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PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO PREPARATION OF SINTERED PHOTO CONDUCTIVE CADMIUM SULPHIDE CELLS

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).

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, all of the Central Electrochemical Research Institute, Karaikudi-3, Madras State, India, all Indian citizens.

The following specification describes the nature of this invention:—

This invention relates to improvements in or relating to the preparation of sintered photo-conductive cadmium sulphide cells.

Photoconductive cadmium sulphide cells either single crystal or polycrystalline are most sensitive among the existing photosensitive cells in the visible region with the maximum at 0.52μ. These cells can be made to handle power levels of several watts. They have a light to dark ratio of the order of one million at high illumination (10,000 Lux). At low levels of illumination (100 lux) the ratio is of the order of 1000. These cells have a multiplicity of uses ranging from relay circuits to gamma ray detection.

The methods of preparation of these layers are (1) by vacuum evaporation and subsequent processing (2) by using sensitized single crystal and (3) by the sintering technique. Of these the latter two methods have been used commercially and particularly of late, the sintering technique is most widely used and popular as it happens to be the cheapest. The major advantages of sintered layers are large area cells can be easily made, incorporation of impurity is easy, the bond between the material and the substrate will be good and the photocurrent varies linearly with applied voltage.

The reported method of preparation of sintered layers, consisted of three steps:— (a) obtaining a very high purity cadmium sulphide powder, (b) sensitizing the same to the required level and (c) sintering the powder on to a suitable substrate. So for ceramic substrate have been used commercially.

The preparation of very high purity cadmium sulphide involves very special and costly techniques and in India we have to import the same. The method of sensitization is critical and is not readily available in published literature and is not also easily reproducible if by chance it is obtained by the reported methods.

The object of this invention is (i) to prepare photosensitive cadmium sulphide powder, (ii) work out an easy method of sensitizing the same and (iii) to standardise the method of sintering.

To these ends, the invention broadly consists in the following:— (a) cadmium sulphide powder is prepared by the interaction of aqueous solution of a soluble cadmium salt of Analar grade like cadmium chloride, cadmium nitrate or cadmium acetate with an aqueous solution of an organic sulphur compound of G. R. grade like thiols, thiourea, substtuted alkyl thiourea, thioacetamide etc., in optimum conditions of pH attained by the addition of a suitable alkali of analytical reagent grade. The participate of cadmium tulphide obtained is filtered, dried and used for sensitization. (b) The powder obtained as above is incorporated with copper and chloride ions of A. R. grade in the required proportions with cadmium chloride A. R. as flux and given a bulk firing at about 550°C to 600°C for about 30 minutes. (c) The powder sensitized as above is well ground and made into a slurry using an organic solvent, for example, hydrocarbon alcohol etc., or even water, to get an optimum consistancy on to an insulating support. For example on to an unglazed porous ceramic or mica the slurry is painted, dried and heated in a furnace between 550°C to 600°C for about 15 to 30 minutes. The ceramic substrate is removed from the furnace and allowed to cool. Adherent and photosensitive layers of cadmium sulphide are thus obtained. After giving suitable ohmic contacts, these layers show very high photosensitivity comparable with the imported ones.

EXAMPLE 1—HIGH RESISTANCE CELL

50 c.c. of 10% aqueous cadmium acetate (A. R.) solution is taken in a beaker and treated with 20 c.c. of 1.5Ml thiourea of reagent grade and stirred magnetically. 10 c.c. of 40% sodium hydroxide (A.R.) solution is added (pH being 10 to 12) and stirring continued for about half an hour. The precipitate is then filtered, washed and dried.

(b) Two grams of the participate is mixed with about 250 mgs of cadmium chloride (A.R.) and 5 to 10 Ml of 1mM of copper chloride (A.R.) solution and made into a slurry. This is fired in a silica dish in a closed furnace at 550°C to 600°C for about 30 minutes. The dish is then removed from the furnace and allowed to cool.

(c) The powder is made into a slurry with water and coated on porous ceramic substrate dried and sintered at 550° to 600°C for about 15 to 30 minutes. The plates are removed from the furnace and allowed to cool. Suitable contacts are given with an electrode spacing of 4 mm. The cell is protected with an optical plastic. The characteristics of the cell thus obtained are as follows:

(i) Dark resistance of the cell—150 M

(ii) For illumination of 60 lux → light to dark ratio is 500

(iii) For an illumination of 5000 lux → -do- -do- $1.5 \times 10^5 \leftarrow 1.5 \times 10^5$

EXAMPLE 2—LOW RESISTANCE CELL

(a) The experiment is carried out exactly as in (a) under Example 1, taking cadmium nitrate (A.R.) in place of cadmium acetate.

(b) Prefiring is carried out exactly as in example 1(b) taking 1 to 5 ml of copper chloride.

(c) The slurry is coated on to a mica substrate, dried and sintered at 550°C to 600°C and processed further as in 1(c).

The cell characteristics:

(i) Dark resistance of the cell—30 M

(ii) For an illumination of 60 lux—light to dark ratio is 100.

(iii) For illumination of 5000 Lux—light to dark rato is 10^4.

These cells compare very well with the commercially available cells.

The following are the main advantages of the invention:

The starting material namely cadmium sulphide of a high grade of purity required for preparing the sintered type of cadmium sulphide photoconductive cells, as well as the finished cells, require to be now imported. The present invention substitutes import of the starting material and the cell and provides a very cheap and easy method of producing the cell itself.

Dated this 4th day of April, 1968.

PATENTS OFFICER,
Council of Scientific and Industrial Research.

COMPLETE SPECIFICATION

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).

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

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

This invention relates to improvements in or relating to preparation of sintered photoconductive cadmium sulphide cells.

A solid state device for converting the varying intensities of light into correspondingly varying intensities of electric currents by the application of a certain voltage to the cell. This invention relates to preparation of photoconductive cadmium-sulphide cell which has the highest sensitivity to visible light.

Photoconductive cadmium sulphide cells are either of single crystal or polycrystalline type. The polycrystalline cells are prepared by i) vacuum evaperation and subsequent processing and ii) by the sintering technique. The major advantages of sintering layers are that large area cells can easily be made, incorporation of impurities known as dopants is easy, the bond between the substrates and the material is good; the photocurrent varies linearly with applied voltage and are superior in their variable ratio of resistances, allowable power loss, spectral response and mechanical strength.

The hitherto known method of preparation of sintered layers consisted essentially of three steps:

(i) obtaining a very high purity cadmium sulphide powder;

(ii) sensitising the same to the required level; and

(iii) sintering the powder on to a suitable substrate. So far ceramic substrates have been used commercially.

The preparation of very high purity cadmium sulphide as a starting material, involves very special and costly techniques and as at present in India, we have to import the same. For example, the preparation of phosphor grade purity of cadmium sulphide requires pure quality of cadmium oxide to be dissolved in hydrochloric acid then further treated by subsequent process requiring the use of vacuum distilled cadmium metal and several subsequent steps required to remove iron, manganese and copper. Not only are the steps quite numerous and require very rigorous control, but the starting material required is to be of a sufficiently high grade of purity, as for example, the cadmium oxide. The method of sensitisation of such high purity cadmium sulphide, as reported in the literature involves two or three repetitions of firings at temperatures and durations which are both critical and not readily available. In addition the reported processes are not easily reproducible.

The object of this invention is i) to prepare photo sensitive cadmium sulphide powder by a simple and easy technique, ii) to work out an easy and reproducible method of sensitising the same and iii) to work out under our conditions a method of preparation of sensitive cadmium sulphide cell.

The principle underlying the invention is as follows:

(a) cadmium sulphide powder is prepared by the interaction of aqueous solution of a soluble salt, o analytical grade like cadmium chloride, cadmium nitrate and cadmium acetate with an aqueous solution of an organic sulphur compound (of guaranteed purity like that of G. R. Merk) like thiols, thiourea, substituted alkyl thiourea and thioacetamide in optimum conditions of pH attained by the addition of a suitable alkali of analytical grade. The precipitate of cadmium sulphide thus obtained, is filtered, dried and used for subsequent sensitisation.

(b) The powder thus obtained, as under (a) is incorporated with copper and chloride ions of analytical grade in the required proportion with cadmium chloride (of analytical grade) as flux and then given a bulk firing at a temperature in the range between 550 and 600°C for about 30 minutes.

(c) The powder thus sensitised as above is well ground and made into a slurry using an organic solvent, for example, a hydrocarbon, alcohol or even water, to get an optimum consistency on to an insulating support. As hitherto used, an unglazed porous ceramic substrate is painted with the slurry, dried and heated in a furnace between 550 and 600°C for about 15—30 minutes, the ceramic substrate is removed and allowed to cool.

(d) Adherent and photosensitive layers of cadmium sulphide are thus obtained. After giving suitable ohmic contacts, these layers show very high photosensitivity comparable with the imported ones. Equally good layers were obtained using mica as a substrate instead of an unglazed porous ceramic substrate.

The first step in the preparation of sintered layers, namely, obtaining the cadmium sulphide of a high grade of purity which means the importation from abroad has been simplified. For the first time, we have found that the method of preparing the cadmium sulphide cells by the interaction of soluable cadmium salt and thiourea in aqueous solutions yeilds a variety of cadmium sulphide which is straight useful for subsequent processing in the preparation of sintered layers.

The second step of sensitisation by the hitherto known process involved multiple firings of at least 2—3 times depending on the grade of purity of the starting material, namely, cadmium sulphide. In our method with the cadmium sulphide prepared as given above, satisfactory sensitisation is obtained with one single firing.

Whereas all hitherto commercially prepared cells were usin ceramic substrates, we could get equally good layers on mica substrates.

The present invention consists of a method of preparing the sintered photoconductive cadmium sulphide cells for measuring the variations of intensity of light in the visible region, comprising of three steps, namely, a) obtaining very high purity cadmium sulphide powder, b) sensitising the same to the required level by multiple firings depending on the grade of starting material and c) sintering the powder on to a suitable substrate, wherein the first step is achieved by a new and simple process of interacting a soluble cadmium salt with thiourea in aqueous solutions and obtaining the cadmium sulphide powder, thus dispensing with a material of a high grade of purity which has otherwise to be imported and by sensitising the cadmium sulphide powder only by a single firing and d) by working out a reproducible method of sintering the powder on to a suitable substrate in a temperature range between 550° and 600°C for about 15—30 minutes.

Whereas hitherto sintering was done only on ceramic substrates, we have been able to make them equally well on mica subserates.

EXAMPLE 1—HIGH RESISTANCE CELL

50 ml. of 10% aqueous cadmium acetate (analar) solution is taken in a beaker and treated with 20 ml. of 1.5 M thiourea of analytical grade and stirred magnetically. 10 ml. of 40% sodium hydroxide (A.R.) solution is added (pH being 10 to 12) and stirring continued for about half an hour. The precipitate is then filtered, washed and dried.

(b) Two grams of the precipitate is mixed with about 250 mg of cadmium chloride (analar) and 5 to 10ml of 1 milli mole copper chloride (analar) solution and made into a slurry. This is fired in a silica dish in a closed furnace at 550°c to 600°c for about 30 minutes. The dish is then removed from the futnace and allowed to cool.

(c) The powder is made into a slurry with water and coated on porous ceramic substrate dried and sintered at 550°c to 600°c for about 15 to 30 minutes. The plates from the furnace and allowed to cool. Suitable contacts like tin or indium are given with an electrode spacing of 4 mm. The cell is protected with an optical plastic. The characteristics of the cell thus obtained are as follows.

(i) Dark resistance of the cell—1500 M

(ii) For illumination of 60 Lux, light to dark ratio is 500.

(ii) For an illumination of 10,000 Lux -do -do- 1.5×10^6.

EXAMPLE 2—LOW RESISTANCE CELL

(a) The experiment is carried out exactly as in (a) under example 1, taking cadmium nitrate (analar) in place of cadmium acetate.

(b) Prefiring is carried out exactly as in example 1(b) taking 1 to 5 ml of copper chloride.

(c) The slurry is coated on to a mica substrate, dried and sintered at 550°C to 600°C and processed further as in 1(c).

The cell characteristics:

(i) Dark resitance of the cell—30 M

(ii) For an illumination of 60 Lux—Light to dark rotio is 100.

(iii) For illumination of 5,000 Lux—Light to dark ratio is 10^4.

These cells compare very well with the commercially available cells.

The following are the main advantages of the Invention:

The starting material namely cadmium sulphide of a high grade of purity required for preparing the sintered type of cadmium sulphide photoconductive cells, as well as the finished cells required to be now imported. The present invention substitutes import of the starting material and the cell, and provides a very cheap and easy method of producing the cell itself.

Photoconductive cadmium sulphide cells are the most sensitive ones in the visible region with a maximum at 0.52 micron. These cells have a multiplicity of use ranging from relay circuits to gamma ray detection.

The methods of preparation of these layers are:

(i) by vacuum evaporation and subsequent processing

(ii) by using sensitised single crystal and

(iii) by the sintering technique.

Of these, the sintered cells are now most popular, as they have all the advantages and are quite cheap.

The reported method of preparation of sintered layers consists of three steps:

(a) obtaining a cadmium sulphide powder of a very high grade of purity, as for example, the phosphor grade of purity not less than 99.999%.

(b) Sensitising the powder by the addition of chloride and copper ions to an optimum extent by a process of multiple firings till high sensitivity is obtained, the number of firings depending upon the grade of purity of the starting material and

(c) Sintering the powder on to a substrate like porous ceramic plate by a technique which is reported more as an art.

In our invention, we have obtained the starting material by precipitating the aqueous solution of cadmium sulphide by the interaction of thiourea and a soluble cadmium salt in optimum conditions of pH and found that this starting material, though not 99.999% purity, just required for the sensitisation involved in the second step only one firing in place of multiple firings done by previous workers. In regard to the third step, of sintering, we have standardised conditions for reproducible sintering, namely, a range of temperature between 550° and 600°C and a duration of time varying between 15 and 30 minutes. Incidentally we could make sintered layers also on mica substrates. The importance of this step lies in the situations where the device is to work in light weight gadgets and conditions of miniaturisation. The cells fabricated by us have a high light to dark ratio of the order of 1 million at high illuminations (10,000 Lux) quite comparable to imported cells.

We claim:

(1) A process for obtaining cadmium sulphide having special characteristics to be used in the successful preparation of sintered photoconductive layers ultimately having high photosensitivity which consists in interacting aqueous solutions of a soluble cadmium salt like cadmium chloride, cadmium acetate, or cadmium nitrate with an organic sulphur compound like a thiol, thiourea, substituted alkyl thiourea or thioacetamide at pH around 12.

(2) A process as claimed in claim (1), by which the precipitated cadmium sulphide thus obtained when filtered, dried and sensitised by optimum doping (addition of small quantities of ions) with copper and chloride ions, by the process of a single firing at a temperature in the range from 550° to 600°C for a duration of about 30 minutes shows finally, after subsequent processing by sintering the sensitised powder on to a substrate, a very high photosensitivity.

(3) A process as claimed in claims (1) and (2) wherein the sensitised powder is made into a slurry (for ease of coating on a substrate) in a solvent like acetone, water or rectified spirit to an optimum consistency, painted on a substrate like an unglazed porous ceramic one, dried and sintered well by heating in a furnace between 550° and 600°C for about 15—30 minutes giving adherent and photosensitive layers of cadmium sulphide, which when used subsequently as a device gives a very high photosensitivity comparable very well with imported cells of the same sintered type, for example, on illumination the resistance of the cell falls to a millionth of that in darkness.

(4) A process as claimed in claims (1)—(3), by which the characteristics mentioned in claim (3) are obtained on conventional unglazed porcelain substrates or on mica.

(5) A process for preparing photoconductive sintered layers of cadmium sulphide cells as claimed in claims (1) to (4).

Dated this 11th day of December, 1968.

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