrom without injury to the emitter surface. For instance, a potassium chloride layer may be applied to an uncontaminated silicon emitter surface and then evaporated off without significant degradation of the surface, even through silicon is a relatively reactive material as compared to, for instance, III–V semiconductor compounds.

Where the emitter bulk is a vapor phase grown semiconductor, it is particularly advantageous to apply the protective layer before the emitter is ever exposed to the atmosphere. For example, potassium chloride may be evaporated on the emitter surface of vapor phase grown gallium arsenide or silicon while the emitter surface is yet in its growth chamber and in a rarified inert atmosphere such as helium. In this way the step of cleaning the emitter surface of contaminants prior to the application of the protective layer is eliminated.

In addition to potassium chloride and cesium iodide there are other materials, such as the other alkali-halide compounds sodium chloride (NaCl) and rubidium chloride (RbCl), suitable as protective layers for emitters. The critical requirements for the protective layer material are that, (1) it does not itself contaminate the emitter surface, (2) it may be removed by evaporation without degrading the tube when it condenses on the inside envelope walls and on internal components (thus for photomultiplier tubes it should be transparent and electrically insulating); (3) it be a chemically stable layer to at least the bakeout temperature required for the tube; (4) as a layer, it be substantially impervious to contaminants in the tube and substantially unaffected by water vapor.

While in the preferred embodiment the emitter surface was activated with cesium and oxygen, the activation may be achieved with any of a number of techniques for lowering the work function. Such techniques generally include the application to the surface of one or more electropositive materials such as potassium, cesium or sodium either alone or together with one or more electronegative materials such as oxygen or fluorine.

The evaporation temperatures for protective layer materials herein are temperatures at which that material will vaporize at a sufficiently rapid rate to remove the layer from the emitter surface within a reasonably short time span, e.g., on the order of minutes. This evaporation temperature is relatively non-critical and is generally a temperature at which the material has a vapor pressure of about 10^{-2} torr to about 10^{-4} torr. Substantially lower temperatures require a much longer time to evaporate such a layer. Where the material is a compound or an alloy, the decomposition temperature is referred to instead of an evaporation temperature. The evaporation temperature for potassium chloride may be taken to be about 450°C or higher but for practical purposes is between 450°C and 500°C. The evaporation temperature for cesium iodide is between about 350°C and 400°C. The decomposition temperature for gallium arsenide is between about 625°C and about 675°C, whereas the evaporation temperature for silicon is upwards of 1,000°C.

While the emitter bodies of EXAMPLES I and II of the preferred embodiments are opaque photocathodes, the novel method is not limited to a particular type of emitter body. Semitransparent photocathodes or electron-multiplying dynodes may also be made by the novel method. In some photoemissive tubes a semitransparent emitter body may itself be a faceplate and thus act as a portion of the envelope, with the emitting surface being inside the envelope. Such an arrangement may require a different means of separately heating the emitter body to remove the protective layer. Although the novel method is particularly advantageous for semiconductor emitter bodies because of the sensitivity of semiconductor surfaces to contamination and the difficulties in evaporating semiconductor layers inside a tube envelope, the novel method is also applicable to where the emitter body is a metal, such as for example tungsten, or an insulator, such as for example magnesium oxide.

I claim:

1. A method of making an electron emitter device, comprising:

coating an uncontaminated electron emitter surface of an emitter body with a non-contaminating protective layer; then

mounting the body so that the coated surface is in the interior of an envelope; then

heating the envelope and the body to a first temperature to drive contaminant gases from surfaces of the envelope interior, while simultaneously pumping out the gases from the envelope interior, the first temperature being low enough that the protective layer remains on the emitter surface; then

heating the body to a second temperature, higher than the first, at which second temperature the protective layer is removed by evaporation from the emitter surface, while maintaining the envelope at a temperature below the first temperature;

activating the emitter surface by the application thereto of a material which lowers the work function.

2. The method defined in claim 1 wherein the protective layer is an alkali-halide compound.

3. The method defined in claim 1 wherein the protective layer is of potassium chloride, the first temperature is about 400°C, and the second temperature is about 450°C or higher.

4. The method defined in claim 1 wherein the protective layer is of cesium iodide, the first temperature is about 300°C, and the second temperature is about 350°C or higher.

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