

March 31, 1964

C. W. RECTOR
PIN-HOLE EVAPORATION CAMERA

3,127,226

Filed Oct. 4, 1960

Fig. 1.

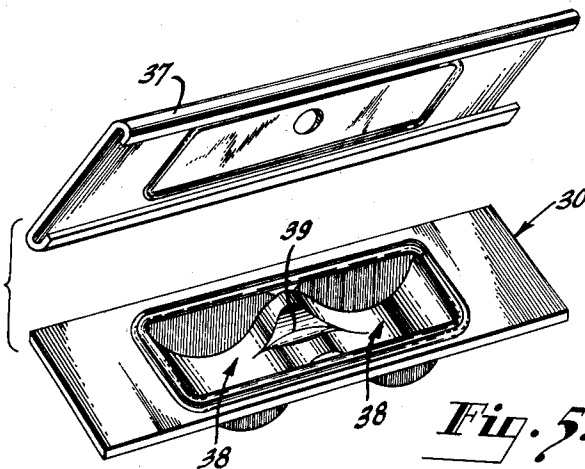
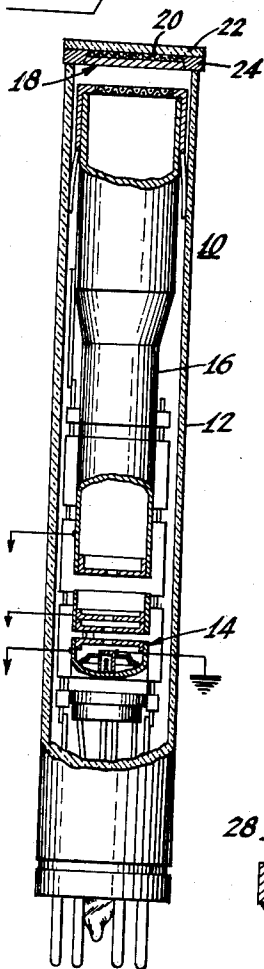


Fig. 5.

Fig. 4.

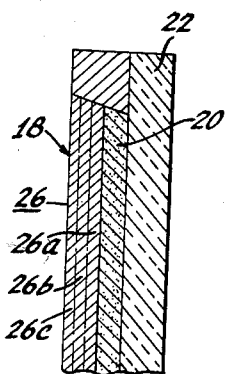
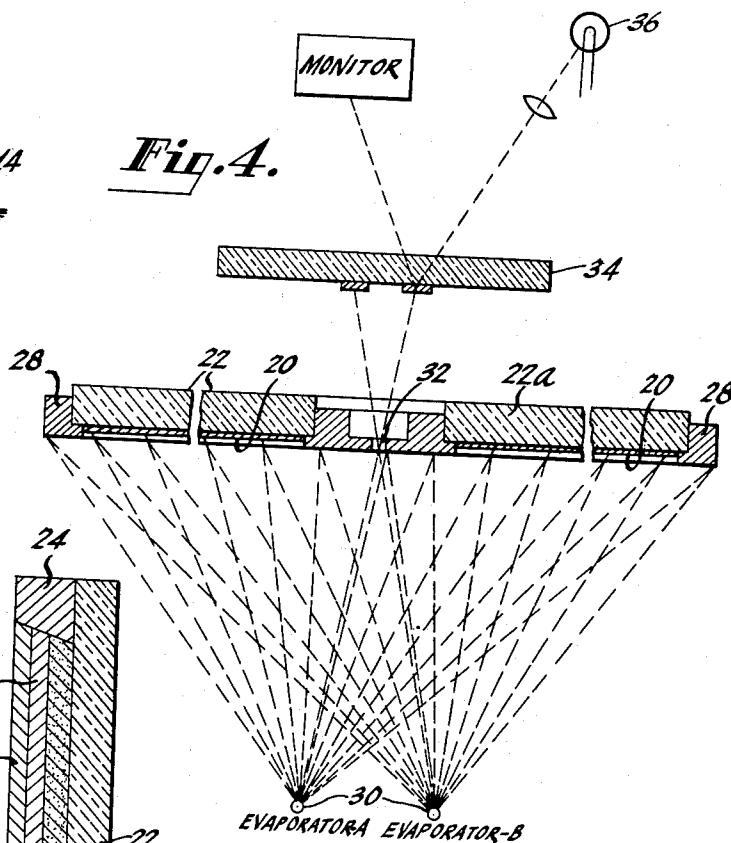


Fig. 2.

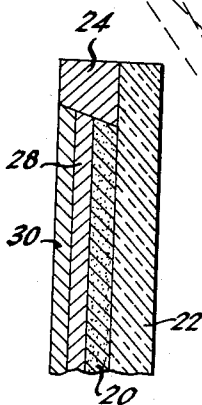


Fig. 3.

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3,127,226

PIN-HOLE EVAPORATION CAMERA

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Filed Oct. 4, 1960, Ser. No. 60,433

3 Claims. (Cl. 316—4)

This invention relates to a method of and means for forming thin deposits. The invention will be described with particular reference to the deposition of thin photoconductive deposits for which it is particularly useful.

In several known electronic devices, e.g., photoconductive pickup tubes and photocells, it is desirable to obtain a photoconductive deposit having a maximum sensitivity combined with a minimum photoconductive lag, maximum speed of response, selected spectral response as well as other preferred parameters of the photoconductive deposit. One of the solutions that has been proposed to obtain the photoconductive deposits having these desired properties is the simultaneous use of two or more different photoconductive materials. For example, it has been proposed to use a photoconductive material including antimony tri-sulfide and antimony oxy-sulfide. At times when using the plural material deposits, it is desirable to deposit the different photoconductive materials as two layers one on top of the other. For other situations it is desirable to deposit the materials as a graded composition in which the composition of each incremental thickness element varies as a function of the distance through the layer.

It is apparent that, without a knowledge of the relative rates at which the various components of the plural photoconductive materials are being deposited, control and reproducibility of a desired photoconductive member would be exceedingly difficult to attain. Since the photoconductive materials are usually deposited by evaporation in some type of vacuum, factors which are known to affect the rate of deposition of a material include the following: (1) the chemical composition of the material; (2) the evaporating temperature of the material; (3) the spacing between the evaporator and the surface on which the material is being deposited; (4) the degree of vacuum through which the evaporation is occurring; (5) the configuration of the evaporator; (6) the length of time of the evaporation; (7) the temperature of the evaporant molecules as they traverse the space between the evaporator and the surface on which the material is being deposited; and (8) the type of gas molecules through which the evaporation is occurring. As is obvious from the length of this incomplete list of factors affecting the rates at which various components are deposited, it is extremely difficult to control the amount of material deposited and therefore the reproducibility of a photoconductive member.

It is therefore an object of this invention to provide a new method of and novel means for monitoring the amount of material deposited.

It is another object to provide a novel method of and means for depositing a photoconductive member, including a plurality of photoconductive materials.

It is a further object to provide a new and improved device having a photoconductive member made by the novel process of this invention.

These and other objects are accomplished in accordance with this invention by providing a novel device which enables the relative amounts of each of the components of a multiple component co-evaporation to be separately monitored while the various materials are being deposited upon a common selected surface. To achieve this, the device includes at least two spaced evaporator sources and an aperture positioned in the evaporant stream from both of the evaporators. By spacing a monitoring plate

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behind the aperture, separate, clearly defined images of the amount of material being deposited on the selected surface, are also deposited on the monitoring plate. By monitoring each component during the evaporation process, such as by counting the interference bands as they are formed on the monitoring plate, the amount of the different materials deposited on the selected surface can be accurately determined. With the separate amounts of the different deposited materials known, rates of evaporation of each component can be adjusted, while the evaporation is taking place, to obtain any desired composition or graded composition through the thickness of the photoconductor deposit.

The invention will be more clearly understood by reference to the accompanying single sheet of drawings wherein:

FIG. 1 is a sectional view of a pickup or camera tube having a target electrode made in accordance with this invention;

FIG. 2 is an enlarged fragmentary sectional view of the target electrode shown in FIG. 1;

FIG. 3 is an enlarged fragmentary sectional view of another embodiment of a target electrode made in accordance with this invention;

FIG. 4 is a partially schematic sectional view of means for obtaining the target electrodes shown in FIGS. 2 and 3 in accordance with this invention; and,

FIG. 5 is a broken away perspective view of an evaporator boat for uses in the means shown in FIG. 4.

Referring now to the drawings in detail, there is shown, in FIG. 1, a photoconductive type pickup tube 10. The pickup tube 10 is an example of a tube wherein this invention is particularly useful and the invention will be explained in detail in connection with this type of tube. The tube 10 comprises an evacuated envelope 12 having an electron gun assembly 14 positioned in one end thereof for producing an electron beam. By means of potentials applied to the electron gun 14 and to an accelerating electrode 16, as well by means of appropriate magnetic fields from conventional alignment coils, focus coils and a deflection yoke, none of which are shown for simplicity of illustration, the electron beam is directed toward and scanned over a photoconductive target electrode 18.

The target electrode 18, which is shown more clearly in FIG. 2, comprises a transparent electrically conductive electrode 20 deposited on a transparent face plate 22. The face plate 22 forms an end of the envelope 12. The transparent electrically conductive electrode 20 is made of a material that is selected for its transparency to radiations of the particular wavelengths of interest and for its electrical conductivity. For the visible range of wavelengths, a layer of tin oxide has been found to be suitable. The transparent conductive coating 20 is deposited in contact with an electrically conductive sealing ring 24 so that, during operation of the device 10, an electrical potential may be applied to the transparent conductor 20 and the transparent conductor may function as a signal plate for obtaining output signals from the device 10.

On the transparent conductor 20 there is deposited a graded composition of photoconductive material 26. In this particular embodiment, the graded composition of photoconductive material comprises a layer 26a of first photoconductive material, a layer 26b of a mixture of the first and of a second photoconductive material, and a layer 26c of the second photoconductive material. The particular chemical compositions selected for the various layers of the graded composition of photoconductive material 26 may be any known chemicals. One example of a graded composition photoconductor is antimony oxy-sulfide used as the layer 26a, antimony tri-sulfide used as the layer 26c, and a mixture of the two for the interme-

diate layer 26b. Other known photoconductive materials, or mixtures of materials, may also be used since, by means of this invention, any selected thickness of a layer, or mixture of layers, may be accurately controlled. Thus, by means of this invention, a photoconductive target electrode 18 may be constructed with the most desirable optical and electrical properties.

Referring now to FIG. 3 there is shown an embodiment of a photoconductive target including two separate distinct layers 28 and 30 of different photoconductive materials. The layer 28 of a photoconductive material may be any selected chemical compound or mixture of compounds and may itself be a graded composition. The layer 30 of photoconductive material may also be any selected chemical compound or mixture of compounds and may be the same as or different from the layer 28. Examples of photoconductive materials which may be used in accordance with this invention and which have been deposited in tubes of the type shown in FIG. 1 include the oxides, sulfides, and selenides of antimony, lead, arsenic and cadmium, as well as mixtures of these materials.

Thus, targets of any number of layers of materials, with each layer being made of one or more chemical compositions, and graded in any desired manner, may be manufactured by using this invention.

An example of a particular means for accurately forming the selected photoconductive layers in accordance with this invention is shown in FIG. 4. In this example two separate face plates 22, 22a are in the process of having a photoconductive target electrode deposited thereon. It should be understood that the photoconductive materials can be simultaneously deposited onto any number of face plates and two are shown for simplicity of illustration. Prior to the manufacturing step shown in FIG. 4, a transparent electrical conductive coating 20 has been deposited on each of the face plates 22, 22a, by any known means.

To deposit the photoconductive target electrodes 18, the face plates 22, 22a, with their transparent conductive coatings 20, are positioned on a jig 28 and in an evacuated chamber (not shown). Also positioned in the evacuated chamber are at least two spaced apart evaporator boats 30. The structure of the evaporator boats 30 will subsequently be explained in detail in connection with FIG. 5. It should be noted that the jig 28 which supports the face plates 22, 22a, includes a small, e.g. approximately 0.07 inch aperture 32. Positioned in spaced relation above the aperture 32 is a monitoring plate 34. The jig 28 may be made of a material such as stainless steel while the monitoring plate 34 may be made of any transparent material, one successfully used example of which is an optically flat transparent glass.

The vacuum chamber is evacuated to a relatively high vacuum, e.g. 10^{-5} mm. of Hg, for some target materials. At this time, current is passed through the evaporator boats 30 to heat these boats to a temperature high enough to evaporate the material contained therein. In the high vacuum, the evaporation process involves essentially a rectilinear propagation of the evaporant. Thus, those evaporant molecules coming from an evaporator boat 30 which pass through the aperture 32 land only on a small region or area of the monitoring plate 34, the extent of which is determined primarily by the dimensions of the object source, the size of the aperture and the distance.

The image formed on the monitoring plate 34 is, in fact, a geometrical representation of the relative rates of evaporation from various portions of the evaporating area. A long evaporation boat, for example, will give a long image; while any "hot spots" in the evaporation boat will show up as heavier deposits in the corresponding parts of the image. In an example of an evaporation unit used for the evaporation of any antimony tri-sulfide antimony oxy-sulfide target, a spacing between boats 30 of 3.3 cm. was used with the boats arranged concentrically around the axis of the aperture 32. With the boats 30 spaced approximately 18.5 cm. below the aperture and the monitor-

ing plate 34 positioned approximately 3.5 cm. above the aperture, the spacing between the deposits of material on the monitoring plate was approximately 6.25 mm.

The amount of material deposited on the monitoring plate 34 is proportional to the amount deposited on the target 18. The amount of material comprising each image on the monitoring plate is most conveniently monitored optically. Thus, a light source 36 directs light onto both of the photoconductor images and the reflected, or transmitted, light from each is monitored either by an observer or electrically.

With transmission monitoring, highly absorbed green or blue light from the source 36 should be used for the important first stages of the evaporation. In the later stages, when an appreciable amount of photoconductive material has been deposited on the monitoring plate, red or near infra red light should be used.

A light source which has been used as the source 36 is a white fluorescence bulb such as used for ceiling lighting fixtures. This offers a fairly continuous light spectrum and, at the distance used, forms a broad area source illuminating the whole of each image on the monitoring plate. The reflection from the image on the monitoring plate shows interference bands, of the deposited material. The interference bands form at the center of the image and expand as separate rings, as the evaporation proceeds. These interference bands, since a "white" light is used, are subtraction colors and occur in the sequence "yellow," "red," "blue." The sequence then proceeds as 1Y, 1R, 1B, 2Y, 2R, 2B, 3Y, 3R, 3B . . . until the termination of the evaporation. With careful observation techniques an 8B band can be detected by the human eye when the material is antimony tri-sulfide. Since the antimony oxy-sulfide is less absorbing, an even greater number of bands can be detected, when using this material. An examination of the monitoring plate with a hand lens after removal from the vacuum system establishes any doubtful final bands.

A specific example of a target for the visible range of the spectrum, made in accordance with this invention, and using available materials, is as follows: The first deposit (deposit 28 shown in FIG. 3) was made of antimony oxy-sulfide and was deposited until the fourth order interference ring was formed. Then, antimony tri-sulfide and antimony oxy-sulfide (corresponding to deposit 30 in FIG. 3) were simultaneously deposited, both at a substantially uniform rate, until the fifth order interference ring of antimony oxy-sulfide and the seventh order interference ring of the antimony tri-sulfide were reached. It should be understood that when materials are used, other than those referred to above, a particular number of interference bands will not necessarily indicate the same thickness of photoconductive deposit. However, with the index of refraction of the selected material known, and the number of interference bands known, the amount of material deposited may be approximately obtained by the following relationship:

$$T = \frac{N\lambda}{2n} \left(\frac{L_2}{L_1} \right)^2$$

where:

N is the number of counted interference bands.

n is the index of refraction of the photoconductive material (3.5 for antimony tri-sulfide and antimony oxy-sulfide).

λ is the light wavelength in air (0.55 micron).

L_1 is the distance from the evaporator boat to the face plate.

L_2 is the distance from the evaporator boat to the monitoring plate.

Thus, in the above example with

$$\left(\frac{L_2}{L_1} \right)^2 = \left(\frac{21.5}{18} \right)^2 = 1.43$$

and the thickness in microns = .112N. The result of this

is that, with the fourth order interference band of antimony oxy-sulfide, the thickness was approximately .45 micron; and the second deposit thickness of a mixture of the two materials ($N=5+7$) was 1.34 microns. It should be understood that this invention is not limited to the above specific example. The total thickness of both layers was 1.79 microns.

The above formula is correct only if the emission area of the evaporator boat is small enough so that the center of the monitor spot receives material from the entire emission area of the evaporator boat. This condition is fulfilled by the evaporator boat of FIG. 5 and the other apparatus used in accordance with this invention.

When the evaporation is complete, the face plate 22, 22a, with its photosensitive target 18, are removed from the evaporation chamber and each is sealed to the open end of two different envelopes 12. A method of and means for forming the seal and other tube processing techniques, after the target 18 has been deposited, is described in a copending application of B. H. Vine, Serial No. 648,094, filed March 25, 1957, now U.S. Patent No. 2,984,769, and assigned to the assignee of this invention.

The use of an open type evaporator boat is undesirable because the evaporants tend to spatter and cause spots on the photosurface. When open boats were used, spot scrap may be as great as 99%. This scrap was reduced to less than 20% by employing an enclosed evaporator which offered no direct line of sight between the evaporant source and target. FIGURE 5 illustrates a type of evaporator boat which has proved very useful. In an evaporation of two different materials, two such evaporators are used, one for each evaporant.

The evaporator boat is directly heated with the ends of the boat 30 clamped to electrical leads (not shown) and current (generally A.C.) passed through the boat. Two evaporant reservoirs are used for symmetry and should be filled with equal amounts of the evaporant. The evaporator is composed of a bottom portion containing reservoirs 38 and vapor channel 39 and a flat lid 37 in the center of which is punched a 0.10" vapor orifice 40. The lid is crimped over the edge of the bottom portion to make the unit vapor tight except for orifice 40. The orifice 40 is large enough to prevent excessive pressure build-up within the evaporator, yet small enough to form approximately a point source for the monitoring system. The evaporator may be formed from .022" tantalum sheet.

The monitoring techniques described above provide a knowledge of the amount and composition gradient of a photosurface as it is being deposited. In order to obtain a pre-specified composition gradient, however, it is necessary to control the relative ratio of evaporation of the component evaporants, using the monitored information to detect deviations from the desired gradient. For satisfactory control several functions must be performed, namely (1) monitoring, (2) computing, (3) controlling, and (4) recording. The monitoring function was described previously and may be performed visually or by the use of known electro-optical techniques. Electro-mechanical equipment (not shown) may be used to perform the functions of controlling and recording as well as certain rudimentary compositions. The evaporation rate, from a boat 30, is a function of the current through the evaporator boat 30. This current may be accurately controlled by means of known variable resistance devices (not shown) in series with the different evaporators and the resistance devices can be controlled so as to either increase or decrease the evaporator current.

In order to provide a predetermined evaporator current schedule, to which minor corrections can be made during the course of the evaporation, a tape (not shown) may be pre-punched with current increase and decrease holes, in accordance with a preferred schedule, and run through an electrical sensing device at a constant rate. Electrical

relays may be used to operate the resistance devices as the current increase or decrease holes pass through the sensing device. Also, corrections in the preferred schedule may be supplied by the monitor, and applied to the tape, so that if trends in the corrections are noted, in several evaporations, the pre-punched schedules can be modified to reduce the number of corrections necessary during a subsequent evaporation. The observed interference bands may also be recorded on a tape as they occur.

The monitor, using the interference bands and knowing the preferred schedule, can apply corrections to the preferred schedules to bring the evaporation into line. The monitor then, by his selection of the amount of correction, is serving as a computer. This function can be performed electronically or electro-mechanically with relatively simple circuitry using only the signal output of the interference band differentials.

The equipment, whose operation is briefly described above, permits satisfactory controlled evaporations to be made by a single operator. By employing electro-optical monitoring, the operation can be made completely automatic. The evaporation could be processed unattended while a complete record of each evaporation was being made.

One of the distinct advantages of some of the composition graded photosurfaces is the high sensitivity of such surfaces. The antimony tri-sulfide, antimony oxy-sulfide photosurface, for example, can be made appreciably more sensitive than photosurfaces prepared from either of the components alone.

Thus, the invention provides a novel method of and means for monitoring the amount and kind of deposit made from a plurality of sources. Since variations may be applied to a preferred schedule, changes that occur in the system, such as a change in vacuum pressure during the evaporation, can be compensated so that the preferred layer may be deposited.

What is claimed is:

1. The method of depositing a photosensitive surface layer on a support, comprising the steps of simultaneously evaporating on said support a photosensitive material from a first evaporator with said first evaporator in a first position and evaporating photosensitive material from a second evaporator with said second evaporator in a second position, positioning a member for receiving material from both of said evaporators, positioning an apertured member for receiving material from both of said evaporators, positioning a monitoring plate on the opposite side of said apertured member from said evaporators for receiving photosensitive material from both said first and second evaporator and passing through the aperture in said apertured member so that said material will land at spaced apart areas on said monitoring surface, and monitoring the amount of photosensitive material deposited on said spaced apart areas.

2. The method of controlling the deposit of photosensitive material on a surface comprising depositing photosensitive material from a first source onto said surface and through an aperture onto a first area of a monitoring member, depositing photosensitive material from a second source onto said surface and through said aperture onto a second area of said monitoring member, said first and said second areas being spaced apart on said monitoring member, and monitoring the amount of material deposited on said monitoring member.

3. The method of making a photoconductive pickup tube comprising depositing a transparent conductive coating onto a transparent face plate, evaporating at least one photoconductive material from at least two evaporating boats spaced apart in a given plane and onto said transparent coating, positioning a monitoring means in spaced relation to said plane to receive said photoconductive material from both of said evaporating boats, positioning a member having an aperture therein between said

monitoring means and said evaporating boats, whereby
 said photoconductive material passes through said aper-
 ture and is deposited on said monitoring means at spaced
 apart areas, positioning an electron gun in an envelope,
 and sealing said face plate with said transparent conduc-
 tive coating and with the evaporated photoconductive
 material to said envelope.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,127,226

March 31, 1964

Charles W. Rector

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 44, for "jib" read -- jig --; column 5, line 63, for "compositions" read -- computations --; column 6, line 12, after "can" insert -- then --.

Signed and sealed this 17th day of November 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents