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SINTERED PHOTOCONDUCTING LAYERS

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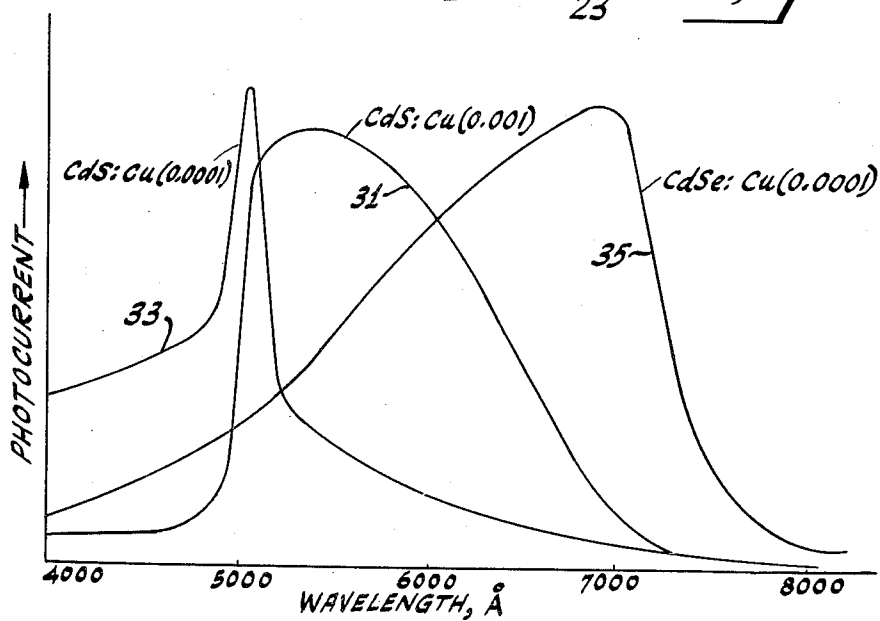
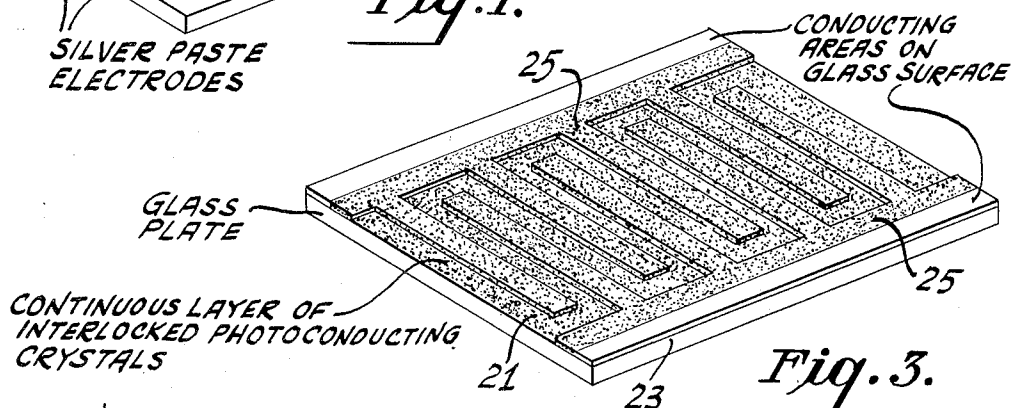
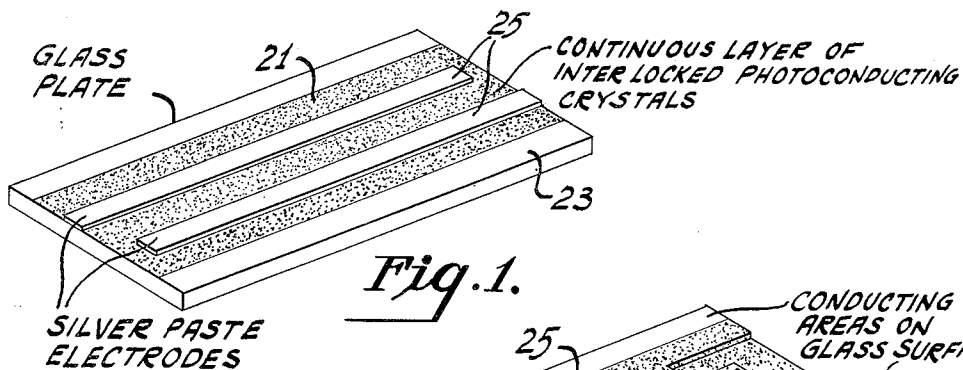


Fig. 2.

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SINTERED PHOTOCONDUCTING LAYERS

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This invention relates to sintered photoconducting layers which are particularly useful in gap type and area type photocells. The invention includes methods for preparing sintered photoconducting layers and devices utilizing the sintered photoconducting layers of the invention.

A photoconductive device is one which displays a reduced resistance to electric current flow when irradiated with light. In its simplest form, a photoconductive device comprises a body of photoconductive material and a pair of electrodes attached thereto. When a voltage is applied to the electrodes, the device displays a decrease in electrical resistance when there is an increase in the intensity of light irradiating the device. An amount of electric current flows through the device which is a function of this electrical resistance.

Ideally, a photoconductive device is a perfect insulator when light to which it is sensitive is absent, and is a perfect conductor when a maximum intensity of light to which it is sensitive is present. Actually, a photoconductive device behaves as a high resistance conductor when light to which it is sensitive is absent and behaves as a lower resistance conductor when light to which the device is sensitive is present.

The difference in conduction produced by the presence of a unit variation of light intensity is referred to as the photosensitivity of the device. The measure of photosensitivity is in terms of photocurrent under standard conditions. The current passed by the device in darkness is referred to as the dark current, the current passed when the device is irradiated is referred to as the light current and the difference between light current and dark current is referred to as the photocurrent.

One type of photoconductive device comprises a single crystal of a photoconductive material and electrodes attached to the crystal. Such single crystal photocells exhibit large photocurrents and high ratios of light current to dark current. However, the crystals are usually small in size and, consequently, the total current passed by a single crystal is small. When greater currents are passed through the crystal, the crystal heats up and the photosensitivity of the crystal is reduced either temporarily or permanently. Furthermore, photoconductive crystals are difficult to grow and are fragile. Thus, the expense of manufacture and maintenance often prohibits the use of single crystal photocells.

Another type of photoconductive device comprises a body including finely-divided photoconducting powder particles and electrodes attached to said body. The body may include, for example, an unbonded photoconducting powder or a photoconducting powder mixed with a binder such as a synthetic resin. Such powder photocells exhibit a broader band of spectral response than single crystal photocells. In addition powder photocells may be prepared in any desired size, shape or current carrying capacity. However, these powder-type devices have had the disadvantage of low photosensitivity, and relatively high resistance when the device is irradiated with light to which it is sensitive.

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The low-photosensitivity and high resistance of powder photocells is generally attributed to the large number of electrical barriers existing between the electrodes. The electric current passing between the electrodes must travel through chains of powder particles. The resistance due to poor electric contact between adjacent particles is multiplied by the number of particles in the chain, partly or completely masking the photosensitivity of the volume of each particle by limiting the maximum amount of current that can be passed by each chain of particles and by heating the particles during the flow of electric current.

An object of the invention is to provide improved photoconductive bodies.

Another object is to provide photoconductive layers having relatively high photosensitivities.

Another object is to provide improved photoconductive devices comprising the improved photoconductive bodies of the invention.

A further object is to provide methods for preparing the improved photoconducting bodies of the invention.

The photoconducting bodies according to the invention comprise a substantially continuous polycrystalline layer of interlocked photoconducting crystals. The crystals may comprise, for example, a predominant proportion of a substance selected from the group consisting of selenides, sulphides, and sulposelenides of cadmium having incorporated therein activator proportions of a halide and activator proportions of a metal selected from the group consisting of copper and silver.

The devices according to the invention comprise a substantially continuous polycrystalline layer of photoconducting crystals according to the invention and at least one electrode attached thereto.

A method for producing a photoconducting layer according to the invention comprises forming a stratum including particles of a material selected from the group consisting of sulphides, selenides and sulposelenides of cadmium, recrystallizing said material in a molten solvent to a desired range of particle sizes, incorporating into said recrystallized material activator proportions of a halide and activator proportions of a metal selected from the group consisting of copper and silver and evaporating said molten solvent, thereby producing a substantially continuous layer of interlocked crystals of photoconductive material.

By producing a substantially continuous layer of interlocked crystals of photoconductive material, the photosensitivity existing in the volume of each particle is "unmasked" and may be observed and utilized for purposes heretofore believed impractical. Such a layer is simple to prepare, reproducible and the devices prepared therewith are rugged and weather resistant.

The invention will be more fully described in the following detailed description when read in conjunction with the drawing in which:

Figure 1 is one embodiment of a photocell according to the invention.

Figure 2 is a series of spectral response curves for typical photocells prepared according to the invention and

Figure 3 is a second embodiment of a photocell according to the invention.

Similar reference characters are used for similar elements throughout the drawing.

Example 1.—An intimate mixture of 100 grams of cadmium sulphide, 10 grams of cadmium chloride, 1.7 milliliters of 0.1 M copper chloride and 500 milliliters of water is prepared. This mixture may be prepared in a blender such as is used for mixing powder with water. The yellow, viscous liquid mixture is applied, as by

spraying or brushing, to a borosilicate glass plate to a desired thickness and then dried. The glass plate bearing a powder coating is fired at 600° C. for about 5 minutes in a restricted volume of air and then cooled. The product will hereinafter be referred to as a sintered photoconducting layer.

During the firing step the cadmium chloride melts dissolving the copper salt and some of the cadmium sulphide. On further heating, substantially all of the cadmium sulphide recrystallizes, and the cadmium chloride evaporates. This recrystallized cadmium sulphide has incorporated therein activator proportions of copper. When substantially all of the cadmium chloride has evaporated, the cadmium sulphide crystals are interlocked with one another forming a substantially continuous polycrystalline layer of interlocked photoconducting crystals on the glass plate. The layer is firmly adherent to the glass.

The sintered photoconducting layer is yellow, fine grained, translucent when thin and firmly adherent to the glass. The photosensitivity is high, comparable with the photosensitivity of single crystals of cadmium sulphide. Unlike cadmium sulphide single crystals, the photoconducting layer is panchromatic in response characteristic, having a peak at the red end of the spectrum and declining to almost zero at the blue end of the spectrum. The sintered photoconducting layers approach single crystals in their speed of response.

In place of cadmium sulphide, cadmium selenide and mixtures of cadmium sulphide and cadmium selenide may be used. Cadmium sulphide and its equivalents will hereinafter be referred to as the host crystal.

Cadmium chloride is introduced into the mixture to act as a solvent for the host crystal. In addition to cadmium chloride, cadmium bromide, and cadmium iodide, for example, may be used as the solvent for these host crystals. In general, any material which is a solvent for the host crystal at the firing temperature may be used. While cadmium chloride is introduced into the coating mixture in the example, it may also be introduced by volatilization in the firing chamber during firing, such that it deposits upon the powder layer for a sufficient period of time to dissolve part or all of the host crystal and recrystallize it.

At the conclusion of the recrystallization step, substantially all of the cadmium chloride, which is volatile at the firing temperature of the example, evaporates, leaving only the interlocked crystals behind. Thus, the solvent for the host crystal should be a material which may be removed, preferably by evaporation during the firing step.

Ammonium chloride may be introduced into the mixture for the purpose of converting any oxides of the mixture to chlorides. Instead of copper, silver may be introduced into the host crystal as the activator. The proportion of copper introduced in Example I is equivalent to about 100 parts per million of copper with respect to the weight of cadmium sulphide. It is preferred to introduce copper in amounts between about 10 to about 1000 parts per million.

The liquid mixture is coated on a borosilicate glass plate in Example 1. Other substrates which are non-conductors, which are non-reactive with the ingredients of the mixture and which will stand the firing temperature of the Example 1 may be used, for example, mica, quartz, glass and ceramic materials.

In addition to recrystallizing the host crystal, it is believed that the following phenomena also take place. The following explanation is given to aid the teaching of the invention. There is no intention that the invention be limited to the explanation.

When cadmium sulphide crystals grow in molten cadmium chloride, some chloride is incorporated into the crystal. Each Cl^{-1} ion that enters the lattice displaces one S^{-2} ion. One free electron also enters the lattice to preserve electroneutrality. The free electrons prob-

ably come from an oxidation of the S^{-2} ions to free sulphur. This reaction does not occur with pure cadmium sulphide. It occurs only while electrons are introduced to compensate for unbalanced charges in the lattice.

If Cu^{+2} ions are present with Cl^{-1} ions during the growth of the host crystal, electrical conductivity is greatly reduced. Each Cu^{+1} probably substitutes for a Cd^{+2} in the host crystal and each Cl^{-1} ion substitutes for an S^{-2} ion. Since each Cu^{+1} makes the crystal deficient in one electron, the excess electron brought into the crystal by each Cl^{-1} ion compensates for this deficiency, thus, preserving electroneutrality in the crystal. Although copper is introduced into the mix as Cu^{+2} , it nevertheless enters the lattice as Cu^{+1} . It is believed that Cu^{+2} is reduced to Cu^{+1} during firing.

Thus, when equal amounts of Cl^{-1} ions and Cu^{+1} ions are present, electroneutrality is established, and the crystal is insulating in the darkness. When light irradiates the crystal, the charge-compensating electrons are easily excited and wander through the lattice imparting a high conductivity to the crystal.

By the method of the invention, a balance of copper and a halide is attained, such that there is a maximum insulating value in the darkness and also an optimum number of photo-excitable electrons in the volume of the crystal. The photosensitivity of the volume of the host crystal is usually masked due to the high resistivity of the contact between the host crystal particles. Treatment of the host crystals according to the invention adapts the surface of each particle to make a low resistance contact with other particles with which it is in physical contact when light is applied thereto.

Example 2.—An intimate mixture is prepared comprising 100 grams of cadmium selenide, 10 grams of cadmium chloride, 1.7 milliliters of 0.1 M copper chloride and 500 milliliters of water. The mixture is coated on a mica sheet, dried and then fired at about 600° C. for about 10 minutes in a restricted volume of nitrogen.

Referring to Figure 1, a sintered photoconducting layer 21 of the invention upon a glass plate may be made into a simple photocell by painting on the surface thereof a pair of silver paste electrodes 25. Such electrodes are well known in the art, comprising a mixture of metallic silver and a suitable resin. The electrodes 25 each have a side equidistantly spaced from the electrode. The gap formed between the two electrodes 25 has two important dimensions: width, which is the distance between the electrodes, and length, which is the distance along which the electrodes are parallel to one another.

In place of painting silver paste electrodes, they may be applied by other printing techniques, such as silk-screening or spraying. Other types of electrodes may be used, for example, aluminum, platinum, silver or gold may be evaporated upon the sintered photoconducting layer of the invention. Similarly, electrode materials may be sputtered in a desired configuration upon the photoconducting layer of the invention.

A voltage is applied between the electrodes, and light is directed into the gap therebetween. The voltage which may be applied to the electrodes and the current which is passed by the photocell is determined by the gap width and the gap length. Thus, the greater the gap width the higher may be the voltage and the greater the gap length the greater may be the current passed by the photocell. The voltage applied to a photocell of the invention may be either alternating or direct current. The specific examples of operational characteristics given herein are in connection with direct current operation although most of such examples are equally representative of low frequency alternating current operation.

The table summarizes typical data for photocells prepared according to the examples and Figure 1. The data is for photocells having a gap 1 cm. long and 0.05 cm. wide with 20 volts D. C. applied to the electrodes. The compositions include the percent by weight of incorpo-

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rated copper with respect to the weight of host crystals, i_D is the photocurrent of the photocell in the darkness, i_1 and i_{50} are the photocurrent microamperes with 1 and 50 foot-candles of light from an incandescent source present respectively, C_D and C_1 are the conductivity in mhos/centimeter of the photocell in darkness and with 1 foot-candle of light present respectively and the curve refers to the spectral response curve of Figure 2 which applied.

Table

Composition	i_D	i_1	i_{50}	C_1	C_D	Curve
CdS:Cu (0.001)-----	0.0001	3	300	10^{-4}	10^{-7}	31
CdS:Cu (0.0001)-----	0.01	30	1,000	10^{-3}	10^{-9}	33
CdSe:Cu (0.0001)-----	0.0001	300	3,000	10^{-2}	10^{-8}	35

Another type of photocell comprises a transparent conducting layer on a glass substrate over which the photoconducting layer of the invention is formed. Such a transparent conductive coating may be prepared by exposing heated glass to the vapors of silicon, tin or titanium chloride and afterwards treating the coating thus formed in a slightly reducing atmosphere. In some cases the glass plate may be treated with a mixture of stannic chloride in absolute alcohol and glacial acetic acid. The electrodes may be in any desired configuration, for example, the electrodes may comprise a simple gap structure comprising two spaced electrodes.

Referring to Figure 3, a photocell of the invention may comprise conducting areas 25 on a glass plate 23 in the configuration of two electrodes having a series of interdigitated fingers extending so that the electrodes are equidistant from one another at every point. Such a structure provides uniform gap width and a relatively long gap length for a given area. A photoconductive layer 21 of the invention is now formed on top of the electrodes 25.

The photoconducting layers of the invention may be used in simple photoconductive devices or in more complicated devices including other structures such as electroluminescent materials and in conjunction with television pickup tubes including cathode ray scanning means.

The sintered photocells of the invention have the advantage over single crystal photocells in that they are cheaper and easier to prepare, are more rugged, exhibit a panchromatic response to light, may be made in any desired size or shape, and may be designed to handle large currents. The sintered photocells of the invention have the advantage over powder photocells in that they are cheaper and easier to prepare, exhibit a greater response to light at the blue end of the spectrum, exhibit a higher speed of response to light and exhibit greater photosensitivity at lower voltages. The sintered photoconductive layers of the invention have the advantage over presently used vidicon targets of greater photosensitivity and are easier to prepare.

What is claimed is:

1. A method for producing a sintered photoconductive layer comprising forming a stratum including particles of a substance selected from the group consisting of sulphides, selenides and sulposelenides of cadmium, recrystallizing said substance in said layer in a molten solvent, incorporating into said recrystallized substance, activator proportions of a member of the group consisting of copper and silver, removing substantially all of said molten solvent and sintering said recrystallized sub-

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stance, thereby producing a substantially continuous layer of interlocked crystals of photoconductive material.

2. A method for preparing a photoconductive layer comprising forming a stratum including particles of cadmium sulphide, recrystallizing said cadmium sulphide in a molten solvent, incorporating into said recrystallized substance activator proportions of chloride and copper, evaporating substantially all of said molten solvent and sintering said recrystallized cadmium sulphide thereby producing a substantially continuous layer of interlocked crystals of photoconductive material.

3. A method for preparing a photoconductive layer comprising forming a stratum including particles of cadmium selenide, recrystallizing said cadmium selenide in a molten solvent, incorporating into said recrystallized substance activator proportions of chloride and copper, evaporating substantially all of said molten solvent and sintering said recrystallized cadmium selenide thereby producing a substantially continuous layer of interlocked crystals of photoconductive material.

4. A process for producing a photoconductive layer comprising coating a substrate with an intimate mixture of about 100 parts by weight cadmium sulphide, 10 parts by weight cadmium chloride, and 0.01 parts by weight of copper and then firing said coating at about 600° C. in an atmosphere that is inert to said coating until a substantially continuous layer of interlocked crystals of photoconductive material is produced.

5. A substantially continuous polycrystalline layer of interlocked photoconducting crystals of cadmium sulphide containing activator proportions of chloride and copper.

6. A substantially continuous polycrystalline layer of interlocked photoconducting crystals of cadmium selenide containing activator proportions of chloride and copper.

7. A substantially continuous polycrystalline layer of interlocked photoconducting crystals, said crystals comprising a substance selected from the group consisting of sulphides, selenides and sulposelenides of cadmium, said crystals having incorporated therein activator proportions of a halide and having activator proportions of an element selected from the group consisting of copper and silver.

8. A photoconductive device comprising a substantially continuous polycrystalline layer of interlocked photoconducting crystals of cadmium sulphide containing activator proportions of chloride and copper and at least one electrode attached to said layer.

9. A photoconductive device comprising a substantially continuous polycrystalline layer of interlocked photoconducting crystals, said crystals comprising a substance selected from the group consisting of sulphides, selenides and sulposelenides of cadmium, said crystals having incorporated therein activator proportions of a halide and having activator proportions of an element selected from the group consisting of copper and silver and at least one electrode attached to said layer.

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