

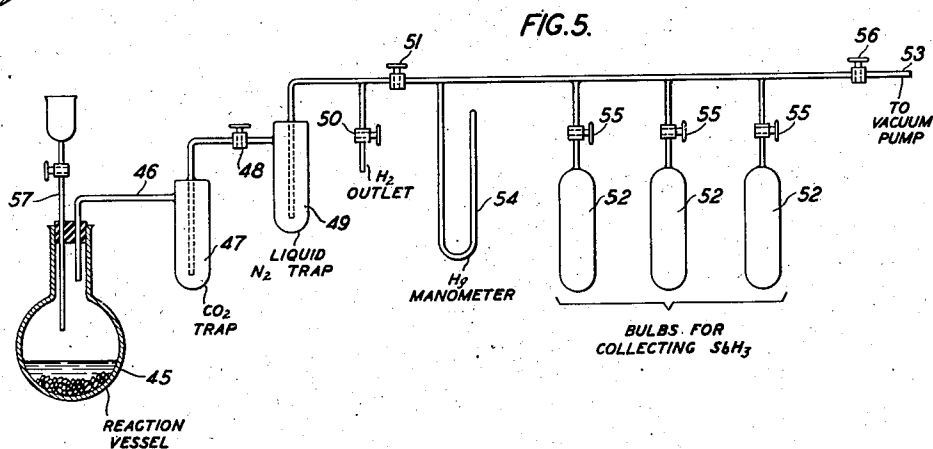
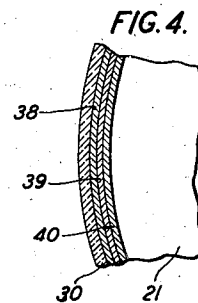
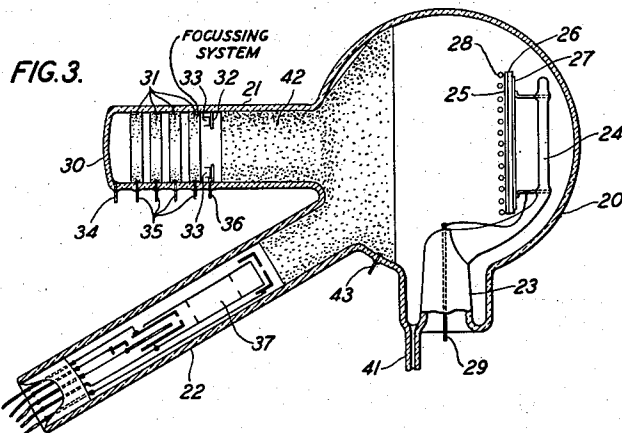
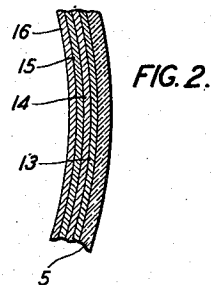
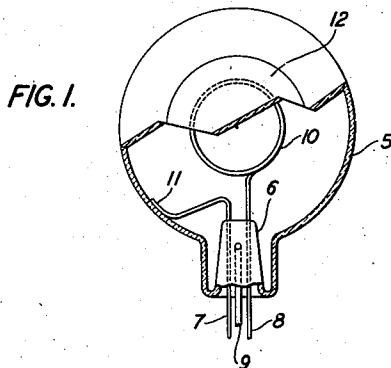
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METHOD OF FORMING LAYERS FOR ELECTRONIC CATHODES

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METHOD OF FORMING LAYERS FOR
ELECTRONIC CATHODES

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This invention relates to methods of producing layers for electronic cathodes and more particularly to the method comprising introducing a gaseous metallic hydride in contact with a cathode carrier to be coated and decomposing the hydride to form a layer of the metal on the carrier.

An object of the invention is to provide an improved method of making electronic cathodes.

In an example of practice of the invention a photoelectric cathode is produced by introducing antimony hydride into a container within which a cathode carrier is supported, such as a silver plate provided with a matrix including cesium oxide and adsorbed cesium. This matrix is heated and the antimony hydride in contact therewith is decomposed to produce a layer of antimony on the matrix. The decomposing temperature is about 150° to 200° C. (centigrade). By controlling both the time of heating and the area which is heated, the amount of antimony deposited may be accurately controlled. The layer of antimony is in intimate contact with the adsorbed cesium.

The antimony may be deposited also directly on glass or on a semitransparent layer of silver, copper or other metal which has been deposited on glass or other carrier. The antimony may also be deposited on metal plates or electrodes. Cesium is deposited on the antimony in intimate contact therewith. Instead of antimony other metals may also be deposited from the gaseous state, such as the volatile hydrides of the elements of the fourth and fifth groups of the periodic table, including among others, bismuth, arsenic, phosphorus, germanium and silicon.

The invention will now be described more in detail having reference to the accompanying drawing:

Fig. 1 shows a photoelectric tube, partly in section, made according to this invention;

Fig. 2 is a fragmentary showing of a portion of the photoelectric tube of Fig. 1 to illustrate the structure of the cathode;

Fig. 3 is a camera tube, partly in section, having a photoelectric cathode made according to this invention;

Fig. 4 is a fragmentary showing of a portion of the tube of Fig. 3 to illustrate the structure of the photoelectric cathode; and

Fig. 5 illustrates schematically apparatus used in the practice of this invention.

The same reference characters are used to indicate identical elements in the several figures.

The photoelectric tube of Fig. 1 is one form

of device which may be made by the method of this invention. It comprises a glass bulb 5, partly in cross section, having a reentrant stem 6 through which cathode lead-in conductor 7 and anode lead-in conductor 8 are sealed and to which exhaust tubulation 9 is connected. The anode 10 in the form of a nickel ring is mounted on the lead-in conductor 8. The cathode is supported on the inner surface of the bulb 5 and in contact with the inner end 11 of lead-in conductor 7. A portion 12 of the bulb 5 is kept clear for the entrance of the energizing light beam.

The nature of the cathode is shown more clearly in Fig. 2. On the inner surface of the bulb 5 a layer 13 of silver or other suitable metal is formed by vaporization and deposition or other suitable process. The surface of the silver layer 13 is then oxidized to form a layer of silver oxide 14. A thin layer 15 of cesium is then deposited on the layer of silver oxide and the evacuated tube is baked to produce maximum photosensitivity. After this baking process the layers 14 and 15 are probably no longer discrete but form a composite matrix on the silver layer 13, which matrix, it is believed, comprises finely divided silver oxide, cesium oxide, pure silver and cesium. A layer 16 of antimony is then formed on this matrix by introducing antimony hydride, SbH_3 , into the evacuated bulb 5 and heating the matrix to a temperature of 150° to 200° C. to decompose the antimony hydride. The effect of this treatment is to improve the spectral sensitivity to wave-lengths in the blue region of the spectrum.

The thickness of the layers 13, 14, 15 and 16, as shown in Fig. 2, is greatly exaggerated for purposes of illustration. In an actual photoelectric tube made according to this invention the silver layer 13 might be even semitransparent while the layers 14, 15 and 16 would be still thinner.

Another device which may conveniently be made by the method of this invention is a so-called camera tube, as illustrated in Fig. 3. It comprises a spherical portion 20, an image portion 21 and an electron gun portion 22, all made of glass. The spherical portion 20 is provided with a reentrant stem 23 having a glass bracket 24 supported therefrom, which bracket supports a mosaic target 25. Target 25 comprises a sheet of mica 26 on which a signal plate 27 is formed by the deposition of evaporated aluminum. The opposite face of the sheet 26 is coated with silver which is heat treated, oxidized and treated with

cesium to form a secondary electron emitting mosaic 28. Sealed through the stem 23 is a lead-in conductor 29 which is conductively connected to the signal plate 27. The image portion 21 is a cylindrical glass tube having a glass end portion 30. The inner surface of the tube 21 is provided with a plurality of conducting ring electrodes 31 and a self-supporting metallic ring electrode 32. Electrode 32 serves as a support for a plurality of evaporator cups 33 used to evaporate a semitransparent layer of silver on the inner surface of the end portion 30 which is sensitized to form a photoelectric cathode. A lead-in wire 34 contacts the silver layer on the end 30. Lead-in wires 35 contact the electrodes 31, respectively, and lead-in wire 36 contacts the electrode 32. The electron gun portion 22 comprises an electron beam producing electrode structure 37. It might also comprise beam deflecting plates.

The nature of the cathode structure on end portion 30 is shown more in detail in Fig. 4. On the semitransparent layer 38 of silver a layer 39 of antimony is formed according to the method of this invention. On the layer 39 a layer 40 of cesium is deposited. This cathode is photoelectrically sensitive so that when an optical image is projected on the photoelectric cathode through the glass end portion 30 a corresponding photoelectron image is formed which may be projected on the mosaic target 25 by the electron focusing electrodes 31 and 32 and a deposited electrode 42 of relatively large extent to which lead-in wire 43 is connected. Electrode 42 covers a considerable portion of the left-hand side of spherical portion 20 and extends into the image portion 21 and the cathode gun portion 22.

The process of sensitizing the camera tube of Fig. 3 is briefly as follows:

The tube is first evacuated and baked at 400° C. to eliminate occluded gases. The evaporators 33 are heated to evaporate the silver which deposits in a semitransparent layer on the end portion 30 in contact with lead-in wire 34. The tube is kept cold as a whole while the end portion 30 is heated to a temperature of 100° to 200° C. by means of a hot-air blast. Antimony hydride gas is admitted through the pump tubulation 41 and is decomposed at the heated portion 30 to deposit antimony on the semitransparent silver layer 38. After a suitable amount of antimony has been deposited the remaining antimony hydride gas is pumped out of the tube and pump station. Oxygen is now introduced into the tube and the mosaic of silver 28 is oxidized by electrodeless discharge. The oxygen is pumped out and cesium is introduced by chemical reaction of a cesium producing pellet. The pellet or pellets, if it is convenient to use more than one pellet, may be mounted within the tube or in a side tube connected to the main tube. After the cesium has been flashed the tube is heated to 150° to 200° C. to distribute the cesium to the oxidized mosaic 28 and to the antimony layer 39 on the end portion 30. The tube is baked and tested alternately until maximum sensitivity is obtained. Any excess of cesium may be taken up by a square of tin oxide painted on the exposed surface of the signal plate 27.

In a modified method of sensitization the antimony layer may be formed on the silver layer 38 by an electrical discharge in the antimony hydride in the vicinity of the silver layer 38, the antimony hydride being decomposed by the discharge. In another modified method of sensi-

zation the semitransparent layer of silver 38 may first be partially oxidized and then exposed to antimony hydride while heated to a temperature of 150° to 200° C. The antimony hydride reacts with the silver oxide and produces Sb_3Ag or Ag and Sb_2O_3 or silver antimonate. Treatment of these surfaces with cesium produces a sensitive photoelectric cathode.

A method of making antimony hydride gas will now be described having reference to Fig. 5. The antimony hydride is formed by chemical reaction in a reaction vessel 45. The gas passes through tube 46 into a carbon dioxide trap 47 used to condense out water vapor. The antimony hydride then passes through a tube including stop cock 48 into a liquid nitrogen trap 49 wherein the antimony hydride is trapped by being solidified during the reaction process. Excess hydrogen produced by the reaction is freed by opening the stop cock 40. During the reaction process the stop cock 51 is closed. The antimony hydride from trap 49 may be collected in gaseous form in bulbs 52 which are first evacuated through pump tubulation 53. The pressure in the bulbs 52 is indicated by a manometer 54. The stop cock 55 controls the bulbs 52 and stop cock 56 controls the connection to the pump tubulation 53.

A suitable reaction for producing antimony hydride results from treating an alloy of antimony and zinc with dilute sulphuric acid, H_2SO_4 , in the reaction vessel 45. At the start of the reaction the vessel 45 is cooled in an ice bath to control the speed of the reaction. The alloy may be prepared by fusing pieces of antimony and zinc in the proportions by weight of 9 grams of antimony to 28 grams of zinc. The antimony and zinc in the form of sticks are broken into pieces about one-quarter inch in length and placed in a porcelain crucible which is covered with another smaller crucible. This combination is heated from below by a Meker burner and from above with a sealing-off torch and a soft flame. The heating requires approximately forty-five minutes, toward the end of which the crucible begins to "bump" as though the mixture were boiling or reacting violently. After cooling the resulting ingot of alloy is removed from the crucible and crushed with a hammer on a steel plate into pieces about the size of peas. The crushed alloy is placed in the reaction vessel 45, together with about 50 cubic centimeters of water. Dilute sulphuric acid, prepared by mixing 25 cubic centimeters of concentrated H_2SO_4 with 100 cubic centimeters of water, is added to the alloy through the stoppered funnel 57 in 25 cubic centimeter portions during the course of about five hours, keeping the reaction vessel immersed in an ice bath. During this reaction the stop cock 51 is kept closed and the stop cock 48 open. Water vapor is collected in the carbon dioxide trap 47 and solid antimony hydride in the liquid nitrogen trap 49. The stop cock 48 is then closed and stop cock 51 opened. The equipment on the right-hand side of stop cock 48 is thoroughly evacuated. The stop cock 56 is then closed to cut off the pump tubulation 53. As the liquid nitrogen trap 49 is allowed to warm up the liquid antimony hydride evaporates and is collected in any one or all of the bulbs 52 under control of the stop cock 55. After the antimony hydride has been collected the stop cock 51 is closed and the antimony hydride in bulbs 52 is ready for use in making devices such as are

illustrated in Figs. 1 to 4. The exhaust tubulation of the device, such as the tube 9 of Fig. 1 or the tube 41 of Fig. 3, is sealed to the pump tubulation 53 of Fig. 5 at any convenient point. By manipulating stop cocks 55 and 56 and other stop cocks in the pump tubulation (not shown) antimony hydride in controlled amounts may be admitted to the sealed-on device from any one or all of the bulbs 52.

Another reaction for producing antimony hydride results from treating an alloy of antimony and zinc with dilute hydrochloric acid, HCl. The crushed alloy is placed in the reaction vessel 45 and the entire system is flushed with tank hydrogen. Dilute HCl is then dropped on the alloy by means of the stoppered funnel 57, keeping the vessel 45 surrounded with an ice bath. The dilute HCl consists of one volume of concentrated HCl mixed with about three volumes of water. About 50 cubic centimeters of the dilute HCl are added immediately. The reaction takes place at a reasonable rate of about one to three bubbles per second. The reaction may continue for several hours. The antimony hydride which is collected in the liquid nitrogen trap may be used in the same manner as hereinbefore described.

Still another reaction for producing antimony hydride comprises dropping a solution of 10 grams of antimony chloride, $SbCl_3$ in concentrated hydrochloric acid, HCl, diluted with an equal volume of water onto granulated zinc and dilute HCl in the reaction vessel 45. The dilute HCl is allowed to react with the zinc for about fifteen minutes to sweep the air out of the system through the outlet tube 50. The antimony chloride solution is then allowed to drop in slowly, the reaction taking place at atmospheric pressure. Here again the antimony hydride is collected as a solid in the liquid nitrogen trap 49. It may be used in the manner hereinbefore described.

What is claimed is:

1. The method of making a light-sensitive cathode which comprises forming on a cathode carrier a deposit of antimony and cesium in intimate contact in an evacuated container, including introducing antimony hydride gas into said container, decomposing said gas, and forming on said cathode carrier a deposit of the antimony resulting from the decomposition.

2. The method of making a light-sensitive cathode which comprises depositing cesium on oxidized silver, heat treating said cesium, silver and silver oxide to form a matrix which is sensitive to light, and further heating said matrix in the presence of antimony hydride gas to a temperature sufficient to decompose said antimony hydride to form a deposit of antimony on said matrix.

3. The method of making a light-sensitive cathode which comprises depositing a silver layer on the inside of an evacuated glass bulb, oxidizing the surface of said silver layer, exposing said oxidized surface to cesium vapor, heating the bulb to cause some of said cesium to react with some of said silver oxide, introducing antimony hydride into the bulb, and heating the bulb to a temperature which decomposes the antimony hydride.

4. The method of making a light-sensitive cathode which comprises depositing a silver layer on the inside of an evacuated glass bulb, oxidizing the surface of said silver layer, exposing said oxidized surface to cesium vapor, heating the bulb to cause some of said cesium to react with some of said silver oxide, introducing antimony hydride

into the bulb, and heating the bulb to a temperature of 150° to 200° C.

5. The method of forming a layer of antimony which comprises depositing a layer of silver on the inside of an evacuated glass bulb, and heating the layer of silver in the presence of antimony hydride to decompose the antimony hydride and deposit a layer of antimony on said silver layer.

6. The method of forming a layer of antimony which comprises depositing a layer of silver on the inside of an evacuated glass bulb, heating the layer of silver in the presence of antimony hydride to decompose the antimony hydride and deposit a layer of antimony on said silver layer, and depositing a layer of cesium on said layer of antimony.

7. The method of making a light-sensitive cathode which comprises depositing a layer of silver on a portion of the inside surface of an evacuated glass tube, oxidizing the surface of said silver layer, exposing said oxidized silver layer to antimony hydride gas, and heating said layer to decompose said gas.

8. The method of making a light-sensitive cathode which comprises depositing a layer of silver on a portion of the inside surface of an evacuated glass tube, oxidizing the surface of said silver layer, exposing said oxidized silver layer to antimony hydride gas, heating said layer to decompose said gas, and exposing said layer of antimony to cesium vapor to form a layer of cesium thereon.

9. The method of forming a metallic layer as a component part of a light-sensitive electrode which comprises evacuating a container, introducing into said container a gaseous hydride of a metal of the fourth and fifth groups of the periodic table, and decomposing said hydride to form a deposit of the metal of said hydride on an electrode carrier inside said container.

10. The method of forming a metallic layer which comprises evacuating a container, introducing into said container a gaseous hydride of a metal of the fourth and fifth groups of the periodic table, decomposing said hydride to form a deposit of the metal of said hydride on an electrode carrier inside said container, and introducing an alkali metal into said container in the form of a deposit on said deposit of metal.

11. The method of forming a metallic layer which comprises evacuating a container, introducing into said container a gaseous hydride of a metal of the fourth and fifth groups of the periodic table, and producing an electric discharge within said container to decompose said hydride to form a deposit of the metal of said hydride on an electrode carrier inside said container.

12. The method of forming a metallic layer which comprises evacuating a container, introducing into said container a gaseous hydride of a metal of the fourth and fifth groups of the periodic table, and heating an electrode carrier inside said container to decompose said hydride to form a deposit of the metal of said hydride on said electrode carrier.

13. The method of forming a metallic layer which comprises evacuating a container, introducing into said container a gaseous hydride of a metal of the fourth and fifth groups of the periodic table, heating an electrode carrier inside said container to decompose said hydride to form a deposit of the metal of said hydride on said electrode carrier, and introducing an alkali

metal into said container in the form of a deposit on said deposit of metal.

14. The method of forming a metallic layer which comprises evacuating a container, introducing into said container a gaseous hydride of a metal of the fourth and fifth groups of the periodic table, producing an electric discharge within said container to decompose said hydride to form a deposit of the metal of said hydride on an electrode carrier inside said container, and introducing an alkali metal into said container in the form of a deposit on said deposit of metal.

15. The method of forming an electrode which comprises forming intimate layers of an alkali metal and another element within an evacuated container, the layer of said other element being formed by introducing into said container a gaseous hydride of an element of the fourth and fifth groups of the periodic table and decomposing said hydride to form the said layer of said element.

16. The method of making a light sensitive cathode which comprises forming a light sensitive layer of cesium, and heating said layer in the presence of antimony hydride gas to a temperature sufficient to decompose said antimony

hydride to form a deposit of antimony on said layer.

17. The method of making a light-sensitive cathode which comprises forming a layer of silver on the inside wall of a vacuum container, oxidizing the surface of said silver, forming a composite layer comprising antimony and caesium in intimate contact with each other on said oxidized surface by introducing antimony hydride gas in said container and decomposing the gas by heating the wall on which the silver is deposited to 150° to 200° C. and by depositing the caesium from caesium vapor, said steps of depositing antimony and caesium being performed one after the other.

18. The method of making a light-sensitive cathode which comprises depositing caesium on oxidized silver, heat treating said caesium, silver and silver oxide to form a matrix which is sensitive to light, and further heating said matrix in the presence of a gaseous hydride of a metal of the fourth and fifth groups of the periodic table to a temperature sufficient to decompose said hydride to form a deposit of said metal on said matrix.

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