United States Patent

[11] 3,627,575

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[21] Appl. No. **775,418**
[22] Filed **Nov. 13, 1968**
[45] Patented **Dec. 14, 1971**

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[54] **PROCESS FOR FORMING PHOTOEMISSIVE SURFACES**
11 Claims, 4 Drawing Figs.

[52] **U.S. Cl.** **117/212,**
29/592, 117/107, 117/211, 117/217, 117/219
[51] **Int. Cl.** **B44d 1/18**
[50] **Field of Search** 117/212,
217, 219, 107, 210, 211; 29/592

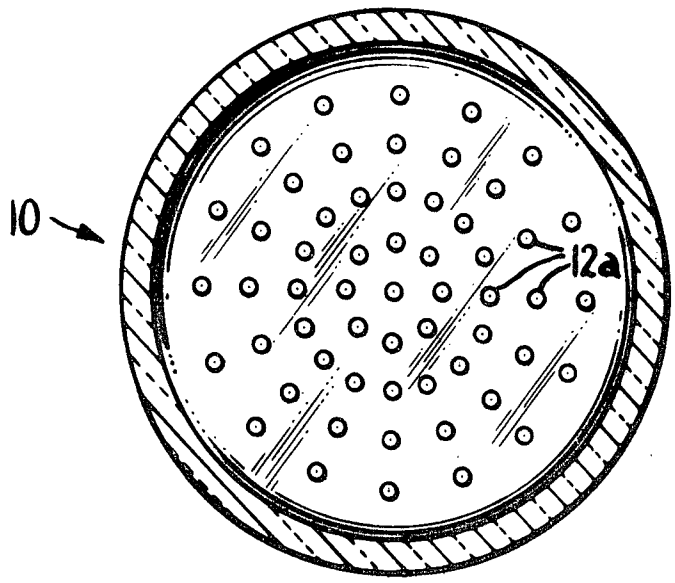
[56] **References Cited**

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3,498,834	3/1970	Rome et al.	117/217
3,508,477	4/1970	Groo	117/217 UX

Primary Examiner—Alfred L. Leavitt
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Attorney—Brumbaugh, Free, Graves & Donohue

ABSTRACT: Photoemitters are formed on selected areas of a substrate or on a normally inaccessible substrate by coating the selected areas or substrate with a layer of a nucleating material having a higher heat of sublimation than the photoemitter base layer (e.g., nichrome if the latter base layer is antimony). The substrate with the selected nucleated areas thereon is sealed into an evacuated envelope and is baked out to remove foreign gases. Antimony is then evaporated inside or caused to diffuse into the envelope at an elevated temperature such that it is deposited only on the nucleated surfaces. An alkali metal (e.g., caesium) is then evaporated within the envelope and it adheres only to the areas where the antimony has previously been deposited, forming photoemitters on the selected area or areas on the substrate.



PATENTED DEC 14 1971

3,627,575

SHEET 1 OF 2

FIG. 1

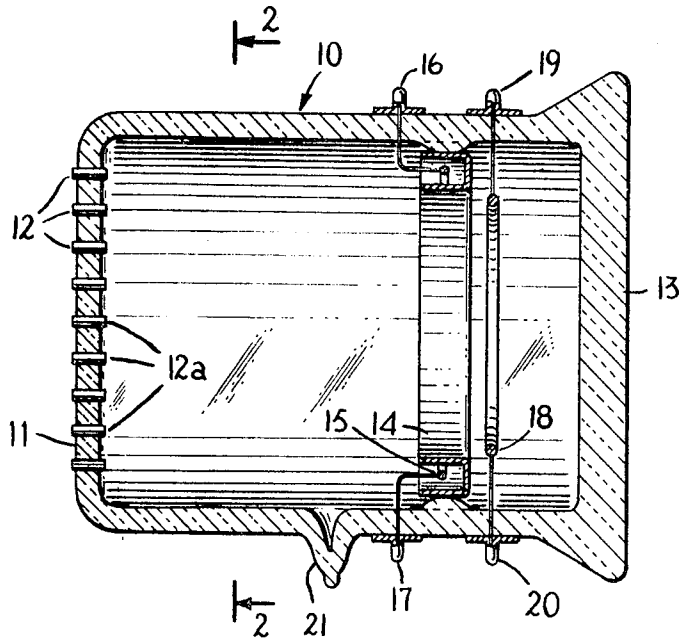
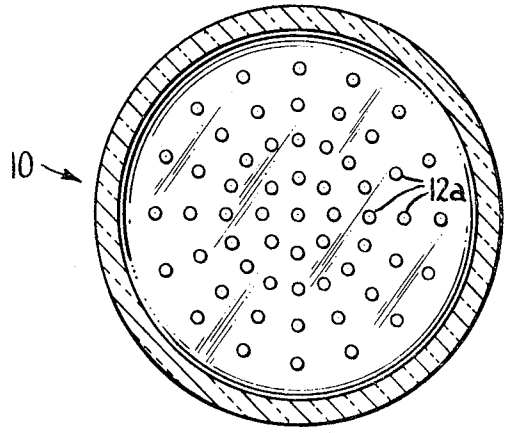


FIG. 2



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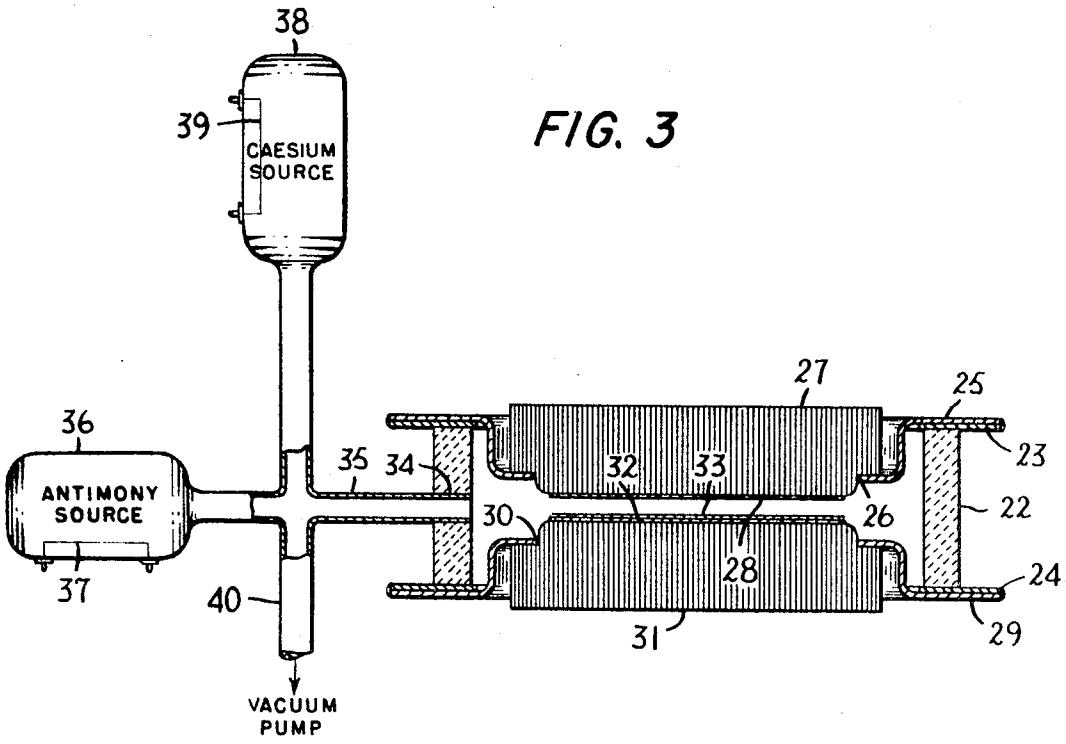
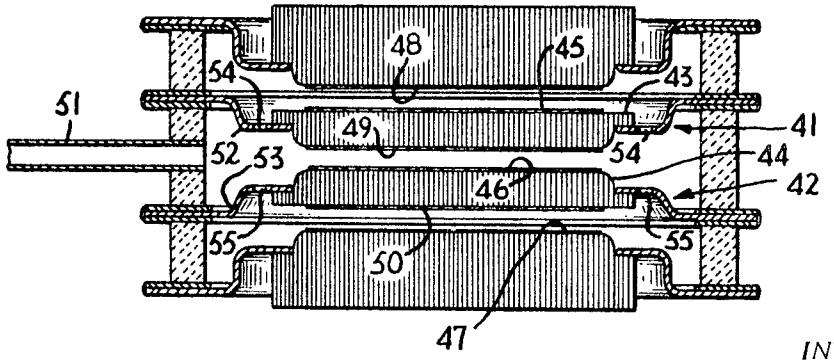


FIG. 3

FIG. 4



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PROCESS FOR FORMING PHOTOEMISSIVE SURFACES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photoemitters and more particularly to a new and improved process for the selective deposition and formation of photoemitters in a simple and highly effective manner.

2. Description of the Prior Art

Photocathodes intended for use in very small interelectrode spaces have been formed heretofore by one of two techniques, viz pre-evaporation or transfer. Pre-evaporation can be effected in several different ways. One way involves depositing the entire photocathode, normally a pure metal (gold, platinum, tungsten, nickel, etc.), and then assembling and evacuating the device. However, the photocathodes so formed are of limited utility because they are only sensitive to ultraviolet wavelengths and their sensitivities are characterized by low quantum efficiencies e.g., 10^{-3} to 10^{-5}).

In the second way, a base photocathode material such as antimony is pre-evaporated in one vacuum system on the surface on which a photoemitter is to be formed. Thereafter, it is exposed to atmospheric conditions and assembled into the final device. Subsequently, the base material is exposed to cesium or other alkali metal vapor and a photoemitter is created. While it is possible to produce photocathodes having a response in the visible spectrum with this technique, exposure of the pre-evaporated base material to airborne debris unfortunately degrades the resulting photoemitter so that the sensitivities are low. Furthermore, this technique is not adaptable to the formation of the higher sensitivity multialkali photocathodes which require more than one antimony deposition during the processing.

Photocathode transfer techniques, on the other hand, permit the formation of all types of photoemitters using conventional deposition procedures. After they are formed in a host chamber, they must be removed and transferred, and vacuum sealed to the final device. All this must be done in a high vacuum system. This method of fabrication is at best very complex and expensive, and is not easily adapted to quantity production, especially where more than one photocathode is required in a single unit.

It has also been proposed to deposit antimony and/or manganese by means of a sliding side arm adapted to introduce a suitable source into a narrow space, and then retract it after the deposition is complete. This technique has been successfully employed in electrostatically focused image intensifiers, but is not suited to proximity focused devices for three reasons. First, it is impossible to get a uniform deposition of any significant size in such a small space; secondly, it is very difficult to keep the evaporants from getting on the output screen; and thirdly, because of the short source to substrate distances, the heat generated by the evaporator during the deposition adversely affects the output screen and the deposition process.

SUMMARY OF THE INVENTION

It is an object of the invention, accordingly, to provide a new and improved process for forming photoemitters which is free from the above-noted deficiencies of the prior art.

Another object of the invention is to provide a new and improved process of the above character for forming photoemitters on selected areas of a substrate without resorting to masking within the evacuated envelope containing the photoemitters.

A further object of the invention is to provide a new and improved process of the above character for forming photoemitters on a selected surface location where in situ photoemitter formation is not possible by existing techniques.

These and other objects of the invention are attained by prenucleating the selected area or areas on a substrate on which the photoemitters are to be formed by coating them with a thin layer of a nucleating material having a higher heat of sublimation than the base layer on which the photoemitter is to be deposited. This can be done in any known manner as by vacuum deposition in a system other than that in which the photoemitters are to be formed, the deposition being restricted to the selected areas by masking or any other conventional technique. The nucleated substrate is then removed from the system and sealed into the envelope which is to contain the completed device, together with charges of the base material and alkali metal from which the photoemitter is to be formed.

With the envelope sealed to a vacuum system, it is first baked out to remove all deleterious foreign gases and other materials. The charge of base material for the photoemitter is then evaporated at an elevated temperature so that it is deposited only on the selected areas that have been prenucleated. The alkali metal or metals constituting the photoemitters are then evaporated from their sources under temperature conditions selected to insure that they will deposit only on the selected areas where the base material has been deposited.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention, reference is made to the following detailed description of several embodiments of the invention as applied to the formation of typical photoemitter devices, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a view in longitudinal section through an electrooptical copier device in which photoemitters are formed according to the invention;

FIG. 2 is a view in section taken along the line 2—2 of FIG. 1, looking in the direction of the arrows;

FIG. 3 is a view, partially in vertical section, showing a system for forming a photoemitter, in situ, in a narrow confined space in an image intensifier; and

FIG. 4 is a view in vertical section how photoemitters may be formed, in situ, in a multistage image intensifier device according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For purposes of illustration, the invention will be described first as applied to the formation of a photoemitter device of the type disclosed in the copending application of Richard H. Groo, III for an "Electrooptical Copier," filed Dec. 6, 1967, Ser. No. 688,524, now Pat. No. 3,508,477. As shown schematically in FIG. 1, the photoemitter device comprises a substantially cylindrical envelope **10** having sealed in at one end a disc **11** in which are mounted a plurality of fine wires **12** extending from the outside to the inside of the cylinder **10**. The cylindrical envelope **10** is sealed at its opposite end by a conventional optical window **13** through which an image of an object to be recorded can be focused on the ends **12***a* of the pins **12** which lie within the cylindrical envelope **10**. For proper operation of the device, it is necessary that the pin ends be photoemitters.

Utilizing the techniques heretofore available, it would be exceedingly difficult to form photoemitters on the pin ends **12***a* in situ within the cylindrical envelope **10** without at the same time coating the adjacent surfaces of the glass substrate in which the pins are mounted. In order to avoid this, it would have been necessary to utilize known masking techniques to mask off these surfaces and then somehow remove the masking before evacuating and sealing the cylindrical envelope **10**. The present invention makes it possible for the first time to form the desired photoemitters on the pin ends **12***a* without utilizing mechanical masking within the device.

According to the invention, the glass disc **11** in which the pins **12** are mounted, before being sealed to the end of the envelope **10**, is thoroughly cleaned to remove any foreign matter which might either provide false nucleating sites or contaminate the subsequent depositions of material. This may be accomplished in any known manner, as by washing the surface

with a 50 percent solution of HCl rinsing with tap water, ultrasonically rinsing in deionized H_2O, rinsing in acetone, drying in hot air, washing in Igepal or other nonionic detergent solution, rinsing in deionized water and then flushing the surface with hot propanol vapors.

The pin ends **12***a* on which photoemitter surfaces are to be formed are then coated with a nucleating material which has a latent heat of sublimation higher than that of the material to be selectively deposited upon it. For antimony, the basic and most common substrate for visible spectrum photoemitters (heats of sublimation 49 Kcal/mole for Sb_4 and 56.4 Kcal/mole for Sb_2) nichrome (heat of sublimation 95–101 Kcal/mole) may be used as the nucleating material. The coating of the pin ends **12***a* with nichrome may be accomplished in any known manner, as, for example, by vacuum evaporation of the nichrome through a mechanical mask in the conventional manner. Only a very thin, invisible coating (less than one monolayer) of the nichrome is required.

After the pin ends **12***a* have been coated with nichrome in the manner described above, the disc **11** is sealed into the end of the enclosure **10** in the conventional manner. At this time, there is also mounted within the enclosure **10** an annular channel **14** of substantially U-shaped cross section, the open end of the U facing the pin ends **12***a*, and containing a narrow filament **15** having antimony thereon which is connected at its ends to the terminals **16** and **17** so that current can be applied to evaporate the antimony.

Also mounted inside the envelope **10** is a caesium strip **18** connected to terminals **19** and **20** through which current can be applied at the proper time for evaporation of the caesium. Since both the U-shaped channel **14** and the caesium strip **18** remain permanently in the device, they are positioned so as not to block the optical path through the window **13** to disc **11** in which the pins **12** are mounted. The nipple **21** is then connected to a suitable vacuum pumping system and the completed device is baked out in the conventional manner to remove all foreign gases and other matter that might adversely affect the photoemitters either during the formation thereof or subsequently in operation. With the pressure reduced to a value in the range from 10^{-5} to 10^{-9} Torr, the entire device is then heated in a suitable oven, for example, to a temperature high enough to prevent any substantial condensation of antimony during evaporation thereof on the glass substrate in which the pins **12** are mounted but not high enough to cause any substantial evaporation of the nucleating nichrome coating on the pin ends **12***a*. A temperature in the range from 200° C. to 400° C., say 300° C. is satisfactory. While the entire device is maintained at this temperature, current is passed through the electrodes **16** and **17** to cause evaporation of the antimony so as to produce an antimony substrate on the pin ends **12***a* inside the envelope **10**. By reason of the elevated temperature within the envelope **10**, however, the antimony does not condense on the glass surfaces in which the pin ends are embedded.

The temperature is then reduced to a value in the range from 130° to 175° C. and current is passed through the electrodes **19** and **20** to evaporate caesium from the strip **18**. The evaporated caesium deposits only on the antimony layers formed on the pin ends **12***a* where it diffuses into the antimony to form caesium antimonide, a good photoemitter. The oven is then removed from the envelope **10**. The envelope is cooled to room temperature and the nipple **21** is sealed off from the vacuum pump. The completed device now has photoemitters formed on the pin ends **12***a* so that it can be utilized for copying purposes in the manner disclosed in the aforementioned Groo Pat. No. 3,508,477.

A wide range of materials in addition to nichrome can be used for the thin nucleating layer. For example, nickel, chromium silver and gold along may be used, as well as nichrome in combination with gold and silver. Other suitable materials include tin, antimony of higher heat of sublimation than the antimony to be used as the photoemitter base, copper rhodium iron, erbium, palladium, platinum, tungsten, molybdenum, tantalum, and alloys or combinations of these metals.

It is also possible to deposit manganese selectively in a manner similar to that described above for nucleated antimony. This is significant because in the formation of some types of photocathodes, manganese is incorporated as a pure metal or as a metal that is subsequently oxidized. In addition, antimony can be selectively nucleated on manganese and manganese oxide. Further, more than one layer can be selectively deposited according to the invention to form complex cathodes by nucleation.

It has further been found that silver, gold, nichrome, nickel and chromium can nucleate manganese in a vacuum of 10^{-5} to 10^{-10} Torr in a temperature range between 300° and 550° C. The manganese can then be oxidized by exposure to oxygen gas, by oxygen ion bombardment, or by means of any other suitable oxidizing agent. The resultant manganese oxide will nucleate antimony when exposed to antimony vapor, and the nucleated antimony subjected to alkali metal diffusion as described above to achieve photoemission.

While the process has been described above as applied to the formation of antimony-caesium photoemitters, it will be understood that it can be applied to other photoemissive materials such as those embodied in antimony-sodium, antimony-potassium, and antimony-sodium-potassium-caesium photoemitters, for example. The technique can be applied to any combination of materials which meet the nucleation requirements for selective deposition and which, thereafter, can be treated to result in a photoemissive surface.

FIG. 3 illustrates how the invention may be utilized to produce a photoemitter in situ in a narrow confined space in a device such as a light intensifier. Referring to FIG. 3, a light intensifier is shown comprising a shallow glass or ceramic cylinder **22** having top and bottom metal flanges **23** and **24** secured thereto by conventional glass to metal seals. Secured to the top flange **23** by a conventional heliarc weld is a ring-shaped member **25** having a central aperture **26** in which is secured a window **27**. The window **27** may comprise an air-tight bundle of fiber optics sealed to the ring-shaped member by a conventional metal to glass seal. The inner face of the window **27** has a nucleating layer **28** of a material such as nichrome which was formed thereon in the manner described, before the ring-shaped member **25** was sealed to the flange **23**.

Secured to the bottom flange **24** is a second ring-shaped member **29** having an aperture **30** therein in registry with the aperture **26** and in which is sealed a fiber optics window **31**. Prior to assembly in the image intensifier, the inner face of the window **31** has formed thereon by sputtering or by the technique disclosed in U.S. Pat. No. 3,314,871 a tenacious luminescent phosphor layer **32** having a conventional non-reflecting overlayer **33** thereon.

The cylinder **22** has a bore **34** formed therein to which a tubulation **35** is sealed. The tubulation **35** communicates with a sealed envelope **36** containing an evaporatable source **37** of a material such as antimony, with a sealed envelope **38** containing an evaporatable source **39** of a photoemitter material such as caesium, and to a conduit **40** connected to a conventional vacuum pump (not shown).

With the apparatus connected as described above and as shown in FIG. 3, the device is pumped down to a low pressure, a conventional oven (not shown) is lowered in place over the equipment, and coatings of antimony and caesium are successively deposited over the layer **28** of nichrome nucleating material from the external sources **37** and **39** essentially in the same manner as described above in connection with FIGS. **1** and **2**. The tubulation **35** is then sealed off in the usual way.

The selective deposition technique of the invention may also be used effectively to form photoemitters in situ in a multistage image intensifier of the type shown in FIG. 4. This device has, in addition to the elements in FIG. 3, two intermediate image intensifier stages **41** and **42** having fiber optics windows **43** and **44**. Prior to assembly in the image intensifier, tenacious luminescent phosphor layers **45**, **46** and **47** and layers of nucleating material **48**, **49** and **50** are formed on the windows in the manner described above. Selective deposition of antimony and caesium, for example, on the nucleated layers

48, 49 and 50 is accomplished in the manner described through the tubulation 51, the rings 52 and 53 holding the windows 43 and 44 being provided with circumferential arrays of holes 54 and 55, respectively, to enable the vaporized materials in the tubulation 51 to reach the nucleated layers 48 and 50.

The process, according to the invention, may also be applied to photocathode operations in which a photocathode is deposited on a surface in one location in a vacuum system and is then moved within the vacuum to its location in the device in which it is to be used.

It will be further understood that the surface of the photoemissive compound formed according to the process may be oxidized in the known manner after it has been formed, to increase its photosensitivity.

The invention thus provides a novel and highly effective process for forming photoemitters in situ in a vacuum. By prenucleating the specific sites where the photoemitters are to be formed, with a material having a heat of sublimation higher than that of the base for the photoemitters, the photoemitter base and active materials can be selectively deposited in situ without the necessity for mechanical masking and in narrow confined spaces out of the line of sight of the evaporating sources.

The specific examples described are intended merely to be illustrative and it will be understood that the process is susceptible of variation both as to materials and operating conditions within the scope of the invention. The invention, therefore, is intended to encompass all such variations as fall within the scope of the accompanying claims.

We claim:

1. The process for forming photoemitters in situ within an evacuated envelope which consists essentially in the steps of coating selected areas of a substrate which it is desired to form photoemitters with a very thin layer of at least one metal having a higher heat of sublimation than the photoemitter component material to be deposited to form said photoemitters, said metal selected from the group consisting of nichrome, nickel, chromium, silver, gold, tin, antimony, copper, rhodium, iron, erbium, palladium, tungsten, molybdenum and tantalum,

assembling said substrate within said envelope,

evacuating said envelope, evaporating a photoemitter component material within said envelope while maintaining said substrate at a temperature to cause said photoemitter component material to deposit only on said selected areas and to thereby produce photoemitters thereat.

2. The process as defined in claim 1 in which said metal is selected from the group consisting of silver, gold, nichrome, nickel and chromium, and the photoemitter component material is manganese.

3. The process as defined in claim 2 in which the manganese is oxidized after deposition on the coated area or areas.

4. The process as defined in claim 3 in which antimony is deposited over the oxidized manganese.

5. The process for forming photoemitters on selected surface areas on a substrate which consists essentially in the steps of coating an area or areas of a substrate surface at which the photoemitters are to be deposited with a very thin layer of at least one metal having a higher heat of sublimation than the photoemitter material to be deposited to form said photoemitters said metal selected from the group consisting of nichrome, nickel, chromium, silver, gold, tin, antimony, copper, rhodium, iron, erbium, palladium, platinum, tungsten, molybdenum and tantalum and

Thereafter placing the said substrate bearing the coated surface areas in an evacuated enclosure, evaporating said photoemitter component material within said enclosure at a temperature to cause deposition of said photoemitter component material on said coated area or areas while preventing deposition of said component material on uncoated areas of said substrate.

6. The process as defined in claim 5, in which the photoemitter component material is antimony.

7. The process as defined in claim 6, in which the temperature at which the substrate is maintained is above about 200° C.

8. The process as defined in claim 4 including the further step of evaporating a second photoemitter component material different from antimony within said evacuated enclosure while maintaining said substrate at a temperature sufficiently high to cause said second material to deposit only on the area or areas having antimony deposited thereon.

9. The process as defined in claim 8, in which said second photoemitter component material is an alkali metal.

10. The process as defined in claim 9, in which said second photoemitter component material is caesium and the substrate is maintained at a temperature in the range from about 130° C. to about 175° C. while the caesium is deposited.

11. The process as defined in claim 10, in which the surface of the antimony-alkali metal compound is oxidized.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,627,575 Dated December 14, 1971

Inventor(s) Robert J. Doyle and Patrick F. Grosso

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 5, lines 32-46, and Col. 6, lines 1-45, the claims should read as follows:

1. The process for forming photoemitters on selected surface areas on a substrate which consists essentially in the steps of coating an area or areas of a substrate surface at which the photoemitters are to be deposited with a very thin layer of at least one metal having a higher heat of sublimation than the photoemitter material to be deposited to form said photoemitters, said metal selected from the group consisting of nichrome, nickel, chromium, silver, gold, tin, antimony, copper, rhodium, iron, erbium, palladium, platinum, tungsten, molybdenum and tantalum, and

thereafter placing the said substrate bearing the coated surface areas in an evacuated enclosure, evaporating said photoemitter component material within said enclosure at a temperature to cause deposition of said photoemitter component material on said coated area or areas while preventing deposition of said component material on uncoated areas of said substrate.

2. The process as defined in claim 1, in which the photoemitter component material is antimony.

3. The process as defined in claim 2, in which the temperature at which the substrate is maintained is above about 200° C.

4. The process as defined in claim 1 in which said metal is selected from the group consisting of silver, gold, nichrome, nickel and chromium, and the photoemitter component material is manganese.

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

5. The process as defined in claim 4 in which the manganese is oxidized after deposition on the coated area or areas.

6. The process as defined in claim 5 in which antimony is deposited over the oxidized manganese.

7. The process as defined in claim 3 including the further step of evaporating a second photoemitter component material different from antimony within said evacuated enclosure while maintaining said substrate at a temperature sufficiently high to cause said second material to deposit only on the area or areas having antimony deposited thereon.

8. The process as defined in claim 7,in which said second photoemitter component material is an alkali metal.

9. The process as defined in claim 8, in which said second photoemitter component material is caesium and the substrate is maintained at a temperature in the range from about 130°C.to about 175°C. while the caesium is deposited.

10. The process as defined in claim 9, in which the surface of the antimony-alkali metal compound is oxidized.

11. The process for forming photoemitters in situ within an evacuated envelope which consists essentially in the steps of coating selected areas of a substrate which it is desired to form photoemitters with a very thin layer of at least one metal having a higher heat of sublimation than the photoemitter component material to be deposited to form said photoemitters, said metal selected from the group consisting of nichrome, nickel, chromium, silver, gold, tin, antimony, copper, rhodium, iron, erbium, palladium, tungsten, molybdenum and tantalum,

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

assembling said substrate within said envelope, evacuating said envelope, evaporating a photoemitter component material within said envelope while maintaining said substrate at a temperature to cause said photoemitter component material to deposit only on said selected areas and to thereby produce photoemitters thereat.

Signed and sealed this 11th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents