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HIGH PERFORMANCE PHOTORESISTOR

Filed Dec. 23, 1963

2 Sheets-Sheet 1

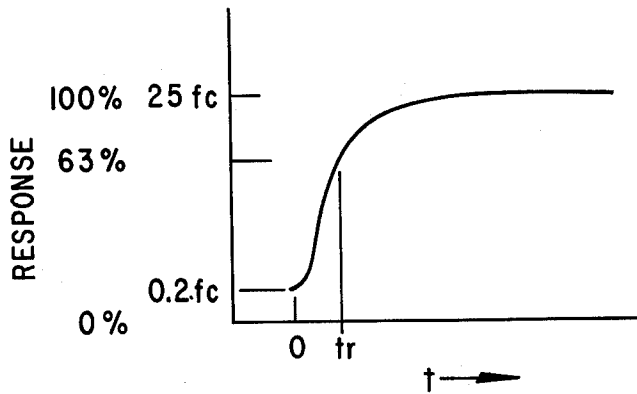


Fig. 1

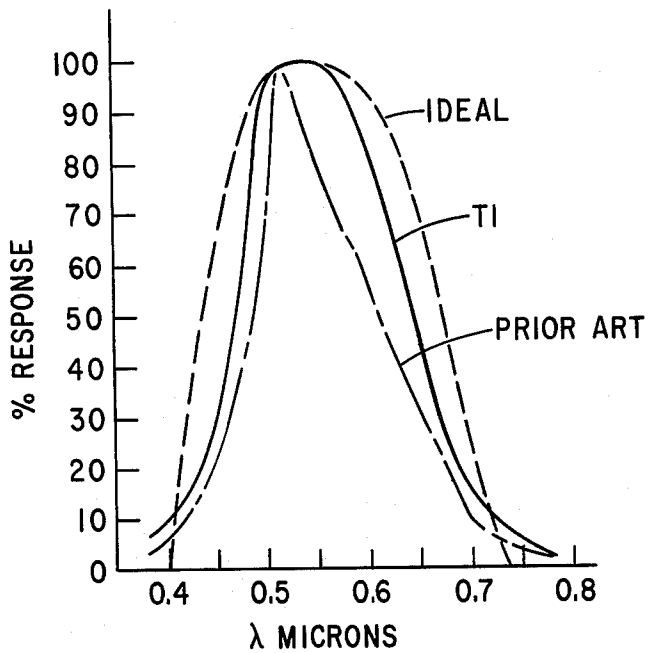


Fig. 2

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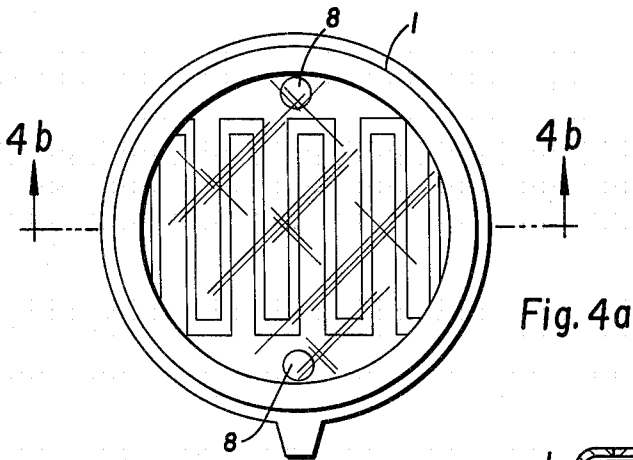


Fig. 4a

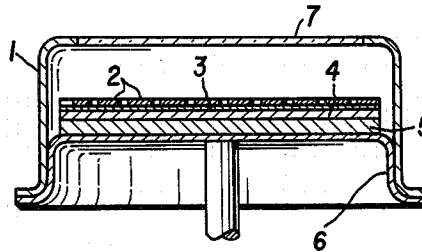


Fig. 4b

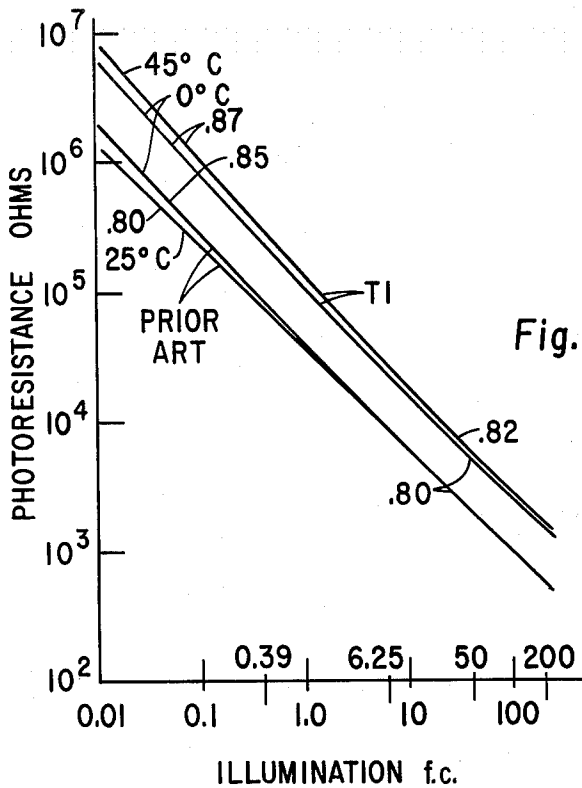


Fig. 3

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15 Claims. (Cl. 338—15)

The photosensitivity of various semiconductive compounds such as cadmium sulfide and selenide, as well as the telluride thereof, both in monocrystalline as well as polycrystalline form is well known. These photoconductive materials have been utilized in many commercial devices and their basic photoconductive mechanisms are fairly well established. The photoconductive effect may be defined as the change of electrical conductivity of the material in response to variations in the intensity of incident radiation. The particular range of wavelengths of radiation to which any given photosensitive material responds is a specific property of the material per se. For cadmium sulfide and cadmium selenide, this photosensitive range includes a substantial portion of the visible spectrum. For this reason, their employment in the field of photoconductive semiconductor devices and elements is particularly advantageous.

Photocells have been developed whose action is based on the internal photoelectric effect occurring in certain semiconductor materials which in darkness are poor conductors. Electrodes are normally fitted to a disc or block of a substance of this kind and depending on the nature of these electrodes, one may obtain a photoconductive cell, or more commonly referred to as a photoresistor. In other words, a device is produced whose electrical conductivity varies with the intensity of the incident light. This is contrasted to a photovoltaic effect which is a device across which differences of electrical potential arise when light falls upon it. The nature of the photoconductivity in the materials of the instant invention, which relates to the II-VI and III-V compounds, can be understood by considering that in a nonconductive solid all electrons are bound to the ions or atoms which comprise the crystal lattice. The free electrons that usually exist in metals and other conductors are absent or, if present, are in very small numbers. This lack of free electrons is also applicable to photoconductive materials such as cadmium sulfide and cadmium selenide when they are not exposed to radiation of the appropriate wavelength. However, when radiation falls on the crystal, the energy of the radiation is absorbed within the lattice. Through the action of this radiation, a number of electrons then become free to move about so that the substance ceases to be an insulator and then converts to a conductor.

Photoconductivity is a process which involves the absorption of energy from light quanta and provides for the excitation of charge carriers from a nonconducting ground state to a higher energy state where these charge carriers are free to contribute to the electrical conductivity, and it also involves the return of these generated charge carriers from the conducting state to their ground state. In other words, photoconductivity processes involve the transition of electrons between different energy states within a crystalline material. A detailed discussion of the various electron processes involved in photoconductivity is provided by Bube, "Photo Conductivity of Solids," John Wiley & Sons, New York, 1960.

Cadmium sulfide and cadmium selenide have been

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found especially useful as photoconductive devices for employment as light amplifiers and image converters as well as other devices. Considerable activity has been expended into increasing the photo response of these materials, and for obtaining new means for providing increased surface areas. The most common method presently employed is the use of powdered layers that have been appropriately sintered to effect bonding. Other methods include various types of powder dielectric material imbedment or the use of evaporated thin films. Sintered layers are preferred for device fabrication inasmuch as they possess superior photosensitivity, high mechanical strength, uniformity of response, as well as ease of formation. While it is well established that the photoconductive properties are directly dependent on the composition and geometry of the unit, it is extremely difficult to provide useful parameters involving fast response and high photocurrents by following techniques disclosed and suggested within the prior art. Photocell rise time and linearity of log resistance versus log light intensity are especially difficult to obtain in accordance with prior art teachings. Furthermore, the range of resistance from dark to light are incompatibly low in the photoconductors of the prior art.

It is an object of this invention to overcome the foregoing and related disadvantages. More specifically, an object is to provide for semiconductor devices having a high photosensitivity and a fast response time, as well as a near linear relationship between log resistance and log light intensity, and being highly responsive to light in the visible and near visible part of the spectrum.

Another object of this invention is to provide for a superior cadmium sulfide-cadmium selenide photoresistor of high performance.

A still further object of this invention is to make available an economical photoresistor having a rise time of less than five milliseconds in response to a change in illumination of 25 ft. candles, or less.

To achieve the above objects, we provide photoresistors based on semiconductor materials and specifically a mixture of cadmium sulfide and cadmium selenide crystals. The cadmium sulfide crystals initially have a diameter of approximately 2 microns with the cadmium selenide particles being 150–200 microns in diameter. We have found that the photoresistor rise time is greatly influenced by film thicknesses as well as film composition. We have found an optimum film thickness range of between 5 to 10 microns as being advantageous with 6 to 8 microns. The thin films may be deposited by employing silk-screening techniques and by carefully controlling the vehicle viscosity and silk-screen mesh size. We have also produced acceptable thin films by air spraying the photoresistor mix and the vehicle. Other printing techniques may also be employed.

We have, furthermore, found that sintering temperatures and sintering times also affect rise times. Also important in the preparation of a photoresistor having a short rise time is homogeneity of the photoresistor mix. This also includes the content with respect to activators. Inasmuch as the activator concentration and ultimate photoconductive mix affects the photoresistivity including the dark resistivity, we have found that the composition of the mix prior to, as well as after sintering, must be closely controlled to effect the desired results. We have, furthermore, found that the spectral response is directly related to the cadmium sulfide-cadmium selenide basic mixture, as well as the use of various activator materials. Further-

more, we have found that the film thickness also greatly affects spectral response. Especially significant insofar as the slope of the log of photoresistance versus the log of illumination, is the copper activator and the cadmium chloride concentration.

The invention may be better understood from the following illustrative description and the accompanying drawings.

FIG. 1 of the drawings is a rise time plot between illumination and time.

FIG. 2 is a spectral response plot of a typical photoresistor manufactured in accordance with the present invention.

FIG. 3 is a plot between log photoresistance and log illumination of typical photoresistors in accordance with the present invention.

FIG. 4 illustrates the structure of a photoresistor of the present invention.

In FIG. 1 is illustrated a typical rise time curve for the devices of the invention where a rise time of about 5 milliseconds or less is secured in response to a change in illumination of from about 0.2 to about 25 ft. candles. The time taken for the resistance to change 63% of the total resistance change is a measure of the response time of the photo device and involves, as shown in the plot, the time for the resistance to reach $1/e$ of its final value, where e is the well known constant associated with Napierian logarithms. Another plot is illustrated in FIG. 2 wherein the spectral response of the instant devices is shown. Readily apparent is the significant improvement over prior art photoresistors and the nearness of the instant invention to an ideal photoresistor. Shifting of the peak of the response to suit the desired wavelength is realized by carefully controlling the composition in accordance with the inventive concept herein, as well as its method of preparation in films of specific thicknesses. Additions of CdSe shift the response peak toward longer wavelengths.

FIG. 3 describes devices of the invention by utilizing a plot between illumination and photoresistance wherein the slope of the curve is found to represent a value between about 0.85 and 1.0 for low illumination levels. The observed slope for higher illumination levels is slightly less with a slope of 0.82 having been realized. For Cu additions reaching up to about 1,000 p.p.m. the log-photoresistance versus log-illumination slope is directly influenced and increases to a value of about 1.8 whereas lower Cu concentrations involving only a few p.p.m. have a smaller slope value. Critical control of the CdSe to CdS ratio has been found necessary since high ratios effect a decreasing slope value. Similarly, CdCl₂ additions adversely affect the slope values. We have found that the devices of the invention, as noted in the two curves having higher slopes as well as higher photoresistance, are superior to those of the prior art wherein slopes of 0.8 are typical. We have also found that even higher slope values can be obtained by critical control of film thickness, with thin film thicknesses also being less sensitive to temperature changes.

FIG. 4a is a top view of a photoresistor mounted within a hermetically sealed metal can 1 positioned underneath a glass window 7. In FIG. 4b, a cross-sectional view, there is shown an active CdS-CdSe film 3 which is deposited, preferably by silk-screening or spraying, onto an alumina disc 4, or the substrate may be other suitable insulating material such as polymeric, refractory organic, or various vitreous materials. After sintering of the composite, suitably conducting contacts 2 such as tin are evaporated through a mask onto the film 3, with external electrical connections being suitably provided through wires 8 extending through optional insulating supporting means 5, disc 4, and film 3, to make connection with the finger shaped contacts 2. Vitreous materials having suitable transparencies to wavelengths of interest, as well as polymeric materials, are especially desirable in lieu of the

can type encapsulation means for special applications and where low cost is important. Hermetic sealing of the device precludes the deterioration normally occurring during operation in even moderately humid ambients. Sealing of the external leads in the epoxy resin, the vitreous material, or other suitable encapsulation means, is also desirable to provide for a complete hermetic seal. The encapsulation means also enhances mounting ease and prevents damaging the active film surface.

The photocells manufactured according to the invention have exceedingly high photoconductivity and have likewise exceedingly fast rise times, broad spectral response, and are functionally stable over a period of time. We have found that a specific narrow range of constituents will provide the required combination of desirable device properties. This composition consists of 66.13 mol percent of CdS, 28.22 mol percent of CdSe, 5.62 mol percent of CdCl₂·2½H₂O, and 0.03 mol percent CuCl₂·2H₂O. This mixture is provided in slurry form and is subsequently dried and ground into fine particles. The mixture is then suspended in a 5% ethyl cellulose toluene solution by ball milling for 30 minutes. The cadmium sulfide-selenide mixture is approximately one-third the weight of the suspending liquid. This suspension is then silk-screened onto alumina wafers and allowed to dry with subsequent baking at a temperature of approximately 550° C. to secure interdiffusion of constituents and film homogeneity.

We have found that one other narrow range of constituents will provide for the desirable combination of photoconductive properties with other compositions being undesirable. A specific composition within this extremely narrow critical range consisted of 87 mol percent CdS, 7.3 mol percent CdSe, 5.7 mol percent CdCl₂ and 0.035 mol percent CuCl₂.

Another photoresistor in this range consisted of a completely diffused homogeneous film of 84 mol percent CdS, 10.6 mol percent CdSe, 5.9 mol percent CdCl₂, and 0.035 mol percent CuCl₂.

We have found that the use of cadmium selenide in a narrow range as an addition element to cadmium sulfide photoresistors will function to decrease rise times and also has a pronounced effect upon dark to light adaptation differences. Our investigations suggest that cadmium selenide introduces traps in cadmium sulfide which normally are nonexistent. This is reasonable since, not only does the cadmium selenide act as a dopant, but boundaries between cadmium sulfide and cadmium selenide granules can also introduce trapping centers. Furthermore, we have found that the oxidation behavior is different for cadmium sulfide and cadmium selenide, and would secure a material containing surface energy levels different than in the absence of cadmium selenide and its normal oxidation products.

We have found that the cooling rate after sintering of the photoconductive film is important. Long cooling periods give better results in that strain-free granular materials are produced having fewer defects with photoresistors having smaller adaptation differences. Prolonged cooling cycles however adversely affect rise time and therefore are undesirable. We have found particularly effective a cool-down cycle having a 15 to 20 minutes duration.

Radioactive isotopes effects suggest that alpha and/or beta, and a low energy gamma radiation can act as a biasing source to maintained filled traps, and thereby function to negate the effects of having to fill and empty these traps as a condition of light change. This approach has been especially useful with CdS photodetectors and has functioned to decrease the light-to-dark adaptation differences as well as to obtain improved rise times. Ti²⁰⁴ as well as Ni⁶³ have been incorporated in the mix as well as secured in the form of a thin film painting on the inner periphery of the encapsulation means. When it is incorporated in the mix, the isotope was less effective due

to vaporization, whereas when incorporated in the encapsulation means, its utility is greater. Good results were obtained by use of these isotopes, even in exceedingly small concentrations. It is simple to determine the amount of activity needed for a particular mix since this can be readily determined by increasing the radioactive isotope concentration until the dark resistance begins to reflect a change.

In the manufacturing processes of the invention, after the sintering operation, the fused thin photoconductor film is provided with an interleaved finger type metallic contact structure on its surface. Exceedingly good results have been obtained by using transparent exceedingly thin contacts of indium and indium-tin oxides. Other thin transparent metallic contacts may also be employed. The device is then provided with a container by mounting into a TO-5 header with an appropriate window, as noted in FIG. 4, or by sealing into a vitreous ceramic or glass or transparent polymeric material.

A particularly desirable method of providing transparent low resistance indium contacts involves the vapor diffusion of indium into the surface of the film. The diffusion step is accomplished under a positive pressure of hydrogen and by heating the assembly to a temperature sufficient to provide a high concentration of indium atoms in the photoconductive surface. It is found highly desirable to maintain a slight temperature gradient of approximately 5° C. per inch which functions to keep the indium vapors from leaving the evaporation chamber. Masking, of course, is employed to provide for the desired electrode configuration. Another method for providing good ohmic transparent nonreflecting contacts utilizes an 82% indium, 18% tin alloy, that is reactively sputtered in an oxidizing ambient onto the film surface. Good results have been obtained with tin concentrations as low as 10% and as high as 30% with the balance being indium. The transmittance characteristics of a sputtered $\text{In}_2\text{O}_3\text{-Sn}$ film provides for an almost 100% transmittance for the wavelengths of interest in the invention.

While superior results are obtained with the specific mixtures disclosed above, we have found that films doped with 100 p.p.m. of copper show spectral response peaking out at approximately 5200 Å. By increasing the copper concentration to 400 p.p.m., the response line is broadened with the peak moving to 5500 Å., silver being useful but less effective. Additional cadmium selenide also functions in the same manner by shifting the peak toward longer wavelengths.

Preliminary evaluations show that the composition employed in the invention is extremely useful for large area photo devices employable in integrated circuits as well as in hybrid microcircuitry involving both active and passive components. Ease of preparing such active and passive components allows for the providing of exceedingly low cost electrical devices per unit function. Thin cadmium selenide films have also been employed for card reader logic circuitry with extremely good results. The photoresistor is also employable into magnetic tape controls as well as in character recognition equipments. Because of its extremely rapid rise times as well as photosensitivity, it is extremely useful in camera aperture control mechanisms as well as in various other visible and ultra-violet region control mechanisms.

While cadmium sulfide single-crystals give better response in the ultra-violet region, economics suggest the use of the invention where low cost is a factor in such applications as check-out equipment as well as in various types of communication techniques employing light of the herein disclosed wavelengths. Its usefulness in various types of logic circuits as well as in automatic counters is only limited by its response time which is about several milliseconds.

It may thus be seen that the invention is broad in scope and includes such modifications as will be apparent to those skilled in the art, and will be particularly appar-

ent after benefiting from the teachings and equivalents disclosed herein and especially in view of those teachings specifically embraced by the instant invention. It is to be understood that the invention is not limited to the specific embodiments hereof excepting as defined in the appended claims. Having thus described our invention, we claim:

1. A photoresistor comprising:

- (a) an insulating substrate,
- (b) a thin film of homogeneous photosensitive material contiguous with said substrate,
- (c) said homogeneous photoconductive material consisting essentially of 60 to 70 mol percent CdS, 20 to 30 mol percent CdSe, 1 to 8 mol percent CdCl_2 , and from 0.01 to 0.05 mol percent CuCl_2 ,
- (d) spaced metal electrodes connected to said thin film of photosensitive material,
- (e) encapsulation means completely surrounding said photoresistor excepting for exposed electrical conducting means making connection to said thin film of photosensitive material.

2. A photoresistor according to claim 1 wherein said homogeneous photosensitive material is 6 to 8 microns in thickness.

3. A photoresistor according to claim 1 wherein the insulating substrate is a thin Al_2O_3 wafer.

4. A photoresistor according to claim 1 wherein the spaced metal electrodes making electrical connection to said thin film of photoconductive material are a transparent indium compound.

5. A photoresistor according to claim 1 wherein the encapsulation means comprises a low temperature vitreous ceramic.

6. A photoresistor according to claim 1 wherein the encapsulation means comprises transparent polymeric material.

7. A photoresistor according to claim 1 wherein the encapsulation means comprises a metal container having a transparent window mounted therein.

8. A photosensitive device comprising:

- (a) an insulating substrate,
- (b) a thin film of homogeneous photoconductive material overlying said substrate, consisting essentially of 84 to 87 mol percent CdS, 7 to 11 mol percent CdSe, 5 to 7 mol percent CdCl_2 , and 0.02 to 0.4 mol percent CuCl_2 ,
- (c) spaced electrodes overlying said photoconductive material,
- (d) encapsulating means surrounding said substrate, photoconductive material, and spaced electrodes, and
- (e) external means making electrical connection to said spaced electrodes.

9. A device according to claim 8 wherein said thin film of homogeneous photoconductive material is 6 to 8 microns in thickness.

10. A device according to claim 8 wherein said spaced electrodes consist of a transparent indium compound.

11. A photosensitive device comprising:

- (a) an insulating substrate,
- (b) a thin film of homogeneous photoconductive material composed of 60 to 87 mol percent CdS, 7 to 30 mol percent CdSe, 1 to 8 mol percent CdCl_2 , and 0.01 to 0.05 mol percent CuCl_2 ,
- (c) spaced electrodes overlying said photoconductive material, and
- (d) encapsulating means completely surrounding said device excepting for exposed electrical conducting means making electrical connection to said photoconductive material.

12. A photosensitive device according to claim 11 wherein said thin film of homogeneous photoconductive material contains radioactive isotopes.

13. A photosensitive device according to claim 11

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wherein said encapsulation means contains a thin film of radioactive isotope material secured thereto.

14. A photosensitive device according to claim 11 wherein said spaced electrodes are a transparent indium compound.

15. A photosensitive device according to claim 11

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wherein said thin film of homogeneous photoconductive material is 6 to 8 microns thick.

No references cited.

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