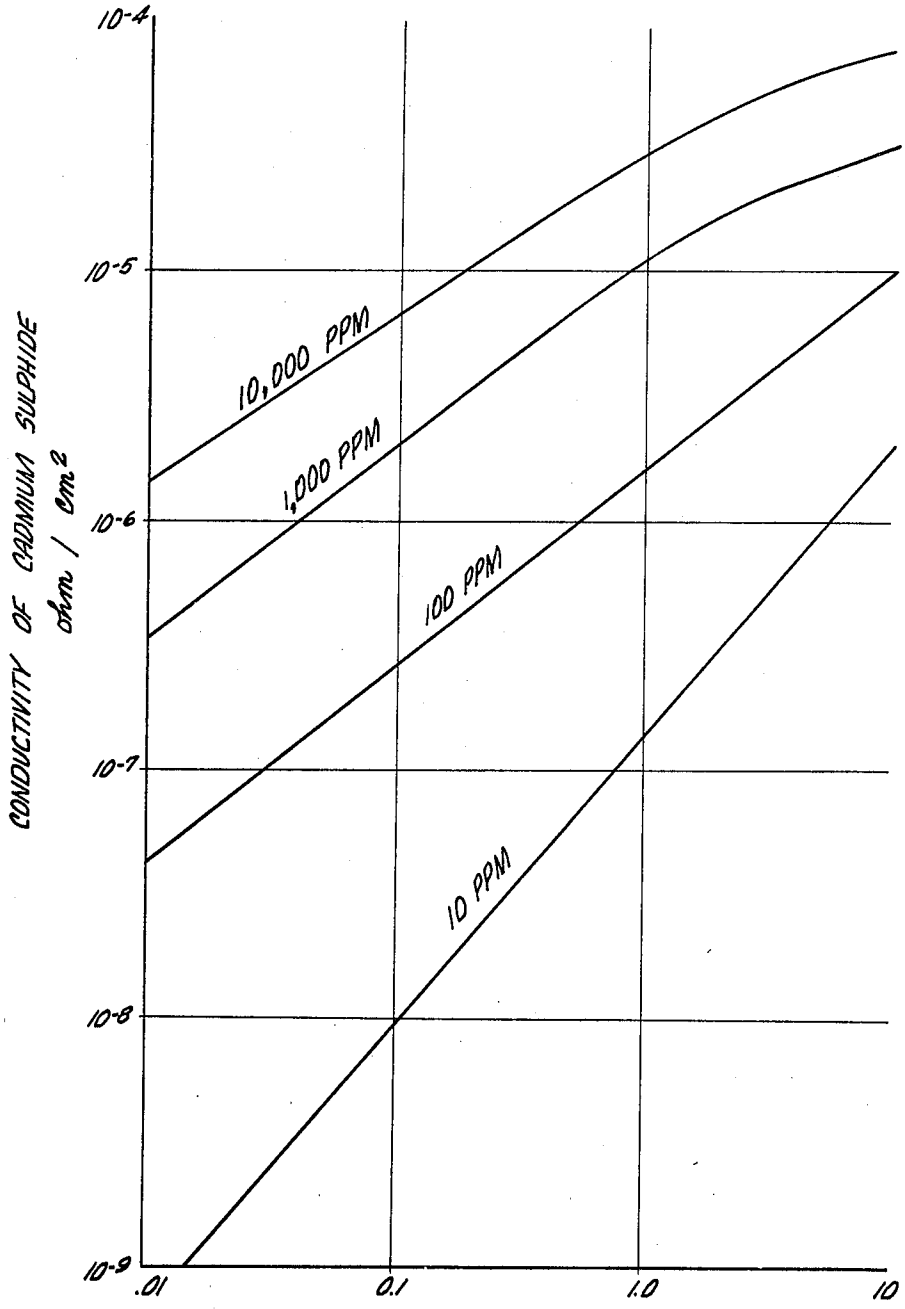
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PREPARATION OF LIGHT SENSITIVE DEVICE OF ENHANCED PHOTOCONDUCTIVE SENSITIVITY

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PREPARATION OF LIGHT SENSITIVE DEVICE OF ENHANCED PHOTOCONDUCTIVE SENSITIVITY

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ABSTRACT OF THE DISCLOSURE

A composition of matter and method for preparing same involving the addition of selected impurities for improving the luminescent and photoconductive properties of certain semiconductor materials. Impurities added are alkali metals in a specified amount. The semiconductors to which the impurities are added are cadmium sulfide, cadmium selenide, zinc sulfide and zinc selenide.

This invention relates to semiconductor materials and in particular to semiconductors of cadmium sulfide, cadmium selenide, zinc sulfide, zinc selenide and alloys of these materials having predetermined amounts of alkali metals incorporated therein.

The use of photocells employing cadmium sulfide and cadmium selenide and mixtures thereof as the photoconductive materials is well known. As is true of many semiconductor materials, small quantities of impurities are frequently found in these materials even after the material has been subjected to refinement. Some of these impurities are alkali metals.

The presence of these alkali metals can be due to several causes. In some cases these metals are present in the cadmium sulfide (CdS) or cadmium selenide (CdSe) used to make the cells and have not been removed by whatever refinement steps were used in preparing the photoconductor. In other cases they are present in the substrate material on which the CdS and CdSe are placed and diffuse into the photoconductor. For much the same reasons, these same alkali metals are also found to be present in the zinc sulfide (ZnS) and zinc selenide (ZnSe) materials which are frequently used in luminescent devices. The presence of alkali metals in these materials has not been regarded as particularly significant nor has there been any indication of an awareness that alkali metals have any particular effect on the properties of sulfides and selenides of cadmium and zinc.

It has now been found, however, that these alkali metals exert a substantial influence on many of the properties of CdS, CdSe, ZnS, and ZnSe and mixtures thereof, and that these various properties differ, depending on the quantity of alkali metal present. The present invention relates to the enhancement of certain properties, e.g., the sensitivity of CdS, CdSe, ZnS, ZnSe and alloys or mixed crystals of these compounds by incorporating into them sufficient quantities of alkali metals such that the total amount of these elements present is within the range of 100 to 10,000 parts (atoms) per million parts (atoms) of cadmium, zinc, sulfur and selenium. In copending application, Serial Number 456,382, filed of even date herewith, the invention disclosed therein is that it has been found that another property, viz, the speed of response of devices using CdS, CdSe, ZnS, and ZnSe and the various alloys thereof is substantially altered if the amount of alkali metals present in such compounds is limited to not more than 30 parts (atoms) per million parts (atoms) of the elements of the semiconductor, viz, cadmium, sulfur, etc.

The effect on one characteristic of a photocell of cadmium sulfide is shown in the drawing which illustrates the direct relationship between the conductivity of the cadmium sulfide and varying concentrations of sodium.

The use of cadmium sulfide and cadmium selenide as photoconductors for the performance of various tasks in research and industry is undergoing a broad expansion at the present time. Photoconductors are currently in use or being considered and developed for use in such widely diverse applications as photocells for measurement of light intensity; automatic exposure and focus control on cameras; detectors for X-rays, alpha and beta particles and gamma rays; automatic automobile headlight dimmers; street light control; oximeters; "noiseless" switches; potentiometers without "moving" contacts; smoke and fire control; detectors and computers; and miscellaneous toys and novelties. The alloys of cadmium sulfide and cadmium selenide with alkali metals according to the present invention result in a substantial improvement in the magnitude of their photoconductivity when compared to unalloyed CdS and CdSe. This improvement in photoconductivity is particularly large at low light intensities and at low temperatures.

Similarly, research directed toward altering the properties of luminescent materials such as zinc sulfide and zinc selenide has become intensified. Alloys of these materials and alkali metals have been found to effect a substantial improvement over the luminescence obtained using unalloyed ZnS and ZnSe. In addition to having useful photoconductive and luminescent properties, alloys of these materials with alkali metals also possess useful acoustoelectric and piezoelectric properties.

Other properties and aspects in addition to those mentioned previously which have been investigated with respect to these semiconductor materials are: spectral response, electrode contact problems, carrier mobility, and surface conductivity. It is the substantial and predictable alteration of all of these properties and particularly the electrical properties of cadmium sulfide, cadmium selenide, zinc sulfide, zinc selenide and the various possible alloys of these compounds with which the present invention is concerned.

The preparation of semiconductors has evolved from techniques for producing layers of semiconductors with properties which approach those of single crystals to three current methods which produce crystalline layers. These three current methods are: preparation by vapor phase reaction of the elements of the desired semiconductor, Phys. Rev., vol. 72, 594 (1947); sublimation or evaporation of a powdered sample of the semiconductor and subsequent recrystallization of the sample, Journal of Applied Physics, vol. 34, 2390 (August 1963); and spraying a slurry of powdered sample followed by sintering to remove the binder materials and promote crystal growth, Rev. of Sci. Inst., vol. 26, 664 (1955).

Addition of quantities of elements from the first periodic group according to this invention can be accomplished during the steps of any of the three methods mentioned above. Another way in which this addition or "doping" can be accomplished is by depositing the CdS, etc. on a substrate of an alkali-containing glass and allowing the proper amount of alkali metal to diffuse from the substrate into the semiconductor.

The term photoconductor as used herein includes materials which are intrinsically photoconductive and those which must be activated by the introduction of impurities into the lattice structure. Cadmium sulfide, for example, belongs in the latter category. In CdS, the sensitizing impurities take the form of halides of silver or copper as is described in U.S. Patents 2,995,474 and 2,997,408.

The additional alloying of alkali metals into the activated cadmium sulfide does not induce photoconductivity but rather enchances it. This enhancement takes the form of substantially greater sensitivity. The increase in sensitivity can be measured by the increase in the conductivity of alloyed versus unalloyed CdS for a given light intensity. The drawing illustrates the variation of conductivity of CdS with given increments of alkali metal impurity. For comparative purposes, four CdS cells containing 10, 100, 1,000, and 10,000 parts atomic (atoms) of sodium respectively were subjected to increasing amounts of light (.01 to 10 footcandles) and the conductivity for that amount of illumination was measured. As shown therein, the conductivity is substantially increased as the amount of sodium in the crystal is increased.

The doping impurity or alloying material heretofore referred to as alkali metals encompasses the following elements: sodium, lithium, potassium, rubidium, cesium, and francium. In addition to the use of these elements singly, it has been found that various combinations of these alkali metals are also quite useful in their contribution to the photoconductive, luminescent, etc., properties of the semiconductor. Specifically, combinations of sodium and lithium, potassium and sodium, and lithium and potassium have been found to add even more significantly to the photoconductivity of the cadmium sulfide in comparison with the use of any one of the elements singly. Similarly, the combination of lithium and sodium affects the luminescent efficiency of zinc selenide in a manner different than either element alone.

In addition to limiting the nature of the impurity to alkali metals, the concentration of the particular metal or combination of metals must also be held within certain quantitative limits depending on the semiconductor being doped. In the case of sodium, it has been found that satisfactory results are obtained when the amount of sodium diffused into semiconductors of cadmium or zinc sulfide is held between the range of one hundred to ten thousand parts (atoms) of sodium per million parts (atoms) of cadmium or zinc and sulfur and between the range of one hundred to one thousand parts (atoms) of sodium per million parts (atoms) of cadmium or zinc and selenium for semiconductors of CdSe or ZnSe. The range of 100 to 10,000 parts per million defines the range in which a substantial change in the properties of the semiconductors is accomplished. Below 100 parts, the sensitivity is too low for many applications, particularly automatic exposure controls.

It is believed that higher sensitivity could be achieved if the selenides and sulfides could be doped with greater quantities of sodium than 1,000 and 10,000 parts respectively. These limits, however, represent upper solubility limits of sodium in the semiconductor materials with which this invention is concerned.

In the case of the other alkali metals, viz., lithium, potassium, rubidium, cesium, and francium, the reduced solubility of these larger molecule elements in the various semiconductor materials with which this invention is concerned further restricts the amount of these elements with which the cadmium sulfide, et al, can be doped. In the case of these latter elements, the upper limit is about one thousand parts (atoms) of at least one of these lower solubility metals per million parts (atoms) of the elements of the semiconductor, a reduction by a factor of ten in comparison to sodium. The lower limit remains the same as for sodium putting the inception of the significant increase in sensitivity due to the presence of these metals at one hundred parts (atoms) per million parts (atoms) of the elements of the semiconductor.

As indicated previously, the present invention also includes the various possible alloys of the sulfides and selenides of cadmium and zinc. By varying the particular constituents and proportions of each constituent in a given alloy, it is possible to obtain a photoconductor whose peak spectral sensitivity is substantially different

from that of cadmium sulfide, cadmium selenide, etc., alone and to tailor the semiconductor to produce a photoconductor with any given spectral sensitivity desired. Where alloys such as these are to be sensitized, the range of alkali metal impurity again varies depending on the constituents of the alloy and the nature of the doping material. For sodium as the dopant and alloys containing sulfides of cadmium and zinc, the range is 100 to 10,000 parts of sodium per million parts of the elements in the semiconductor material. The upper limit of the range depends on the amount of sulfide present in the alloy. As the amount of sulfide present in the alloy increases, the solubility of sodium approaches an upper limit of 10,000 parts per million; as the amount of sulfide diminishes, the solubility of sodium is reduced, and the upper limit is likewise diminished down to but not below 1,000 parts per million, a condition which occurs where only trace quantities of the sulfides are present in the alloy.

In the case of the alkali metals less soluble in these semiconductor materials, viz., lithium, potassium, rubidium, cesium and francium, the useful range is the same for alloys of the semiconductor as it was for crystals of CdS, CdSe, etc. alone, i.e., 100 to 1,000 parts of at least one of the alkali metals per million parts of the elements in the semiconductor alloy regardless of the particular composition of the alloy.

Where the alloy is doped with sodium and lithium or potassium, the range is 100 to 10,000 parts of these alkali metals for alloys including sulfides and 100 to 1,000 parts for those alloys in which little or no sulfide is present. Where the dopant is potassium and lithium, the suitable range of concentration is 100 to 1,000 parts atomic of potassium and lithium per million parts atomic of the elements in the semiconductor material regardless of the particular amount of selenides and sulfides present in the material.

The preceding ranges can be summarized by the following tables:

TABLE I.—DOPANT

	Na	Li, etc.
Semiconductor:		
CdS	100–10,000	100–1,000
CdSe	100–1,000	100–1,000
ZnS	100–10,000	100–1,000
ZnSe	100–1,000	100–1,000
CdS-CdSe	100–10,000	100–1,000
CdS-ZnS	100–10,000	100–1,000
CdS-ZnSe	100–10,000	100–1,000
CdSe-ZnS	100–10,000	100–1,000
CdSe-ZnSe	100–1,000	100–1,000
ZnS-ZnSe	100–10,000	100–1,000
CdS-CdSe-ZnS	100–10,000	100–1,000
CdS-CdSe-ZnSe	100–10,000	100–1,000
CdS-ZnS-ZnSe	100–10,000	100–1,000
CdSe-ZnS-ZnSe	100–10,000	100–1,000
CdSe-CdS-ZnS-ZnSe	100–10,000	100–1,000

TABLE II.—DOPANT

Semiconductor	Na and Li	Na and K	Li and K
CdS	100–10,000	100–10,000	100–1,000
CdSe	100–1,000	100–1,000	100–1,000
ZnS	100–10,000	100–10,000	100–1,000
ZnSe	100–1,000	100–1,000	100–1,000
CdS-CdSe	100–10,000	100–10,000	100–1,000
CdS-ZnS	100–10,000	100–10,000	100–1,000
CdS-ZnSe	100–10,000	100–10,000	100–1,000
CdSe-ZnS	100–10,000	100–10,000	100–1,000
CdSe-ZnSe	100–1,000	100–1,000	100–1,000
ZnS-ZnSe	100–10,000	100–10,000	100–1,000
CdS-CdSe-ZnS	100–10,000	100–10,000	100–1,000
CdS-CdSe-ZnSe	100–10,000	100–10,000	100–1,000
CdS-ZnS-ZnSe	100–10,000	100–10,000	100–1,000
CdSe-ZnS-ZnSe	100–10,000	100–10,000	100–1,000
CdSe-CdS-ZnS-ZnSe	100–10,000	100–10,000	100–1,000

One specific application for the high sensitivity photoconductive cells of this invention is as light-sensing devices, in particular, as devices for detecting very small values of light intensity. For example, a camera with automatic exposure control through its lens requires a photocell which operates at an intensity of less than one foot candle. A photocell equipped with an alloy of alkali

metals and cadmium sulfide according to this invention possesses the required degree of sensitivity.

As indicated earlier, alloys of the present invention display marked changes in many characteristics relative to their unalloyed counterparts. The immediately preceding example illustrated the enhanced photoconductivity of alloyed cadmium sulfide. Another property substantially effected is the luminescence of these semiconductors. For example, where zinc selenide is doped with from ten to one thousand parts (atoms) of lithium per million parts (atoms) of zinc and selenium or with one hundred to one thousand parts of lithium and sodium per million parts (atoms) of zinc and selenium, its luminescent efficiency can be increased by a factor of between 10 to 100. The piezoelectric characteristic of these doped zinc selenides also makes them useful in acoustic amplifiers.

What is claimed is:

1. A method for preparing a light sensitive device for detecting small values of light intensity which comprises:
providing a solid substrate for said device;
providing a semiconductor material selected from the class consisting of sulfides and selenides of cadmium;
incorporating an activator and a halide coactivator in the semiconductor material;
depositing on said substrate a layer of the activated semiconductor material;
incorporating an alkali metal salt wherein the alkali metal is selected from the class consisting of sodium, lithium, rubidium, cesium and francium in said layer of semiconductor material in sufficient amount to provide from 100 to 10,000 parts atomic of said alkali metal per million parts atomic of the elements in the semiconductor material; and heating the layer of semiconductor material to form a photoconductive layer on said substrate.

2. The method of claim 1 wherein the alkali metal is sodium.

3. The method of claim 2 wherein the semiconductor material is cadmium sulfide.

4. A method for preparing a light sensitive device for detecting small values of light intensity which comprises:
providing a mixture of a semiconductor material selected from the class consisting of sulfides and selenides of cadmium and an activator-coactivator material selected from the class consisting of halides of silver and copper to produce an activated photoconductive material;
depositing the activated photoconductive material and an alkali metal salt on a substrate, the alkali metal being selected from the class consisting of sodium, lithium, rubidium, cesium and francium in sufficient amount to provide from 100 to 10,000 parts atomic of alkali metal from the class per million parts atomic of the elements in the semiconductor material; and
sintering the deposited material.

5. The method of claim 4 wherein the alkali metal is sodium.

6. The method of claim 5 wherein the semiconductor material is cadmium sulfide.

References Cited

UNITED STATES PATENTS

2,958,932	11/1960	Goercke	252—501 X
3,133,888	5/1964	Oikawa et al.	252—501
3,324,299	6/1967	Schuil	252—501 X
3,130,341	4/1964	Johnson.	

OTHER REFERENCES

Kroger—Sodium & Lithium as Activators of Fluorescence in Zinc Sulfide—Journal of the Optical Society of America, vol. 39, No. 8, August 1949, pp. 670–672.

RICHARD D. LOVERING, Primary Examiner

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252—62.3, 62.9, 301.6, 501