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PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO PROCESS OF MAKING PHOTOSENSITIVE SILVER SULPHIDE THIN FILM DEVICE"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, An Indian registered body incorporated under the Registration of Societies Act (Act XX, of 1860)

The following Specification describes the nature of this invention :—

This is an invention by :

CHITTARI VENKATA SURYANARAYANA Scientist

NARASIMHAN RANGARAJAN Senior Scientific Assistant

KRISHNAMOORTHY NAGARAJA RAO Senior Scientific Assistant

MARY JULIANA MANGALAM Senior Scientific Assistant

Nationality : INDIANS

Central Electrochemical Research Institute, KARAIKUDI-3.

This invention relates to improvements in or relating to Silver sulphide photosensitive cells.

Hitherto only photo voltaic silver sulphide cells are known and they were used mainly in spectrophotometers. Photo-conductive silver sulphide cells have not been in vogue.

Photo-voltaic cells in general give less signal than if the same cells can be worked as a photo-conductive one. The photo-voltaic signal obtainable theoretically is limited in the case of Silver Sulphide to about 900 mV. As a photo-conductor, signal voltages obtainable depend on the applied voltage limited only by the breakdown voltage of the semi-conductor. Silver sulphide cells were not used as photo-conductive ones for the reason that due to ionic conduction the dark resistance values would drift and also give rise to small signals.

The object of this invention is to obviate these disadvantages by processing the Silver sulphide cell as a photo-conductive one without the disadvantages mentioned above.

To these ends, the invention broadly consists in the following observations and modifications by us mentioned below :

(a) Silver sulphide cell (undoped) behaves as a stable photo-conductor, when a low d.c. of the order of one tenth of a microampere or a.c. of the order of one micro-ampere or less is passed.

Alternatively when doped suitably, not only the sensitivity increases about two fold but also the cell remains stable when d.c. of about 1/5th micro ampere or a.c. of any higher value of the order of milliamps is passed.

(b) That this signal obtained is dependent on the frequency of the applied a.c.

(c) That a frequency in the range 20-60c/s gives good signals.

(d) That about 10 V a.c. of 50c/s. applied voltage gives enough signal to be measured by a meter.

(e) That the overall sensitivity in the entire spectral range can be improved by doping with the following two groups of combinations.

(i) Ions of group II(b) (zinc, cadmium, mercury) in the periodic classification with selenium or/and teleurium,

(ii) Antimony or/and bismuth and alkali-halides,

(iii) Other ions of group I B in the periodic classification with alkali halides.

A proper choice is to be made between sensitivity and stability of dark resistance with time.

(f) Heat treatment of the deposited layers in a range of temperature between 120-175°C in an atmosphere of oxygen for a few minutes resulted in additional augmentation of sensitivity in the entire spectral region.

The following typical examples are given to illustrate the invention :

Example 1

Applied Bias 13V, 50 c/s
Electrode spacing=5 mm
Resistance of the cell 15 MegΩ
d=distance between the cell and source

Cell	Philips Infraphil lamp (red) (150 watts) d=50 cms signal	white light (60 watts) d=25 cms. signal
Ag_2S	400 mV	90 mV
Ag_2S (doped)	900 mV	100 mV

Example 2

Applied Bias 13 V, 50 c/s
Electrode spacing=4 mm
Resistance 12 MeΩ

Cell	Infra-phil Lamp 150 Watts d=50 cms	White light 60 watts d=25 cms
Ag_2S	350 mV	70 mV
Ag_2S (doped)	1400 mV	220 mV

Example 3

(Effect of frequency)

Applied bias 13 V.
Electrode Spacing 5 mm
Resistance 15 MegΩ
Source :Infraphil Lamp at 50 cm.

Frequency	5 c/s	20 to 60 c/s	500c/s	1000 c/s
S l in MilliVolts :	360	400	190	70

The following are among the main advantages of the invention :

1. By suitable doping the response as well as the stability of the cells in the entire range have been enhanced considerably.

2. Doped Silver sulphide thin film photosensitive layers could be used as stable photo-conductive cells in the region 0.4 micron to 1.4 micron by applying 10 volts a.c. in the range of 20-60 c/s.

3. By balancing the dark current, even small signals obtained for low levels of illumination could be amplified.

Dated this 23rd day of June, 1967.

(Sd./-)

PATENTS OFFICER,

Council of Scientific & Industrial Research.

COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO PROCESS OF MAKING PHOTOSENSITIVE SILVER SULPHIDE THIN FILM DEVICE"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi 1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by CHITTARI VENKATA SURYANARAYANA, Scientist, NARASIMHAN RANGARAJAN, Senior Scientific Assistant, KRISHNAMOORTHY NAGARAJA RAO, Senior Scientific Assistant and MARY JULIANA MANGALAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, all Indian citizens.

This invention relates to improvements in or relating to silver sulphide photoconductive cells, and has particular reference to a photosensitive silver sulphide thin film device for measuring low levels of illumination (100 to 1000 Lux) in the spectral range of 0.4 to 1.4 microns.

Hitherto these photosensitive thin layers of silver sulphide have been deposited by the method of vacuum evaporation. Photoconductive silver sulphide cells have not been in vogue. On the other hand, only photovoltaic silver sulphide cells sensitive in the range from 0.4 to 1.4 microns are known and they were used mainly in spectrophotometers.

The vacuum evaporation method is governed by several critical factors, such as the degree of vacuum, the nature of the heating element which keeps the material to be evaporated, the current to be passed through the heating element wire, the disposition of the glass plates on which the material is to be evaporated and is also costly. Moreover uniformity of deposition and reproducibility are rather difficult to achieve by vacuum evaporation.

The photosensitive silver sulphide layer when used to form a junction with other suitable materials like a layer of antimony, works as a photovoltaic cell when the junction is shone with light in the region of its response, namely, 0.4 to 1.4 microns. Normally the same material without forming a junction when used as thin layer with two identical electrodes in electrical circuits should behave as a photo resistor. But in the particular case of silver sulphide, due to ionic conduction, the dark resistance values would drift and therefore the material could not be used as a photoconductor. It was used only as a junction material in a photovoltaic device.

The photovoltaic signal obtainable theoretically is limited in the case of silver sulphide to about 900 mV. When used as a photoconductor, signal voltages obtainable, if the material works well, depend on the applied voltage limited only by the breakdown voltages of the semiconductor. Silver sulphide layers were not used as photoconductive ones for the reason given, namely, that due to ionic conduction the dark resistance values would drift and also give rise to small signals.

The object of this invention is to obviate these disadvantages by processing the silver sulphide layers as photo-conductive ones without the disadvantages mentioned above (namely the ill effects of ionic conduction of silver ions).

The main finding underlying the invention is that the silver sulphide layer can be deposited on ground glass substrates by an easy and reproducible chemical method by using silver nitrate, thiourea and ammonium hydroxide as starting materials. The doping is done by adding the dopant to the chemical bath in the beginning itself. The cell thus obtained behaves as a stable photoconductor, when a low d.c. of the order of not more than 1 microampere or a.c. of the order of 70 microamperes and more are passed (limited only by the undesirable heating effects).

The new result flowing from the new finding in quantative terms :

1. The signal obtained depends on the frequency of the applied a.c.
2. A frequency in the range of 10-100 c/s gives good results.
3. 10-100 volts of 50 c/s applied bias gives enough signal to be measured by a meter and the sensitivity will also be a high optimum.

Other new findings :

(a) Improvement in the overall sensitivity in the entire spectral range could be achieved by appropriate doping with the following groups of combinations using (i) with (ii) or (iii) :

 (i) Ions of group II (b) (zinc, cadmium, mercury) in the periodic classification with selenium or/and tellurium,

 (ii) Antimony or/and bismuth and alkali-halides;

 (iii) Other ions of group I (b) in the periodic classification with alkali halides.

(b) Additional augmentation of the sensitivity in the entire spectral range has been observed on heat treatment of the deposited layers in air in a range of temperature between 120 and 175°C for about ten minutes.

According to the present invention, the process for making a photosensitive silver sulphide thin film device for measuring low levels of illumination (100-1000 Lux) consists in introducing dopants into the silver sulphide layer by adding the dopants to the bath (consisting of thiourea, a soluble silver salt made alkaline to pH around 9.5) during chemical deposition, namely, (a) ions of group II (b) (zinc, cadmium, mercury) in the periodic classification with selenium or/and tellurium, (b) antimony or/and bismuth and alkali halides, and (c) other ions of group I (b) in the periodic classification with alkali halides and subsequently heat-treating the deposited layers in air in the range between 120° and 175°C for ten minutes whereby is obtained a thin sensitive layer of silver sulphide which can act as a stable photoresistor in a.c. circuits.

Thus, thin layers of silver sulphide of about 3 microns thickness are deposited on ground glass plates of dimensions 10 mm × 5 mm and heat-treated between 120°—175°C subsequently, which results in the layers acquiring high sensitivity.

Gold is vacuum evaporated on to the plate leaving a strip of 4 mm × 5 mm area of silver sulphide layer for the incidence of radiation and on to the gold electrodes thin wires are soldered using indium solder. The sensitive part of silver sulphide is protected from atmospheric humidity by using an optical plastic as for example polymethyl methacrylate.

The device is used for measuring low levels of illumination (100-1000 Lux) in the following manner: The device is kept in an electrical circuit with a load resistor of about 1/2 megohm in value (the resistance of the cell being around 2 megohms), the biasing a.c. voltage being in the range of 10-1000 volts at the frequency ranging from 10-100 c/s, and a milli-voltmeter is connected across the load resistor, whereby when the light in the given spectral range falls on the cell, a signal by way of a change in the voltage across the load resistor is recorded (as per circuit diagram given in Fig. 1 of the accompanying drawings).

Gold is vacuum evaporated on to the plate leaving a strip of 4 mm × 5 mm area of silver sulphide layer for the incidence of radiation. On to the gold electrodes, thin wires are soldered using indium solder. The sensitive part of silver sulphide is protected from atmospheric humidity by using an optical plastic such as polymethyl methacrylate. The result of the above process is that these layers obtained showed good photoconductive effects with a.c. bias allowing currents of about 70 microampere to pass through the cell at optimum sensitivity.

But for the dopants introduced into the silver sulphide layers during deposition and subsequent heat-treatment, the layers could only be used for the construction of a photovoltaic device which means smaller d.c. signals. By the above process, the sensitive layers could stand 70 microamperes of a.c. current passing through them without allowing a drift either in darkness or after illumination. The advantage of using the cell as a photoconductor with a.c. biasing is that it enables amplification of even low signals to desired levels.

Example 1

Deposition bath consists of 15 ml of 0.5 M silver nitrate solution and 40.0 ml of 1.5 M thiourea solution diluted to 100 ml with distilled water. The perspex holder containing the affixed plates is immersed in the bath and contents stirred with a magnetic stirrer. A mixture of 5.0 ml of liquor ammonia (specific gravity—0.91) and 5.0 ml of distilled water is gradually added to the bath when a bright mirror is formed on the sides of the beaker, followed by 10 ml of liquor ammonia till the pH reached 9.5. The mirror is violet in colour in the beginning and turns dark grey towards the end. The plates are allowed to remain inside the beaker for about 30 minutes. The holder is then removed, washed with distilled water and plates are wiped with cotton-wool soaked in distilled water. The plates are removed and dried at 110°C. For introducing dopants such as mercury, 5 ml of 10^{-5} M mercuric chloride solution is taken along with thiourea solution and the rest of the steps are the same.

The characteristics:

Applied bias	20 volts, 50 c/s	
Illumination	5000 Lux (Tungsten filament lamp)	
Load resistance	0.42 megohm	
Cell	Resistance	Signal across the load
Silver sulphide	15 megohm	400 mV
Silver sulphide (doped)	3 megohm	1300 mV
Silver sulphide (doped and heat-treated)	5 megohm	1600 mV

Example 2

The preparation steps are the same as before excepting that the concentration of the dopant (mercury) has been increased to 10 ml.

The characteristics:

Applied bias	25 volts
Resistance of the cell	7 megohm
Load resistance	0.42 megohm
Illumination	5000 Lux
Frequency in c/s	Signal across the load in mV
10	1700
50	1700
100	1700
1000	1050
5000	200
10000	100
15000	100

WE CLAIM:

1. A process for making a photosensitive silver sulphide thin film device for measuring low levels of illumination (100-1000 Lux) which consists in introducing dopants into the silver sulphide layer by adding the dopants to the bath (consisting of thiourea, a soluble silver salt made alkaline to pH around 9.5) during chemical deposition, namely, (a) ions of group II (b) (zinc, cadmium, mercury) in the periodic classification with selenium or/and tellurium, (b) antimony or/and bismuth and alkali halides, and (c) other ions of group I(b) in the periodic classification with alkali halides and subsequently heat-treating the deposited layers in air in the range between 120° and 175°C for ten minutes whereby is obtained a thin sensitive layer of silver sulphide which can act as a stable photoresistor in a.c. circuits.

2. A process as claimed in claim 1 wherein thin layers of silver sulphide of about 3 microns thickness are deposited on ground glass plates of dimensions 10 mm × 5 mm and heat-treated between 120°—175°C subsequently, which results in the layers acquiring high sensitivity.

3. A process as claimed in claim 1 or 2 wherein gold is vacuum evaporated on to the plate leaving a strip of 4 mm × 5mm area of silver sulphide layer for the incidence of radiation and on to the gold electrodes thin wires are soldered using indium solder, the sensitive part of silver sulphide is protected from atmospheric humidity by using an optical plastic as for example polymethyl methacrylate.

4. A device for measuring low levels of illumination whenever obtained by the process given in any of the preceding claims 1 to 3.

5. A photosensitive silver sulphide thin film device of silver sulphide photoconductor for measuring low levels of illumination substantially as described in the examples.

6. A photosensitive silver sulphide thin film device for measuring low levels of illumination substantially as hereinbefore described.

Dated this 3rd day of February, 1968.

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