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METHOD OF MAKING A BIALKALI PHOTOCATHODE WITH IMPROVED SENSITIVITY AND HIGH TEMPERATURE OPERATING CHARACTERISTICS

United States Patent 3838304

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A bialkali photocathode is made by a series of alternate evaporations of antimony, sodium and potassium. The disclosure includes a photocathode made by the method described.

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US Patent References:

[ELECTRON EMISSIVE DEVICE](#)[INCORPORATING A SECONDARY](#)[ELECTRON EMITTING MATERIAL OF](#)[ANTIMONY ACTIVATED WITH](#)[POTASSIUM AND CESIUM](#)

Sommer - August 1973 - 3753023

[METHOD OF MAKING A MULTIALKALI](#)[PHOTOCATHODE WITH IMPROVED](#)

SENSITIVITY TO INFRARED LIGHT AND
A PHOTOCATHODE MADE THEREBY

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Claims:

What I claim is

1. Method of making a photocathode, comprising in order:
2. The method defined in claim 1 and wherein said step of forming said base layer includes:
3. The method defined in claim 1 and wherein said substrate is maintained at a temperature of between 200°C. and 250°C. during said steps b through g.

4. The method defined in claim 1 and wherein said sensitizing includes:
5. The method defined in claim 4 wherein step 1 is performed at the intermediate temperatures of: 200°C., 190°C., 180°C., and 170°C.
6. An electron emissive photocathode made by the method defined in claim 1.
7. An electron emissive photocathode made by the method defined in claim 2.
8. An electron emissive photocathode made by the method defined in claim 3.
9. An electron emissive photocathode made by the method defined in claim 4.
10. An electron emissive photocathode made by the method in claim 5.

Description:

BACKGROUND OF THE INVENTION

This invention relates to the art of making photoemitting surfaces. A previous type of photoemitting surface is a semitransparent multialkali photocathode such as described in U.S. Pat. Nos. 2,770,561 to A. H. Sommer and 3,372,967 to F. R. Hughes. Generally, photocathodes of this type which have been sensitized with cesium (cesiated photocathodes) have substantially higher sensitivities of response than non-cesiated photocathodes. However, such cesiated photocathodes have been found inadequate for certain applications. For example, photomultiplier tubes having cesiated photocathodes, have been used for scintillation counting, in applications, such as, for example, geophysical exploration in which the ambient temperature of operation approaches 150°C. At such temperatures, the cesiated photocathode appears to decompose and the expected useful life of the device is severely restricted. Moreover, high temperature operation in general, above 85°C., of conventional photomultiplier tubes with non-cesiated photocathodes, tends to make the tube extremely sensitive to higher operational voltages, which, if applied to the device are known to cause spurious scintillation counts, and general instability of the processed signal due to regenerative effects within the tube. Photocathodes are desired which exhibit improved sensitivity and high temperature operating characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIG. 2 is a sectional view of a phototube having a photocathode made by the method of FIG. 1.

FIG. 3 is a graph comparing the spectral response of the photocathode made by the present method.

DESCRIPTION OF THE PREFERRED EMBODIMENTS GENERAL TUBE STRUCTURE AND PROCESSING EQUIPMENT

FIG. 1 is a flow chart of the steps used for practicing a preferred embodiment of the novel method. By these steps, a phototube 26, shown in FIG. 2, is provided with an improved bialkali photocathode surface 28 having improved sensitivity and improved high temperature operating characteristics. The tube 26 has a tubular glass wall section 30. One end of the wall section 30 is closed by a glass faceplate 32, which is flat on the outside and concave on the inside with a radius of curvature of about 1.9 inches. The other end of the wall section 30 is closed by a stem 34 having a number of electrical lead-in pins 35. Along the interior of the tube are spaced a series of dynodes 36. Near the dynodes 36 are spaced two channels 38, 40 of tantalum foil containing, respectively, substances for evaporating potassium and sodium. The potassium channel 38 contains potassium chromate, zirconium, and tungsten. The sodium channel 40 contains sodium chromate, zirconium, and tungsten. A resistance filament 42 situated near the faceplate has two antimony alloy beads 43 attached to it for evaporating antimony. The channels 38, 40 and the filament 42 are suitably connected by internal leads to electrical current sources through the pins 35 so that they can be activated separately by electrical resistance heating.

Light transmission through the faceplate 32 is monitored by directing light from an incandescent tungsten filament at an angle through the faceplate 32 and wall 30 to a light sensing tube. Photoemissive sensitivity of the interior faceplate surface is monitored by collecting the emitted electrons with one or more of the internal electrodes, such as the electrode 44. For such collection, the electrode 44 is impressed with a voltage of between 50 and 150 volts positive with respect to the photocathode 28 through a lead 46 going from a lead-in pin 35 to the photocathode 28 and through lead 48, also from a lead-in pin 35, to the electrode 44. The sensitivity is expressed in terms of microamperes of emitted electron current per lumen of light incident on the photocathode 28.

During processing, the tube is continuously evacuated through exhaust tubulation 50 in the stem and preferably maintained at a vacuum of 10^{-6} torr. In general, vacuums of 10^{-5} torr to 10^{-7} torr are considered suitable. The tubulation leads directly to a titanium evaporation ion vacuum pump having a pumping speed of about 250 liters per second.

Processing Steps

Referring now to FIGS. 1 and 2, processing steps for preparing the photoemissive surface are as follows with ranges of parameters given in parentheses immediately after a preferred value:

1. The tube is baked for about 5 (3 to 6) hours at about 400°C. to clean and degas the interior.
2. After the tube is cooled to room temperature, the filament 42 is heated and antimony is evaporated from the antimony leads 43 until the light transmission of the faceplate 32 is about 70 percent (65 -75 percent). The transmission of the faceplate 32 before evaporation is defined as 100 percent.
3. The tube 26 is placed in an oven which has been preheated to about 190°C. (160°C.-200°C.).
4. While the tube 20 is heating to oven temperature, the channels 38, 40 are preheated to clean and degas them. Then the potassium channel 38 current is set so that the channel will release potassium vapor when the faceplate 32 temperature reaches about 190°C. (160°C.-200°C.).
5. Potassium is evaporated on the antimony layer until maximum sensitivity is reached. The maximum is generally about 1.5 (1-5) microamperes per lumen.
6. The oven temperature is increased to about 210° (200°-250°)C. and the sodium channel 40 current adjusted so that sodium vapor will be released when the faceplate 32 reaches about 210° (200°-250°)C.
7. Sodium is evaporated until a substantially maximum sensitivity is reached. The maximum is generally about 35 (20-60) microamperes per lumen.
8. Antimony is evaporated until a maximum sensitivity is passed at about 40 (30-60) microamperes per lumen and sensitivity has decreased to a substantially fixed value between 30 and 50 percent of that maximum.
9. Potassium is evaporated until a maximum sensitivity is reached.
10. Antimony is evaporated until a maximum sensitivity is passed and sensitivity has decreased to a substantially fixed value between 30 and 50 percent of that maximum.
11. Sodium is evaporated until a maximum sensitivity is reached.
12. Antimony is evaporated until a maximum sensitivity is passed and sensitivity decreases to a substantially fixed value between 30 and 50 percent of that maximum.

13. Potassium is evaporated until the sensitivity passes a maximum and decreases to about 60 to 70 percent of that maximum.
14. The tube 26 is baked at 220°C. (210°-250°) until a new maximum sensitivity is reached.
15. The tube is slowly cooled at a rate of about 4° (2°-10°)C. per minute.
16. When the tube has reached 200°C., step 13 is repeated.
17. When the tube has reached 190°C., step 13 is repeated.
18. When the tube has reached 180°C., step 13 is repeated.
19. When the tube has reached 170°C., step 13 is repeated.
20. With the photocathode 28 completed, the tube 26 is slowly cooled to room temperature at a rate of about 4°C. (2°-10°) per minute and removed from the oven. After the exhaust tubulation 47 is sealed off, the tube 26 is operative.

GENERAL CONSIDERATIONS

Techniques for monitoring sensitivity and light transmission during processing as well as for evaporating photocathode materials are further described, for instance in the U.S. Pats. to A. H. Sommer and F. R. Hughes, referenced above, and also in U.S. Pat. Nos. 2,914,690 to A. H. Sommer and 2,676,282 J. J. Polkosky.

Light transmission of the faceplate, for the purpose of monitoring the thickness of the antimony layer, is measured by conventional means. Its measurement is not critical.

Sensitivity of the evaporated layers is measured separately for visible light and blue light. It is desirable to be able to measure both visible and blue sensitivity almost simultaneously so that the photocathode may be processed to give a favorable relative value of both sensitivities. For this purpose, two separate incandescent tungsten light sources are used, each about 0.1 lumen in output and operated at approximately 2,854°K. The sources are spaced apart a short distance from the faceplate. Interposed between one source and the faceplate is a glass light filter apssing primarily blue light. For instance, a Corning CS5-58 bandpass filter passing approximately 20 percent at 380 nanometers wavelength, 40 percent at 400 nanometers and about 20 percent at about 440 nanometers is suitable. The sensitivity of the photocathode to both visible and blue light may be measured separately and almost simultaneously by manual switching from one light source to the other.

The rates of evaporation of the evaporated elements are limited by the speed and accuracy at which the sensitivity can be monitored. A relatively slow evaporation rate makes the monitoring less critical.

Maximum sensitivity is determined from the first derivative of the increasing sensitivity function. The first derivative takes a zero value at the peak of a sensitivity curve. A computer can be used to continually calculate the derivative of the sensitivity function, or a human operator can simply observe a plotted curve of the sensitivity and note when its tangent is horizontal to indicate a peak. However, in the course of an alkali metal evaporation there are often a number of spurious peaks in the sensitivity which are of lower values than a later highest maximum peak. In order to discriminate these spurious peaks from the maximum it is necessary to continue evaporation until the sensitivity has fallen to a value of about 80 percent of the sensitivity at the peak in question. It may then be assumed that the peak was the highest attainable for that evaporation and is therefore a maximum. A reference herein to evaporation of an alkali metal to a "substantially maximum sensitivity" means an evaporation past the maximum to at least 15 percent of the sensitivity at the maximum. Excess alkali metal evaporated after a maximum is reached generally evaporates off again during subsequent baking.

During certain evaporation steps of the novel method, the magnitudes of sensitivities (given as a percentage of each maximum sensitivity), once established, tend to change. Wherever such changes are critical and require reevaporation to establish a fixed percentage of sensitivity relative to the

maximum sensitivity achieved, the terminology specifies a "substantially fixed" percentage. A sensitivity is considered "substantially fixed" whenever its magnitude remains relatively stable, within the ranges specified, over a period of 5 to 10 seconds.


While in the preferred embodiment evaporation was done by heated channels inside the tube, external processing, such as is described in the aforementioned patents, can also be used to practice the novel method. Thus, the novel method can be used to form bialkali photocathodes having improved response in tubes, such as image tubes for which internal processing may not be as useful as external processing because of possible contamination of electrodes.


The novel method results in a bialkali photocathode having improved high temperature operating characteristics and improved sensitivity over similar photocathodes processed by conventional methods. The curves 52 and 54 in FIG. 3 represent the approximate response characteristics of two competing photocathodes made by present methods for high temperature operation and utilizing the same materials (Sb, Na, and K). Curve 56 represents the approximate response characteristic of a photocathode made by the novel method. It is seen that the sensitivity is considerably higher over the entire response region and extends as far as 700 nanometers. Moreover, photomultipliers utilizing the novel photocathodes have been found to maintain stable response characteristics even at temperatures approaching 150°C. When used for high temperature scintillation applications at temperatures approaching 150°C., these photomultipliers exhibit a counting ability relatively insensitive to operating voltages as high as 2,000 volts, without significant spurious scintillation counts being generated. Also, at such operating temperatures, the photocathode did not appear to decompose and the expected useful life of the device was greatly improved.


Although the novel photocathode is made by a series of evaporations, it is presently not possible to define precisely the actual finished structure, since there is an alloying of the evaporated substances. The chemical compositions of the various thickness portions of the photocathode are not known. Therefore, the novel photocathode can presently be best described as the product of the novel method.


The novel photocathode may be used as a photoemitter on an opaque substrate or as a secondary electron emitting surface.

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