United States Patent

Stoudenheimer et al.

[15] **3,697,794**

[45] **Oct. 10, 1972**

[54] **PHOTOCATHODE COMPRISING LAYERS OF TIN OXIDE, ANTIMONY OXIDE, AND ANTIMONY**

[72] Inventors: **Richard G. Stoudenheimer,** Lancaster; **Rodger P. Dourte,** Manheim, both of Pa.

[73] Assignee: **RCA Corporation**

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Related U.S. Application Data

[63] Continuation of Ser. No. 622,293, March 10, 1967, Pat. No. 3,436,164.

[52] **U.S. Cl.** **313/94,** 117/217, 313/102

[51] **Int. Cl.**.....**H01j 39/06,** H01j 39/00

[58] **Field of Search** ....313/65, 94, 102, 66; 117/215, 117/217 A

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Primary Examiner—Robert Segal
Attorney—Glenn H. Bruestle

[57] **ABSTRACT**

In a photocathode comprising a substrate of tin oxide having thereon a photoemissive coating including antimony, a layer of antimony oxide is interposed between the tin oxide substrate and the photoemissive coating.

5 Claims, 5 Drawing Figures

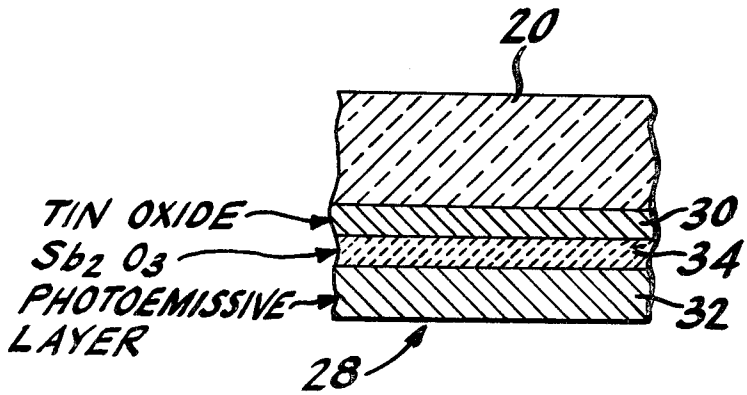


Fig. 1.

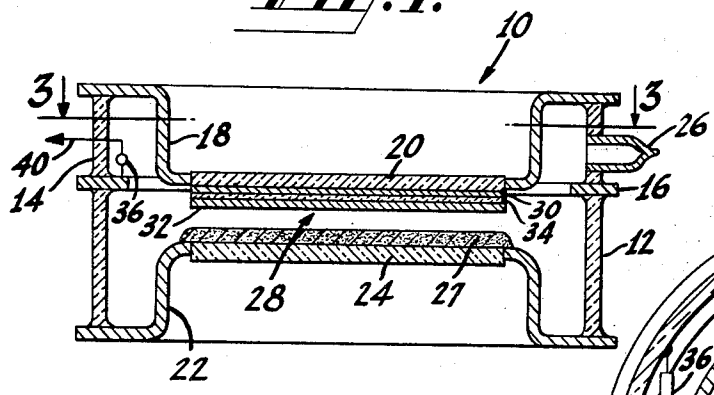


Fig. 2.

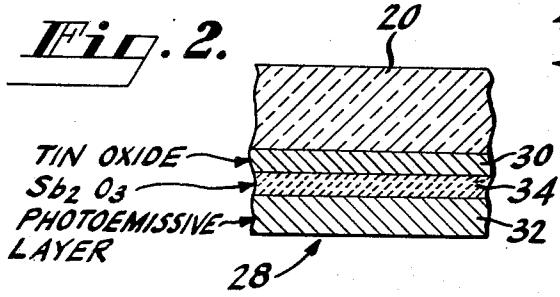
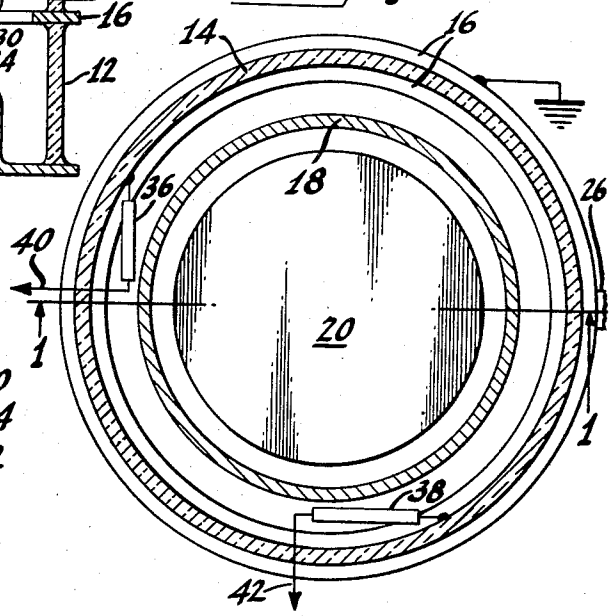


Fig. 3.



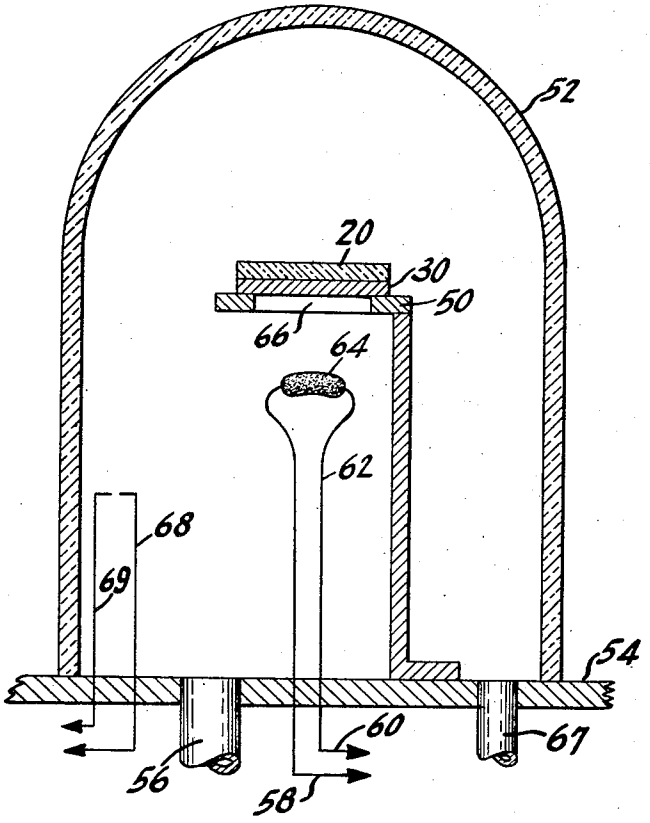


Fig. 5.

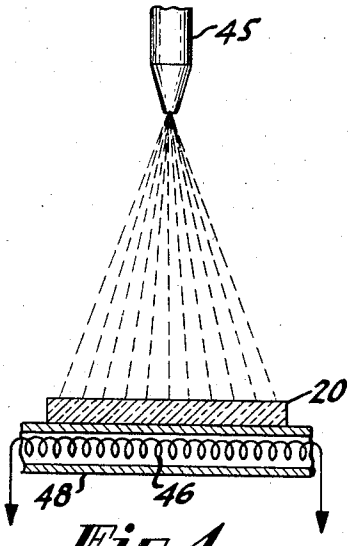


Fig. 4.

Inventors:
RICHARD G. STOUDENHEIMER &
ROGER P. DOURTE

By L. A. Larsen
Attorney

PHOTOCATHODE COMPRISING LAYERS OF TIN OXIDE, ANTIMONY OXIDE, AND ANTIMONY

RELATED APPLICATION

This is a continuation of U.S. Patent application Ser. No. 622,293 filed Mar. 10, 1967 now U.S. Pat. No. 3,436,164.

BACKGROUND OF THE INVENTION

1. Field of the Invention

Our invention relates to photocathodes of the type including antimony and one or more alkali metals, and particularly concerns a cathode of this type that is characterized by reduced lateral resistance without adversely affecting its sensitivity, and to a method of making the same.

2. Description of the Prior Art

Some photocathodes that include an initial deposit of antimony and one or more alkali metals comprise the antimony-cesium photocathode, the antimony-potassium-cesium photocathode, and the antimony-potassium-sodium-cesium photocathode. Photocathodes of this type find use in a number of applications including image tubes, phototubes and camera tubes.

Photocathodes of this type are characterized by relatively high resistivity. The antimony-cesium photocathode has a resistivity near 10^6 ohms per square; the resistivity of antimony-potassium-cesium photocathode is near 10^7 ohms per square; and the resistivity of the antimony-potassium-sodium-cesium photocathode is near 10^5 ohms per square. The term "ohms per square" is defined in U. S. Pat. No. 2,849,538 issued to N. Pritikin on Aug. 26, 1958 as "the resistance of a square area to current passing between opposed edges of such square, the size of the square being of no consequence since the width of the current path varies directly with the length of the current path, and is, in fact, equal thereto."

When a photocathode is deposited directly upon an insulating substrate, such as a glass faceplate of a tube, it is usually caused to overlap, at its periphery, a conductive layer connected to a source of suitable electrical potential, such as ground. Such conductive layer serves to replenish emission electrons lost by the photocathode in operation. However, because of the relatively high lateral resistivity of the photocathode, several problems arise.

One of these problems presented by the relatively high lateral resistivity of the photocathode concerns a relatively large voltage gradient produced across the photocathode in operation. This voltage gradient distorts an electrostatic focusing field adjacent to the photocathode so as to adversely affect the focusing function of such field with consequent distortion and loss of resolution in the electron image. Tube types in which electron focusing is critical and in which the voltage gradient referred to is particularly objectionable are image tubes, photoemissive camera tubes and phototubes.

The magnitude of the aforementioned voltage gradient across the photocathode can be reduced to acceptable limits by reducing emission from the photocathode. However, such reduction in emission requires a reduction in the light magnitude to which the photocathode is exposed. Such reduction in light adversely affects the level of the output screen brightness

in the case of image converter tubes, or the magnitude of the output signal in the case of phototubes or camera tubes.

A particular problem resulting from the relatively high transverse or lateral resistivity of photocathodes of the type under consideration, is evidenced in tube operations where the light input to the tube and the photoemission from the photocathode is a high intensity pulse. In these applications there is a demand during each pulse for a current throughout the photocathode to replenish the emitted electrons. To avoid an intolerable change in voltage on the photocathode during the pulse and a consequent defocussing of the electron image, the resistance of the photocathode must be sufficiently small so that the product of peak pulse current and cathode resistance is less than the maximum tolerable voltage change on the photocathode.

In another type of application a voltage pulse is applied to electrodes adjacent to the photocathode so that emission current may be withdrawn from the photocathode only during a very short selected time interval. Because the cathode and any adjacent electrodes form a capacitor a current must flow into the capacitor (through the photocathode) wherever the potential difference between the two electrodes is changed. While the capacitor charging current is flowing through the photocathode, the potential at the center is different from the applied voltage at the edge of the photocathode. Consequently for a short time interval after the adjacent electrode voltage is pulsed, the center of the photocathode is subjected to a transient defocusing voltage pulse which decays to the applied DC voltage at the edge of the cathode with a decay time constant equal to RC where R is the effective cathode resistance and C is the effective capacitance between the central area of the photocathode and the adjacent electrode to which the pulse voltage is applied. The time duration of the voltage pulse which draws electrons from the photocathode is called pulse width, and in some cases exposure time. Where C is in the range of 10 to 30 picofarads and pulse widths are in the range of 10 nanoseconds, the effective resistance of the photocathode should be less than 1000 ohms per square.

Prior attempts to solve the problem of relatively high lateral resistivity of photocathodes of the type made by initially depositing antimony on a substrate, have involved the provision of a conducting substrate for the photocathode. However, such attempts have not been successful. The only known conductive material that possesses the required lateral conductivity when applied to a thinness for acceptable light transmission, is tin oxide. However, it has been found that tin oxide poisons a photocathode of the type requiring an initial deposit of antimony followed by processing temperatures in excess of about 180° C. during manufacture, as in the case of the photocathodes referred to before herein. Such poisoning of the photocathode appreciably reduces its sensitivity to an unacceptable level.

SUMMARY OF THE INVENTION

In accordance with the present disclosure, the foregoing problems are avoided. Desired low lateral resistivity of a photocathode formed by first deposition

antimony, is achieved by a novel substrate comprising a layer of tin oxide (Tic) having thereon a layer of antimony oxide (Sb_2O_3). When a photocathode is formed on such substrate by first depositing antimony, the lateral resistivity of the photocathode is as low as 100 ohms per square. The layer of antimony oxide deposited directly on the tin oxide layer, effectively isolates the photocathode from the tin oxide layer and prevents a poisoning of the photocathode by the tin oxide.

Photocathodes made in accordance with the present disclosure are therefore characterized by a sufficiently low lateral resistivity so as to avoid any appreciable voltage gradient across the photocathode with its attendant adverse effects on focusing, and so as to have a sufficiently fast electron replenishment for advantageous use of the photocathode in relatively fast pulse applications. These advantages are realized with an appreciable increase in the sensitivity of the photocathodes under consideration. Such increase in sensitiviy is from 10 microamperes per lumen without the antimony oxide layer, to from 40 to 140 micro-amperes per lumen with the antimony oxide layer.

Another advantageous effect produced according to the present disclosure by a layer of antimony oxide over a layer of tin oxide, resides in the fact that the resistivity of the tin oxide layer is reduced by a value of from about 5 to about 10 percent. Such reduction in lateral resistivity of the tin oxide is accompanied by several advantages. It permits a reduction in the thickness of the tin oxide layer without sacrificing conductance, with attendant increase in light transmission. It may be desirable to employ a tin oxide layer of a conventional thickness in which event the reduced resistivity thereof is accompanied by the advantages of contributing to further decrease in the voltage gradient across a photocathode, and a more rapid replenishment of emission electrons in pulse application.

The reason for the decrease in resistivity of the tin oxide layer when placed in contiguous relation with respect to a layer of antimony oxide is not clearly understood, particularly since antimony oxide is characterized by an appreciably higher resistivity than tin oxide. However, tests have revealed that a 5 to 10 percent reduction in resistivity of a tin oxide coating occurs when a layer of antimony oxide is placed thereover. One explanation may be that an interface is formed between the tin oxide and antimony oxide layers of such low resistivity that the interface in combination with the tin oxide layer, is of lower resistivity than the tin oxide layer alone. Another way of looking at it is that charge carriers become highly concentrated in one of or both the tin oxide layer and the antimony oxide layer near the common interface boundary of the two layers. This results in a lowered resistivity there.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing to which reference is now made for an exemplary embodiment of the invention:

FIG. 1 is a section of a proximity-focus type of image tube having a photocathode in accordance with the present disclosure;

FIG. 2 is an enlarged fragmentary sectional view of the photocathode and its supporting substrate shown in FIG. 1;

FIG. 3 is a transverse sectional view taken along the line 3—3 of FIG. 1;

FIG. 4 is a sectional view of a photocathode substrate and illustrates a step of coating a surface of the substrate with tin oxide while heating the substrate; and

FIG. 5 is a sectional and partly schematic view of apparatus that may be used in forming a layer of antimony oxide over a tin oxide coated substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Photoemissive cathodes of the type in which a photoemissive layer is formed by first depositing a layer of antimony on a substrate and in connection with which the subject matter disclosed herein is useful are of many kinds and find many applications such as in image tubes, photoemissive camera tubes and phototubes. However, in the interests of simplicity the embodiment of the disclosure selected for illustration comprises a proximity-focus type of image tube **10** shown in FIG. 1 and having a photoemissive layer of antimony, potassium and cesium.

The tube **10** includes a cylindrical side wall formed by two cylinders **12, 14** having adjacent ends sealed hermetically to a metal ring **16**. The cylinders **12, 14** are made of insulating material such as glass or ceramic.

To the free end of cylinder **14** is hermetically sealed a reentrant structure comprising a metal flange **18** and a transparent glass faceplate **20** hermetically sealed to the flange **18**. To the free end of cylinder **12** is hermetically sealed another reentrant structure comprising a metal flange **22** defining an opening across which is sealed a transparent glass faceplate **24** in vacuum tight manner. The envelope defined by cylinders **12, 14**, flanges **18, 22** and faceplates **20, 24**, is suitably evacuated through an exhaust tubulation **26** which is shown closed. The tube **10** may have a length of **2.6** inches and a diameter of 2.6 inches.

Upon the inner surface of the faceplate **24** is a phosphor screen **27** comprising a relatively thin conductive electrode made of a material such as aluminum or tin oxide and a layer of phosphor thereover that responds in light to electron impingement thereon. The phosphor may comprise silver activated zinc sulfide.

The inner surface of the faceplate **20** supports a photocathode **28**. As shown more clearly in FIG. **2**, the photocathode **28** comprises several layers. A first layer **30** directly engaging the faceplate **20** comprises tin oxide. The thickness of layer **30** may be from 0.1 to 1.0 micron. An outer photoemissive layer **32** comprises antimony, potassium and cesium and has a thickness of about 500 Angstroms.

Photoemissive cathodes such as the photoemissive cathode **28**, including antimony are made by initially depositing a layer of antimony on a substrate and sensitizing the antimony layer by one or more layers or alkali metals. When the initial antimony layer is deposited directly on tin oxide and subsequent processing temperatures are in excess of about 180° **75** C., it is found that the tin oxide poisons the photocathode by reducing its sensitivity to unacceptable levels.

In order to prevent such poisoning of the photocathode, there is interposed, in accordance with

the present disclosure, a layer **34** of antimony oxide between the tin oxide layer **30** and the photoemissive layer **32**. The antimony oxide layer **34** preferably comprises several sublayers of this material. For best performance the antimony oxide layer **34** may comprise from **3** to **5** such sublayers. It is believed that the aforementioned best performance when multiple sublayers are applied, is due to a reduction in pin holes in the resultant antimony oxide layer **34** effected by the multiple application of the antimony oxide. While the presence of such pin holes in the antimony oxide layer **34** adversely affects the performance of the photocathode, such adverse performance is appreciably better than it would be if the intermediate layer **34** of antimony oxide were completely eliminated. Therefore, while the formation of the layer **34** in a single application is not as advantageous as when the layer is formed in a plurality of the applications, the single layer may be satisfactory in certain applications. However, increasing the number of such layer applications beyond **5** does not contribute any increased advantage. Of course, where a single layer is used, its thickness should be equal substantially to the combined thickness of the sublayers. Such combined thickness may be about from 100 to 300 Angstroms.

In order to realize a proximity-focus of photo-electrons from the photocathode **28** the free surfaces of the photocathode **28** and the phosphor screen **26** should be relatively closely spaced with respect to each other. Such spacing may be about 100 mils.

As shown best in FIG. **3**, the tube **10** also contains two alkali metal generators **36, 38**. Each generator may comprise an elongated metal channel known in the art containing materials from which the desired alkali metal may be generated. In the present example, the channel of generator **36** may contain potassium chromate, aluminum and tungsten, for generating potassium. The channel generator **38** may contain cesium chromate and silicon for generating cesium. When the metal channels are heated as by passing electric current therethrough, the materials therein react to provide the desired alkali metal. For so heating the channels one end of each channel is connected to the metal ring **16** which may be grounded. The other ends of the generator channels **36, 38** are connected by leads **40, 42** to suitable current sources, not shown. Further description of the formation of the several layers of the photocathode **28** including the potassium and cesium layer will be presented in the following.

During operation of tube **10** the photocathode **28** and the phosphor screen **27** are operated at a relatively high voltage difference. The cathode potential may be ground and the phosphor screen voltage may be +15,000 volts. In order to form a nearly closed chamber shielded from the relatively high electrostatic field produced by the aforementioned voltage difference, the ring **16** is positioned substantially in the plane of faceplate **20** and extends inwardly of the tube envelope to partly enclose a space **44** as shown in FIG. **1**. The alkali metal generators **36, 38** are positioned in this space. Such positioning is accompanied by advantages in respect of preserving the generators from unwanted alkali metal generation in response to the aforementioned electrostatic field and preventing undesired effects by the generators upon such field. The spacing between the inner edge of metal ring **16** and a flange **18** should be sufficient to permit vapors generated by the generators **36, 38** to travel freely to the region between the faceplates **20, 24** for deposit on the photocathode **28**. Such spacing may be about from 0.050 to 0.120 inch.

In making the photocathode **28** (FIGS. **1** and **3**) certain layers thereof are formed on the faceplate **20** prior to incorporation of the faceplate in the structure of tube **10**. Such preformed layers comprise the tin oxide layer **30**, the antimony oxide layer **34** and the unoxidized antimony layer incorporated in the photoemissive layer **32**. No strata indentifying the several materials of the photoemissive layer **32** are shown in the drawing since it is not known how these materials are oriented in the layer **32**. It may be that the materials used form into spaced globules or even molecules and they may also chemically combine with each other.

The layer **30** of tin oxide may be formed by spraying a relatively low viscosity solution of tin oxide in alcohol by a spray gun **45** upon one surface of the glass plate **20** as shown in FIG. **4**. In order to contribute to smoothness of the resulting tin oxide layer, the glass faceplate **20** is heated to a temperature of about 500° C. during this spraying step. The heating may be effected by means of a resistive wire structure **46** supported in a recess in a support **48** for the faceplate. The wire structure **46** is connected across a suitable electric current source, not shown. The thickness of the tin oxide coating so formed on a surface of the glass faceplate **20** may be controlled in one of several ways. One way in which the thickness control may be effected, is to spray a given amount of tin oxide solution that has been empirically determined to provide the desired coating thickness of about from 0.1 to 1.0 micron. Another way is to support the glass faceplate **20** in such a manner that light occlusion therethrough may be measured as the spraying operation takes place in the manner described in U. S. Pat. No. 2,676,282 issued to J. J. Polkosky. The spraying of the tin oxide solution upon the faceplate **20** may take place at atmospheric pressure.

After the faceplate **20** has been coated with tin oxide to a thickness of about from 0.1 to 1.0 micron, the faceplate so coated is positioned on a support **50** shown in FIG. **5**, with the faceplate so oriented that the tin oxide layer **30** is on its underside. The support **50** is enclosed by a bell jar **52** made of glass for example, and hermetically sealed to a table **54**. The bell jar **52** is suitably evacuated through an exhaust tubulation **56** to a pressure below 10^{-6} torr.

The terminals **58, 60** of a filament **62** supporting a mass **64** made of a platinum-antimony alloy are connected to a suitable current source not shown for heating the filament **62** to a temperature at which a portion of the antimony from the antimony alloy source **64** vaporizes. In order that the antimony vapors may travel to the faceplate **20** the support **50** is cut away at **66** to expose the tin oxide coated side of the faceplate as shown in FIG. **5**.

Where five applications or sublayers are desired in forming the antimony oxide layer **34** (FIG. **2**) each sublayer of antimony may be applied to a thickness measured by a reduction in light transmission therethrough to a value of 90 percent of the original

light transmission prior to application of the sublayer. After each of the five sublayer applications is completed in accordance with the foregoing, oxygen is admitted into the bell jar **52** through a duct **67** to a pressure of from 0.1 to 1.0 torr, and by means of a glow discharge in the oxygen ambient, the antimony sublayer is oxidized. The glow discharge may be provided by suitably electrically energizing electrodes **68, 69** by a power supply (not shown) of from 400 to 2000 volts at a current of from about 5 to about 50 milliamperes. The power source connected to the electrodes **68, 69** is preferably interrupted to provide from 5 to 15 short duration pulses.

After each antimony subcoating has been applied to the faceplate **20**, and oxidized, the bell jar **52** is pumped out to a pressure below 10^{-6} torr in preparation for the next sublayer of antimony. Antimony oxide layers formed according to the processes described above are necessarily non-porous layers because of the relatively low ambient pressure in which the formation takes place.

After the fifth sublayer of antimony oxide has been formed on the tin oxide coated faceplate **20** to constitute the layer **34** (FIG. **2**) of antimony oxide and after the pressure within the bell jar **52** has been reduced to a value below 10^{-6} torr, a final layer of antimony is deposited on the antimony oxide layer **34** to a thickness determined by a reduction in light transmission of from 50 to 70 percent of the light transmission prior to the application of the final layer of antimony. This final layer of antimony is not oxidized.

Where two sublayers of antimony oxide are desired, each sublayer of antimony is deposited to a thickness determined by a **50%** reduction in light transmission through the coated faceplate. The final layer of unoxidized antimony, however, has the same thickness whether applied over an antimony oxide layer formed by five sublayers or less.

Furthermore, if it is desired that the antimony oxide layer **34** be formed of three or four sublayers, this can be accomplished by determining the thickness of each sublayer by a light transmission reduction intermediate the aforementioned 90 and 50 percent of light transmission. For example, where three layers are used, the thickness of each layer may be determined by a light transmission of 76 percent, while for four sublayers, each sublayer should have a thickness to permit a light transmission of 86 percent.

After application of the final unoxidized layer of antimony for forming a portion of the photoemissive layer **32**, the pressure within the bell jar **52** is reduced to atmospheric and the faceplate **20** having thereon a tin oxide layer, an antimony oxide layer over the tin oxide layer and a layer of unoxidized antimony over the antimony oxide layer, is removed from the bell jar. The exposure of the coated faceplate **20** to air and a sealing of the same to the metal flange **18** of tube **10** do not harm the coatings applied to the faceplate **20** in accordance with the foregoing.

After the coated faceplate **20** is incorporated in the structure of tube **10**, the tube is evacuated to a pressure of about 10^{-8} torr through the exhaust tubulation **26**, and baked at a temperature of from 200° C. to 250° C. for about one and one-half hours. While maintaining a tube temperature of 160° C., the lead **40** is then connected to a current source of about 5 amperes for heating the channel **36** to release potassium therefrom until the sensitivity reaches a first maximum. The lead **42** is then connected to a current source of about 5 amperes for heating the channel **38**, while maintaining tube temperatures aforementioned, to release cesium therefrom until the sensitivity reaches a second maximum. Further evolution of potassium and cesium is terminated by disconnecting leads **40, 42** from the current sources referred to. The tube **10** is then baked at a temperature of at least 160° C. until the photosensitivity of the photoemissive layer **32** reaches another peak. The tube is then cooled and ready for use.

We claim:

1. An electron tube comprising:
   a. a transparent insulating substrate,
   b. a photocathode of reduced lateral resistance on said substrate, said photocathode comprising:
      1. a layer of tin oxide on said insulating substrate,
      2. a layer consisting of non-porous antimony oxide on said tin oxide layer, and
      3. a photoemissive layer including antimony on said antimony oxide layer.

2. The tube defined in claim **1** and wherein said tin oxide layer has a thickness of about 0.1 to 1.0 micron and said layer of antimony oxide has a thickness measured by light transmission of the unoxidized antimony that is about **50%** of that through said insulating substrate and said tin oxide layer prior to application of said layer of antimony oxide.

3. A photocathode of reduced lateral resistance comprising:
   a. a substrate comprising tin oxide,
   b. a photoemissive layer over said substrate and comprising sensitized antimony, and
   c. a layer consisting of non-porous antimony oxide about 100 to 300 Angstroms thick intermediate said tin oxide substrate and said photoemissive layer, for isolating said photoemissive layer from poisoning effects of said tin oxide substrate.

4. An electrode for an electron tube comprising a structure including:
   a. a tin oxide substrate,
   b. a layer of antimony oxide about 100 to 300 Angstroms thick on said substrate, and
   c. a layer of photoemissive material on said antimony oxide layer, said structure having a resistivity that is from 5 to 10 percent less than the resistivity of the tin oxide substrate alone.

5. The electrode defined in claim **4** having a photoemissive layer containing antimony on said antimony oxide.

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