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CADMIUM SELENIDE-ZINC SELENIDE PHOTOCONDUCTIVE ELECTRODE AND METHOD OF PRODUCING SAME

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Fig. 1.

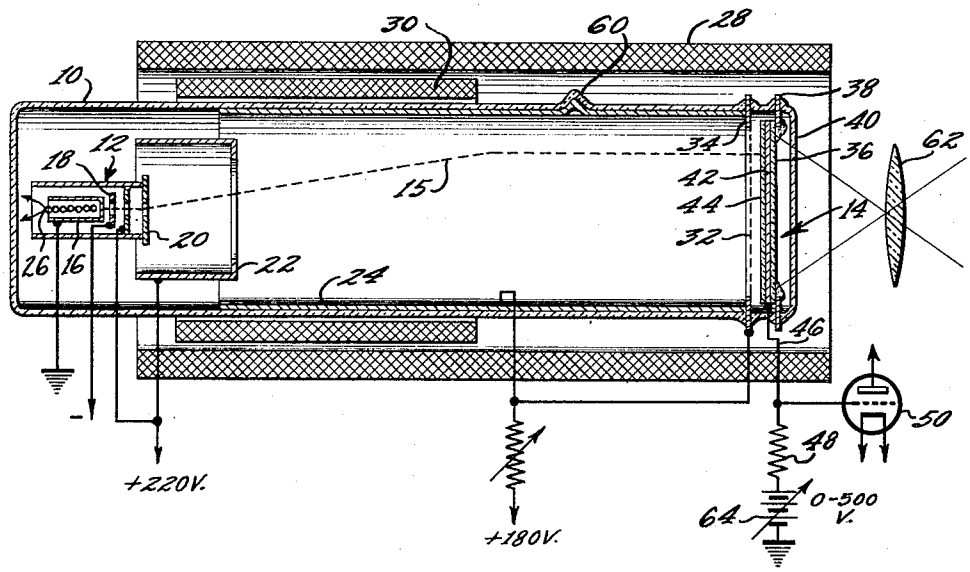
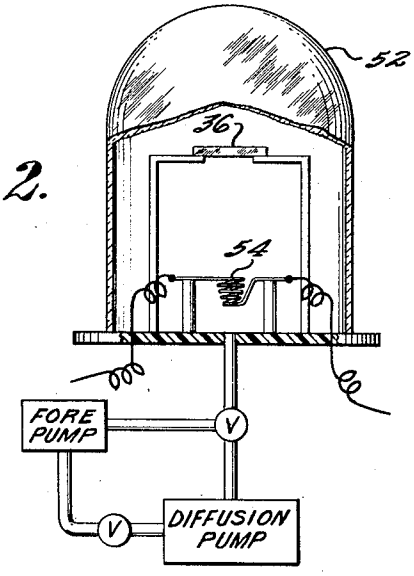


Fig. 2.



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CADMIUM SELENIDE-ZINC SELENIDE PHOTOCONDUCTIVE ELECTRODE AND METHOD OF PRODUCING SAME

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Application January 2, 1951, Serial No. 204,045

10 Claims. (Cl. 117—211)

This invention is directed to a pickup or camera tube for television and more specifically to an improved photoconductive target, therefor.

An example of a photoconductive pickup tube is one having a target formed with a supporting transparent sheet portion, which is first coated with a conductive film or signal plate and then, secondly, with a layer of known photoconductive material, over the conductive film. This target electrode is mounted within an evacuated envelope with the photoconductive coating facing an electron gun structure, which produces a high velocity (in the order of 500 volts) electron beam, substantially normal to the target surface. Either electrostatic fields or electromagnetic fields can be used to cause the electron beam to scan, in closely spaced parallel lines, over the surface of the photoconductive target layer. The scanning of the electron beam over this photo-conductive layer provides a secondary electron emission from the target surface. The number of secondary electrons leaving the target surface is normally controlled by an adjacent collector electrode, whose potential will be approached by the surface of the target. This potential of the target surface, acquired by secondary electron emission, may be considered an equilibrium potential. A potential, that is several volts different from the equilibrium potential established on the photoconductive surface is applied to the conductive signal plate of the target. In this manner, then, a difference of potential is established across the two surfaces of the photoconductive film. Due to the photoconductive properties of the target material used, when light is focused upon the photoconductive film, a current flow will take place through the film in the illuminated areas, and will change these areas toward the potential of the conductive film. Areas of the target not illuminated by the light will have little or no current flow depending upon the resistivity of the photoconductive material in the dark and will thus remain at the equilibrium potential established by the beam. The electron beam upon scanning over the target areas illuminated by light, will return the illuminated target areas to equilibrium potential. Since the signal plate is capacitively coupled with the scanned surface of the target, the instantaneous charging of the target by the beam to equilibrium potential will be evidenced by a voltage change in the circuit of the signal plate. This voltage change becomes the output signal of the tube. The above described operation is that in which a high velocity scanning beam is used. The operation of a similar tube using a low velocity beam (substantially gun cathode potential) is described below.

A photoconductive material, in order to be effectively used for a pickup tube target, must exhibit sufficient dark resistivity to give storage during tube operation. A desirable photoconductive material would be one having not only the required dark resistivity but also one having high conductivity when illuminated by light. A photoconductive material having a low resistivity in the dark cannot be used in pickup tubes, since the equilibrium potential charge established on the surface areas of the target scanned by the electron beam must be maintained in unilluminated target areas. That is, the dark current through the material will discharge the target in these areas, thus masking the light output signal derived from the illuminated areas.

The photoconductive properties of cadmium selenide and zinc selenide are well known. However, both of these materials have certain deficiencies, which limit their use in pickup tubes of the type described. Cadmium selenide has a specific resistance less than 10^{11} ohms per centimeter, which is too low to allow for full storage necessary for pickup tube operation. Furthermore the spectral response of cadmium selenide is peaked in the red and has a low blue response. Cadmium selenide however, has a very large change in current with light change, which would provide a high sensitive photoconductive target, if the material had a sufficiently high specific resistance. Zinc selenide on the other hand has a high specific resistance much greater than 10^{11} ohms per centimeter and more than adequate to allow for storage, in pickup tube applications. Zinc selenide on the other hand has a spectral response peaked towards the blue and a low red response. Also, zinc selenide provides only a moderated change in current with light change, and of several orders of magnitude less than that of the cadmium selenide.

Thus, it would be advantageous to provide the desired photoconductive properties of cadmium selenide and zinc selenide and eliminate their undesirable photoconductive properties. That is, a material having the high dark resistivity of the zinc selenide, the large change in current to light change of the cadmium selenide, and a spectral response between the red and the blue and preferably in the green region would be a desirable photoconductive material.

It is therefore an object of my invention to provide an improved photoconductive material of cadmium selenide and zinc selenide for use in a pickup tube.

It is a further object of my invention to provide an improved photoconductive material of cadmium selenide and zinc selenide having a high specific resistance greater than 10^{11}.

It is another object of my invention to provide a photoconductive material of zinc selenide and cadmium selenide having a spectral response peaked between the red and blue portions of the spectrum.

It is another object of my invention to provide a method of forming an improved photoconductive material for use in a pickup tube.

It is a further object of my invention to provide a photoconductive pickup tube having an improved target formed of zinc selenide and cadmium selenide.

The invention is specifically that in which an improved photoconductive material of cadmium selenide and zinc selenide is formed and is used as a target material in a camera pickup tube. To form the photoconductive material, cadmium selenide and zinc selenide are mixed together with the cadmium selenide in the mixture varying from 20 percent to 50 percent, the remainder of the mixture being zinc selenide. The mixture is fired in a neutral atmosphere between 900° C. and 1200° C. for approximately fifteen minutes. The fired material is then cooled and evaporated, in a vacuum, as a coating film onto a target support member to form a photoconductive film of zinc and cadmium selenide. The coated target support is mounted as the target electrode within a pickup tube to be used in the manner described above.

While certain specific embodiments have been illustrated and described, it will be understood that various

changes and modifications may be made therein without departing from the spirit and scope of the invention.

Figure 1 is a cross sectional view of a photoconductive pickup tube using a zinc-cadmium selenide target, in accordance with my invention.

Figure 2 is a partial sectional view of an evaporation chamber for evaporating zinc-cadmium selenide onto a support member.

Figure 1 discloses a photoconductive pickup tube having an evacuated envelope **10**, within which is positioned an electron gun structure **12** and a target electrode **14**. The electron gun **12** provides an electron beam **15** which can be scanned over the surface of the target **14**. The electron gun is of conventional design and consists essentially of a cathode electrode **16**, a control grid **18** and an accelerating electrode **20**. Electrodes **22** and **24** are beam focusing electrodes. Cathode **16** is essentially a tubular electrode closed at one end facing the target electrode **14**. The closed cathode end is coated with thermionic emitting material, which is heated preferably by a non-inductive heater coil **26** to provide an electron emission. This emission is formed in a well known manner by electrodes **18** and **20**, into the electron beam **15**.

The electrons of beam **15** are magnetically focused to a well defined point of the surface of target electrode **14** by a magnetic coil **28**, which encloses the tube envelope **10**, as is shown. A yoke structure, indicated at **30**, comprises essentially two pairs of coils, with the coils of each pair connected in series and respectively to sources of saw-tooth currents for providing line and frame scansion of beam **15** over the surface of target **14**. Such a deflection system is well known, and does not constitute a part of this invention. During tube operation, voltages are applied to the several electrodes, as is indicated. These voltages represent appropriate values for tube operation and operation of the tube need not be limited to these values.

Accelerating and focusing electrode **24** may comprise a conductive coating on the inner wall of the tube envelope **10**. The conductive coating **24** extends to a point closely adjacent to target electrode **14**. Conductively connected to coating **24** is a fine mesh screen **32**, which is mounted in the tube envelope across the opening of a ring **34** sealed in the tube envelope **10**. Target electrode **14** comprised essentially of a supporting insulating transparent plate **36**, such as glass, for example, which is sealed to a mounting ring **38**, which is in turn sealed in the tube envelope **10** as shown. Envelope **10** is closed, at the target end thereof, by a face plate **40** closely spaced from the target supporting sheet **36**. The glass sheet **36** is coated on its surface facing the electron gun **12** with a transparent conductive film or signal plate **42**. Such a conductive film may be formed from evaporated metal or of conducting material as stannic oxide. The conductive film **42** is coated with a thin layer **44** of photoconductive zinc and cadmium selenide.

During tube operation, appropriate voltages are applied to the several electrodes within the tube. The electron beam **15**, which is formed, is scanned over the surface of the photoconductive material **44**. As will be described below, the surface of photoconductive coating **44** facing the electron gun **12** will assume an equilibrium potential. The conductive signal plate **42** is connected by lead **46** through a resistance **48** to a source of potential, to be described below, to establish on signal plate **42** a potential different from the equilibrium potential established on coating **44**. When light is focused upon the target **14**, portions of the photoconductive film **44**, illuminated by the light, will become conductive and because of the potential difference across film **44**, a current will flow in these areas. This flow of current will discharge the scanned surface of coating **44** towards the potential of signal plate **42**. As the scanning beam **15** passes over the discharged areas of the screen, it tends to rapidly restore these areas to equilibrium potential. This almost instantaneous charging of a discharged area of the target to the equilibrium potential provides rapid change in potential across resistance **48**, since signal plate **42** is capacitively coupled to the photoconductive film **44**. The change in potential across resistance **48** is detected and amplified, in a well known manner, by an electron tube **50** connected, as is shown, to lead **46**. This provides the video signal or output signal of the pick-up tube.

In the above described operation of the tube of Figure 1, it is necessary for successful tube operation that there be little or no current flow between the surfaces of the photocathode coating **44** in those areas of the target which are not illuminated by light when a picture is focused upon the target **14**. It is obvious that if there is a large "dark" current flow in the unilluminated areas of the target, then all of the scanned surface of photoconductive film **44** will become discharged to the potential of signal plate **42**. Beam **15**, then, in scanning across the target surface will provide little or no distinguishing potential changes across resistance **48** to provide a video or picture signal from the tube.

Up to the present time, very little success has been obtained in using cadmium selenide as a photoconductive material in pickup tubes of the type described above. Although the photoconductivity of cadmium selenide is good, when illuminated by a light source, it is true that in the dark, the material also has considerable conductivity. For storage type of pickup tube operation, with a $\frac{1}{30}$ second scanning (frame) frequency, a dark resistivity greater than about 10^{11} ohm-centimeters is required. This insures that the scanned target surface, in the dark areas, will not be discharged by an appreciable flow of dark current in the frame scanning time. Sublimed or evaporated layers of cadmium selenide have consistently fallen far short of this resistivity, so that the inherent high light sensitivity possible from cadmium selenide has not been fully utilized.

Zinc selenide has an excellent dark resistivity greater than necessary for pickup tube applications. It is desirable that a photoconductive target material for a pickup tube of the type described have good change of current with light characteristic and a spectral response having a relatively flat curve between red and blue or preferably peaked in the green region of the spectrum, between the red and the blue. Zinc selenide has a high blue spectral response coupled with a low red spectral response. Also zinc selenide has only a moderate change of current with light change. Cadmium selenide on the other hand has a spectral response peaked in the red and with low blue response. Cadmium selenide has a large change in conductivity with light change.

In accordance with my invention, zinc selenide and cadmium selenide materials in the desired proportions are thoroughly mixed and fired in a neutral atmosphere at a temperature between 900° C. and 1200° C. for fifteen minutes or more. The fired material is then put down as a thin film on a supporting base by evaporation, sublimation, or settling.

Specifically, the target is formed as follows: for example, 30 mole percent of cadmium selenide is mixed with 70 mole percent of zinc selenide. By this, is meant that the ratio of the number of moles of cadmium selenide used to the number of moles of zinc selenide used, is 3:7. The materials are mixed and ball milled as a dry powder for at least 15 minutes. The milled mixture is placed in a silica boat or dish and then covered with a layer of zinc sulfide which is absorbent to oxygen. The silica boat is placed in an oven and baked at a temperature between 800° C. and 1200° C. for from 15 minutes to an hour or more depending upon the amount of the batch. By packing the mixture in the zinc sulfide, an oxygen-free atmosphere is provided immediately surrounding the zinc selenide and cadmium selenide mixture. This prevents any deleterious reaction of the mixture with the oxygen of

the air. The fired material is cooled and then put down as a thin film or a supporting base, to form a photoconductive target.

The optimum temperature for firing a batch of the mixture is around 900° C. Higher temperatures result in larger crystal formations, while lower temperatures will require a longer firing time. One five gram batch of the mixture was fired for about 20 minutes at 900° C. The time of firing depends upon the size of the batch fired, a larger batch requiring a longer firing time.

A preferred firing method is given above, however, the mixture may be fired in any neutral or oxygen free atmosphere without the use of oxygen absorbent zinc sulfide material. For example large batches may be fired in a crucible having a close fitting lid and a neutral atmosphere. A neutral atmosphere, however, may still have traces of oxygen which react with the zinc and cadmium of the mixture to form a brownish metal oxide mixture on the surface of the fired batch. After firing, the brownish contaminated portion can be removed before forming the photoconductive target.

The mixture prepared as described above is evaporated onto the target plate **36**. The target plate is first coated with a conductive film or signal plate **42**. This signal plate may be of a transparent metal film or of a conductive film of a material such as stannic oxide. The coated plate **36** is placed in an evacuated chamber **52**, as shown in Figure 2. A crucible can be formed from tungsten filament, which is coated with aluminum oxide. The wire is formed in a conical spiral to form a cup **54**, as shown in Figure 2. The zinc selenide-cadmium selenide mixture is placed in this cup **54**. Upon evacuation of chamber **52** to a pressure of around 10^{-5} mms. of mercury, a current is passed through the filament wire to heat the cadmium selenide-zinc selenide mixture until it evaporates. Evaporation is continued until a film around 0.1 mil thickness of the zinc and cadmium selenide is formed on the surface of target plate **36**. Such a film thickness is required by the desired capacity-time lag for the pickup tube, as described above. Since the beam current of tubes of this type is around .1 microampere, it can be easily determined that the desired thickness of the target film should be in the order of 0.1 mil for a target diameter in the order of 0.75 inch. By counting interference fringes from the film, when it is illuminated during its formation by a monochromatic light, such as a sodium light, it can be determined when the film has reached the desired thickness. The target is then removed from chamber **52** and mounted in the tube envelope substantially as shown in Figure 1.

The forming of the zinc and cadmium selenide film on the target support plate **36** need not be limited to the method of evaporating the material. Such a film may also be formed by sublimation in the manner described in my copending application Serial No. 197,019 filed November 22, 1950, and now Patent No. 2,688,564. In this described manner, the zinc and cadmium selenide mixture is placed within a tube, through which hydrogen gas is passed. Upon heating the material to its sublimation point, the material sublimes and is carried over onto the target support plate, also arranged within the tube. The photoconductive film may also be formed on plate **36** by settling the zinc and cadmium selenide mixture from an aqueous suspension of the mixture onto the support plate **36** to form the photoconductive film **44**. An electrolyte such as potassium silicate may be used in the suspension to provide a binder for the selenide mixture to the target plate **36**. Upon drying the film is tightly adherent to plate **36**.

I have found that there is an optimum range of percentages of zinc selenide in the material which provides the desired photoconductive properties. This range is that in which the mole percent of zinc selenide in the mixture is between 50 percent and 80 percent. Within this optimum range, the photoconductivity of the material is satisfactory for use in pickup tubes in the type described. The operative sensitivity of the material, which may be defined as the difference between the light current and the dark current of the material is good, and more than enough for tube operation. Also within this range of percentages, the spectral color response of the material is relatively flat from blue to red. The peak of the color response is in the green. This is desirable, since it corresponds to the color response of the eye. Within this range of percentages, the specific resistance of the mixture is satisfactory and lies between 10^{11} ohms centimeters and 10^{13} ohms centimeters. It has also been found that the cadmium and zinc selenide photoconductive material has a longer life than the cadmium selenide material alone. One sample target has been used for more than 100 hours with no falling off of photoconductive properties.

The tube of Figure 1 may be operated in any one of several ways. For example, if the lead **46** of signal plate **42** is connected through a variable voltage source **64** to ground, the operation of the tube can be that of an orthicon in which beam **15** is caused to approach target **14** at very low velocity. The adjustable voltage source **64** may be regulated so that the potential of the signal plate **42** is established at about 20 volts positive relative to the potential of gun cathode **16**. The electron beam **15**, then upon approaching the target **14**, will be slowed down to substantially zero velocity and will deposit electrons upon the scanned surface of the cadmium sulphide film **44** to drive that surface down to an equilibrium potential, which is very close to that of the gun cathode **16**. At this potential, the electrons of the beam **15** will be repelled back toward the accelerating anode **20** of the gun. Since the signal plate electrode **42** is at about 20 volts positive relative to the cathode, and the scanned surface of cadmium sulphide film **44** is at substantially gun cathode potential, there is established a potential difference between the two surfaces of the photoconductive film **44**. This is the condition of the target **14**, when no light is focused upon the target. If now, a scene or picture is focused on target **14**, photoconductivity will be established through film **44** between the surfaces, thereof, and in the areas illuminated by the light of the scene or picture. In these illuminated areas a current flow will take place across film **44** and proportional to the amount of light falling upon each illuminated target area. The illuminated areas of photoconductive film **44** will, on the scanned side, be charged toward the potential of the signal plate **42** and in an amount corresponding to the amount of light falling on each respective target area. Areas of the target not illuminated by the light will have little or no current flow and this will remain near equilibrium potential established by the beam. The electron beam upon scanning over the target will return those areas illuminated by light to equilibrium potential. As the signal plate **42** is capacitively coupled with the scanned surface of the target, the instantaneous charging of the target to equilibrium potential by the beam will be evidenced by a voltage change in the circuit of the signal plate. This voltage change is amplified by tube **50** and becomes the output signal of the tube.

The above description of the operation of the tube of Figure 1, is limited to the use of a low velocity electron beam. Tube operation using a high velocity scanning beam is also possible. Such an operation is described in the above cited copending application Serial Number 197,019.

While certain specific embodiments have been illustrated and described, it will be understood that various changes and modifications may be made therein without departing from the spirit and scope of the invention.

I claim:

1. The method of making a photoconductive electrode, said method comprising the steps, of mixing zinc selenide material with cadmium selenide material, said cadmium selenide being between 20 and 50 mole percent of the

mixture, firing said mixture in an oxygen-free atmosphere at a temperature between 800° C. and 1200° C., applying said fired material as a thin film onto a supporting member.

2. The method of forming a photoconductive target for a pickup tube, said method comprising the steps of, mixing zinc selenide material with cadmium selenide material, said cadmium selenide being between 20 and 50 mole percent of the mixture, firing said mixture in an oxygen-free atmosphere and at a temperature between 800° C. and 1200° C., applying said fired mixture as a thin film onto a target support plate.

3. The method of making a photoconductive electrode, said method comprising the steps of, forming a mixture of zinc selenide and cadmium selenide with the mole percentage of zinc selenide between 50% and 80% of the mixture in any oxygen-free atmosphere, firing said mixture at a temperature between 800° C. and 1200° C., applying said fired material as a thin film to a supporting member.

4. The method of forming on a support member a photoconductive target for a pickup tube, said method comprising the steps of, forming a mixture of zinc selenide and cadmium selenide with the mole percentage of zinc selenide between 50% and 80% in the mixture in an oxygen-free atmosphere, firing said mixture at a temperature between 800° C. and 1200° C., evaporating said fired material as a thin film onto said support member.

5. The method of forming on a support member a photoconductive target for a pickup tube, said method comprising the steps of, forming a mixture of 30 mole percent of cadmium selenide and 70 mole percent of zinc selenide, firing said mixture at a temperature between 800° C. and 1200° C. in an oxygen-free atmosphere, and evaporating said fired mixture as a thin film onto said support member.

6. The method of forming on a support member a photoconductive target for a pickup tube, said method comprising the steps of, forming a mixture of zinc selenide and cadmium selenide with the mole percentage of zinc selenide between 50% and 80% of the mixture in an oxygen-free atmosphere, firing said mixture at a temperature between 800° C. and 1200° C., settling said fired mixture from a liquid suspension thereof to form a thin film on one surface of said support member.

7. A photoconductive target electrode for a pickup tube, said electrode comprising, a transparent sheet of insulating material, a thin conductive coating on one surface of said transparent sheet, and a photoconductive film of a mixture of zinc selenide and cadmium selenide on said one surface of said supporting sheet and covering said conductive film, said cadmium selenide being between 20 and 50 mole percent of the mixture.

8. A photoconductive target electrode for a pickup tube, said electrode comprising, a transparent sheet of insulating material, a thin conductive coating on one surface of said transparent sheet, and a photoconductive film of a mixture of substantially 30 mole percent of cadmium selenide and 70 mole percent of zinc selenide on said one surface of said supporting sheet and covering said conductive film.

9. A photoconductive electrode comprising, an electrically conductive supporting member and a photoconductive film over one surface of said conductive supporting member, said photoconductive film formed of a mixture of zinc selenide and cadmium selenide, and an electrically conductive film between said support member and said photoconductive film said mixture formed with the mole percent of cadmium selenide lying between 20 and 50 percent.

10. A photoconductive electrode comprising, an electrically conductive support member and a photoconductive coating over a portion of said support member, said photoconductive coating including a mixture of zinc selenide and cadmium selenide formed with the mole percentage of zinc selenide lying between 50% and 80% of the mixture.

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