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PROVISIONAL SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO PREPARATION OF LEAD SULFIDE PHOTOCONDUCTIVE CELLS FOR INFRARED DETECTION"

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, HOLAVANAHALLY NARAYANA RAO VENKOBA RAO, Scientist, KURUMATHU KRISHNA PILLAI JANARDHANAN PILLAI, Senior Scientific Assistant, VENKATASUBRAMANYA SUBRAMANIAN, Junior Scientific Assistant, KANDAN RAMAKRISHNAN, Senior Laboratory Assistant and YELLAMRAJU VENKATA PURNA RAMACHANDRA ROW, Scientist, all of the Central Electrochemical Research Institute, Karaikudi-3 India, all Indian citizens.

The following Specification describes the nature of this invention:—

This invention relates to improvements in or relating to preparation of lead sulfide photoconductive cells for infrared detection.

The lead salts namely, the lead sulfide, the lead telluride and the lead selenide are well known infrared radiation detectors. The lead sulfide detector is responsive in the wave length region between 1 and 3.5 microns and is the best and the most rugged one for use at normal room temperature. The lead telluride and the lead selenide are meant for extending the region of response beyond 3.5 microns.

The lead sulfide polycrystalline layers were prepared hitherto both by vacuum evaporation and by chemical deposition. However, of late, the method of chemical deposition is the most widely followed one in the world. This method of chemical deposition, though outlined by Kicinski (Chem. Industry, p. 54 (1948) has not given enough workable detail in published literature. The principle of the method consists in the reaction between lead acetate and thiourea in aqueous solutions on the addition of a very strong alkali when a mirrory deposit of lead sulfide occurs on the ground glass plates intended to be coated. Even at the concentrations of thiourea and lead acetate given in the literature, the method of the addition of alkali, namely, the rate and the quantity as well as the rate of stirring of constituents at a given temperature of deposition is very critical in obtaining satisfactory sensitivity in the deposited layers of lead sulfide.

The sensitivity of these cells as deposited, is actually quite low and no further step for sensitisation is indicated therein.

The sensitised layers of lead sulfide do not keep up their sensitivity if left open to the atmosphere. They therefore require to be protected and no specific mention of protective varnishes or lacquers easily available are cited in the previous literature.

After providing the prepared cells with suitable ohmic contact no mention is clearly made in previous literature of soldering leads to the ohmic contacts.

In this background, the object of this invention is :

(1) To modify the technique of chemical deposition,

(2) Subsequent sensitisation,

(3) Lacquering the sensitive surface of protection against atmospheric action and

(4) Soldering leads to the metallic contacts.

To these ends, the invention broadly consists in the following :

(1) *Chemical desposition :* To a suitable mixture of lead acetate and thiourea kept stirred, sodium hydroxide is added slowly in two instalments. The contents are kept stirred at a moderate speed of about 200 r.p.m. for 10 minutes. After deposition, the plates are treated with 1% solution of ammonium sulfide and dried.

Addition of 1-2 gms. of lead monoxide either to the depositing bath or to the alkali being added for deposition has contributed considerably to increasing the sensitivity of the detector. Similarly addition of alkali halides particularly bromides and iodides helped in giving uniform resistivity to all the cells prepared in one batch and also in augmenting the sensitivity of the plates.

(2) *Sensitisation :* These deposited plates are heat treated in an atmosphere of oxygen at one atmospheric pressure at a temperature ranging 500-600°C for a period of 5–15 minutes.

(3) *Protective coating to the sensitive layers :* Optical plastic having window characteristics in the region of 0.6-4 microns particularly in the group of styrene compounds has been used for providing the seal to the sensitive area.

(4) *Soldering :* Soldering could be successfully done by using indium solder with a low voltage iron using a stainless steel bit and copper sulfate as the flux.

The detectors thus prepared have been found to be sensitive upto a wave length of 3.5 microns. The maximum response of these cells is around 2.1 microns. The sensitivity of our detectors is comparable with the generally claimed sensitivities of such detectors manufactured for applications like pyrometry and on-off switching arrangements. The sensitivities obtained are around 1/4th (or sometimes even better) of the best commercial cells having specially high sensitivities, used in some special devices for communication systems ; for example, the signal obtained from one of the

best commercial cells at 2.1 microns is around 230 mV whereas under identical conditions our best cells have given around 60–80 mV according to our invention.

The following typical examples are given to illustrate the invention :

EXAMPLE 1

Deposition bath consists of a mixture of 30 c.c. of 40% lead acetate, 10 c.c. of 12% thiourea to which are added 50 c.c. of water and kept stirred for 5 minutes at moderately high speed. The ground glass plates attached to a Perspex holder is kept immersed in the bath. After sometime, a first instalment of 2 c.c. of 66% sodium hydroxide is added and after about 1/2 minute a second instalment of 8 c.c. of sodium hydroxide is added and kept magnetically stirred for about 10 minutes at a relatively moderate speed. 1 gram of lead monoxide and 3 c.c. of 0.01% solution of potassium iodide were added during the deposition. After 10 minutes the holder with the plates was removed, the plates washed with distilled water and immersed in a 1% solution of ammonium sulfide for 15 minutes and washed and dried. The dried plates were heated to 500°C for 10 minutes in oxygen at one atmospheric pressure and quenched to the room temperature. After cooling, the cells are provided with gold contacts in a vacuum evaporation unit using a suitable mask. Immediately after gold deposition, the cells are given protective coating with an optical plastic and allowed to age for about a fortnight, by which time the sensitivity gradually increases to a maximum. Tinned copper leads are spot-soldered to the gold electrodes using an indium solder as mentioned earlier. The characteristics of a representative sample of our cells as reported after testing in the Defence Science Laboratory at New Delhi are as follows :

1. Spectral response-visible to 3 microns.
2. Signal to Noise Ratio-1000.
3. D* (800°C, 500 CPS, 2 CPS)—2.8 x 10^9 cm. (C.P.S.)$^{1/2}$/Watt.

For comparison, the following data for the lead sulfide cell quoted by Infratron, U.S.A. is given below :

1. Spectral response—visible to 3.5 microns.
2. Signal to Noise Ratio—600.
3. D* (Peak, 750, 1)—2.0—2.8 x 10^{10} cm. (C.P.S.)$^{1/2}$/Watt.

D* is pronounced as 'dee star' and is the detectivity of the infrared detector expressed as the reciprocal of the incident radiation power required to give a signal to noise ratio of unity rendered independent of the area of the sensitive layer and frequency of test measurement

EXAMPLE 2

Deposition bath consists of a mixture of 30 c.c. of 40% lead acetate, 10 c.c, of 12% thiourea to which are added 50 c.c. of water and kept stirred for 5 minutes at moderately high speed. The ground glass plates attached to a Perspex holder is kept immersed in the bath. After sometime, a first instalment of 2 c.c. of 66% sodium hydroxide is added and after about 1/2 minute a second instalment of 8 c.c. of sodium hydroxide is added and kept magnetically stirred for about 10 minutes at a relatively moderate speed. 2 grams of lead monoxide and 6 c.c. of 0.01% solution of potassium iodide were added during the deposition. After 10 minutes the holder with the plates was removed, the plates washed with distilled water and immersed in a 1% solution of ammonium sulfide for 15 minutes and washed and dried. The dried plates were heated to 500°C for 10 minutes in oxygen at one atmospheric pressure and quenched to the room temperature. After cooling, the cells are provided with gold contacts in a vacuum evaporation unit using a suitable mask. Immediately after gold deposition, the cells are given protective coating with an optical plastic and allowed to age for about a fortnight, by which time the sensitivity gradually increases to a maximum. Tinned copper leads are spot-soldered to the gold electrodes using an indium solder as mentioned earlier. The characteristics of a representative sample of our cells are as in example 1.

The following are the main advantages of the invention :

(1) A detailed scheme modifying the chemical deposition method, giving reproducible physical and electrical characteristics of deposited layers (not available in literature) is worked out.

(2) Sensitisation by oxygen treatment has been introduced as an easy step for obtaining sensitive infrared detectors having a maximum response at 2.1 microns.

(3) Indigenously available optical plastic having good infrared transmission belonging to the styrene group provides a good sealing against any deleterious atmospheric effects.

(4) Soldering of tinned copper leads to the gold electrodes, with indium solder, on lead sulfide have been made easy by using a new flux, namely copper sulfate and using a stainless steel bit.

(5) These cells can now be prepared indigenously whereas for they have been imported.

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Industrial Research

Dated this 25th day of June 1968.,

COMPLETE SPECIFICTION

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 iniention by CHITTARI VENKATA SURYANARAYANA, Scientist, HOLAVANAHALLY NARAYANA RAO VENKOBA RAO, Scientist, KURUMATHU KRISHNA PILLAI JANARDHANAN PILLAI, Senior Scientific Assistant, VENKATASUBRAMANYA SUBRAMANIAN Junior Scientific Assistant, KANDAN RAMAKRI SHNAN, Senior Laboratory Assistant and YELLAMRAJU VENKATA PURNA RAMACHANDRA ROW, Scientists, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens

This 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 lead sulphide photoconductive cells for infrared radiation detection.

The lead sulphide infrared radiation detector is responsive in the wavelength region between 1 and 3.5 microns with a peak around 2.1 microns and is the best and the most rugged one for use at normal room temperatures. Hitherto the lead sulphide polycrystalline layers were prepared either by vacuum evaporation or by chemical deposition. Of these two methods, the former has become obsolete and the latter, namely, the chemical deposition method is widely adopted all over the world. This method of chemical deposition, for example, the one outlined by Kicinski (Chem. Industry, p. 54 (1948) depends on the reaction between lead acetate and thiourea in alkaline medium. In some cases the bath solution contained oxydizing agents. The deposited layers were reported to be sensitive without any further subsequent treatment.

The chemical method of deposition reported in literature is rather critical in the sense that as per directions given either in published papers or patent literature, the cells prepared do not exhibit photosensitivity claimed by the workers Further, after the deposition of thin layers of lead sulphide, any sensitivity, however small obtained by the hitherto known process of chemical deposition, requires to be protected against deterioration from atmospheric humidity and contamination, by a protective coating which also transmits infrared radiation in the wavelength region between 1 and 3.5 microns to which the layers are sensitive. The nature and the material of this protective coating is not clearly mentioned in the previous literature. The method of giving contacts to the gold electrodes on lead sulphide layer is not available in a straight forward way in the existing literature.

The main objects of the invention are :

(i) to work out clearly various steps in chemical deposition;

(ii) to evolve and standardise the process of subsequent sensitisation so that finally lead sulphide layers of high sensitivity are obtained;

(iii) to find out a good protective material to seal off the layers from atmospheric effects; and

(iv) to provide a suitable solder contact on gold electrodes for purposes of mounting the cell.

The main finding (the new principle) underlying the invention :

(a) The basic principle of chemical deposition remains the same as in the hitherto known process, namely, the reaction between lead acetate and thiourea in an alkaline medium. Our modifications consist in :

(i) the addition of 1 to 2 gms of lead monoxide either to the depositing bath or to the alkali being added for deposition.

(ii) addition of alkali halides, particularly bromides and/or iodides which contribute towards obtaining uniform resistivity in all the prepared cells in a given bath. Both the steps (i) and (ii) augment the sensitivity of the cells.

(b) The deposited layers are heat-treated in an atmosphere of oxygen at one atmospheric pressure at a temperature ranging from 500-600°C for a period of 5-15 minutes. Without this heat-treatment, the layers as chemically deposited are very little sensitive.

(c) We have found polystyrene having good window characteristics in the wavelength region of 1-3.5 microns as a very good sealant on the lead sulphide surface; and

(d) To the gold electrodes vacuum deposited on the lead sulphide layers, soldering of tinned copper wires was a problem and we could successfully do it by using indium solder with a low voltage iron using a stainless steel bit and copper sulphate as the flux.

The *new result* flowing from the new finding :

The chemically deposited cells hitherto claimed to be sensitive without further subsequent treatment have been found by us to be really not so. By the introduction of a subsequent step of heat treatment in oxygen mentioned above, we have obtained good infrared radiation detectors. They are comparable with the sensitivities and the spectral range of response claimed by commercial manufacturers useful for applications like pyrometry and on-off switching arrangements. The sensitivities obtained are around 1/4th (or sometimes better) of the best commercial cells having specially high sensitivities, used in some special devices for communication system; for example, the signal obtained from one of the best commercial cells at 2.1 microns, is around 230 mV whereas under identical conditions. our best cells have given around 60-80 mV according to our invention.

Other new findings :

(i) Addition of alkali halides like the iodides and bromides to the deposition bath enhance the sensitivity of the deposited cells;

(ii) Addition of lead monoxide to the deposition bath or to the alkali being added for deposition enhances the sensitivity of the deposited layers;

(iii) We have found polystyrene having good window characteristics in the wavelength region of 1-3.5 microns as a very good sealant on the lead sulphide surface ; and

(iv) Technique of soldering tinned copper wires to the gold electrodes using indium solder and staintess steel bit and copper sulphate as flux makes the soldering process easier.

According to the present invention, the process for the production of infrared sensitive lead sulphide photoconductive cells is characterised by the following steps :

(a) the lead sulphide layer is produced on a ground glass plate by chemical deposition by dipping the ground glass plate in an alkaline bath where lead acetate is reacted with thiourea, in the presence of added lead monoxide and alkali halide such as bromide or iodide and (b) subsequent heat treatment of the lead sulphide deposit in oxygen at one atmospheric pressure in temperature range of 500–600°C for period of 5–15 minutes resulting in the production of infrared sensitive lead sulphide layer.

Thus, there is provided a process for the production of lead sulphide photoconductive cells comprising of lead sulphide layer on glass substrates wherein the lead sulphide is produced by the reaction of lead acetate and thiourea in an alkaline bath by the following steps :

(a) the addition of lead monoxide to the bath, (b) addition of an alkali halide such as bromide or iodide to the bath and (c) subsequent heat treatment of the resultant lead sulphide layers on glass substrates in oxygen at one atmospheric pressure in a range of temperature from 500–600°C for a duration ranging from 5–15 minutes each of the said steps contributing to an increase in sensitivity and resulting in the production of infrared sensitive lead sulphide layers.

An indigenously available plastic material belonging to the styrene group is used for protecting sensitive layers against deleterious atmospheric action.

Vacuum evaporated gold contacts are provided on the lead sulphide layer and tinned-copper wires are spot soldered on the vacuum evaporated gold contacts on the lead sulphide layers by using indium solder and a stainless steel bit and copper sulphate as flux.

A few typical examples to illustrate how the invention is carried out in actual practice :

Example 1

Deposition bath consists of a mixture of 30 c.c. of 40% lead acetate, 10 c.c. of 12% thiourea to which are added 50 c.c. of water and kept stirred for 5 minntes at about 8000 r.p.m. speed. The ground glass plates attached to a Perspex holder are kept immersed in the bath. After some time, a first instalment of 2 c.c. of 66% sodium hydroxide is added and after about 1/2 minute a second instalment of 8 c.c. of sodium hydroxide is added and kept stirred for about 10 minutes at a speed of about 5000 r.p.m... one gm of lead monoxide and 3 c.c. of 0.01% solution of potassium iodide are added during the deposition. After 10 minutes the holder with the plates is removed, the plates washed with distilled water and immersed in a 1% solution of ammonium sulphide for 15 minutes and dried. The dried plates are heated to 500°C for 10 minutes in oxygen at one atmospheric pressure and quenched to the room temperature. After cooling, the cells are provided with gold contacts in a vacuum evaporation unit using a suitable mask. Immediately after gold deposition, the cells are brush coated with polystyrene in amyl acetate and allowing the latter to evaporate and allowed to age for about a fortnight, by which time the sensitivity gradually increases to the maximum. Tinned copper leads are spot-soldered to the gold electrodes using a stainless steel bit and indium solder with copper sulphate as flux as mentioned earlier The characteristics of a representative sample of our cells as reported after testing in the Defence Sciece Laboratory at New Delhi are as follows :

1, Spectral response-visible to 3 microns.

2. Signal to Noise Ratio-1000

3. D* (800°C, 500 CPS, 2 CPS)—2.8×10^{9} cm. $(C_{,}.PS.)^{1/2}$/watt.

For comparison, the following data for the lead sulphide cell quoted by Infratron, U.S.A. are given below :

1. Spectral response—visible to 3.5 microns

2. Signal to Noise Ratio—600

3. D* (Peak, 750, 1)—2.0—2.8×10^{10} cm $(C.P.S.)^{1/2}$/watt.

D* is pronounced as 'dee star' and is the detectivity of the infrared detector expressed as the reciprocal of the incident radiation powder required to give a signal to noise ratio of unity rendered independent of the area of the sensitive layer and frequency of test measurement.

Example 2

Deposition bath consists of a mixture of 30 c.c. of 40% lead acetate, 10 c.c. of 12% thiourea to which are added 50 c.c. of water and kept stirred for 5 minutes at about 8000 r.p.m, speed. The ground glass plates attached to a Perspex holder is kept immersed in the bath. After sometime, a first instalment of 2 c.c, of 66% sodium hydroxide is added and after about 1/2 a minute a second instalment of 8 c.c. of sodium hydroxide is added and kept stirred using a magnetic stirrer for about 10 minutes at a speed of about 5000 r.p m. Two gms of lead monoxide and 6 c.c. of 0.01% solution of potassium iodide are added during the deposition. After 10 minutes the holder with the plates is removed, the plates washed with distilled water and immersed in a 1% solution of ammonium sulphide for 15 minutes and dried. The dried plates are heated to 500°C for 10 minutes in oxygen at one atmospheric pressure and quenched to the room temperature. After cooling, the cells are provided with gold electrodes in a vacuum evaporation unit using a suitable mask. Immediately after gold deposition, the cells are brush-coated with polystyrene in amyl acetate and allowing the latter to evaporate and allowed to age for about a fortnight, by which time the sensitivity gradually increases to the maximum. Tinned copper leads are spot-soldered to the gold electrodes using stainless steel bit and indium solder with copper sulphate as flux. The characteristics of a representative sample of our cells are as in example 1. The main advantages of the invention are :

1. The chemical deposition reported in patent and published literature, which was not yielding photosensitive lead sulphide layers has been modified to yield really sensitive layers by slightly modifying bath conditions and introducing an additional step of subsequent heat treatment in oxygen atmosphere which was not done hitherto. By these modifications lead sulphide layers of sensitivities claimed in general by commercial firms have been obtained. The material required for sealing off the sensitive layers from deleterious atmospheric action has been found to be one among the indigenously available materials. The soldering of tinned copper wires on to the gold electrodes for purposes of subsequent mounting has been entirely worked out by using indium solder and stainless steel bit and copper sulphate as flux.

All the above steps make for the indigenous production of lead sulphide infrared detecting cells in our country without having to import them any more.

We Claim :

1. A process for the production of infrared sensitive lead sulphide photoconductive cells which is characterised by the following steps :

(a) The lead sulphide layer is produced on a ground glass plate by chemical deposition by dipping the ground glass plate in an alkaline bath where lead acetate is reacted with thiourea, in the presence of added lead monoxide and alkali halide such as bromide or iodide and (b) subsequent heat

treatment of the lead sulphide deposit in oxygen at one atmospheric pressure in temperature range of 500—600°C for period of 5—15 minutes resulting in the production of infrared sensitive lead sulphide layer.

2. A process as claimed in claim 1, wherein a plastic material belonging to the styrene group is brush coated there on for protecting the said sensitive layer against deleterious atmospheric action.

3. A process as claimed in claims 1 & 2, wherein to the gold electrodes provide on the said sensitive layer by the usual vacuum deposition method, tinned wires are spot-soldered by using indium solder and a stainless steel bit and copper sulphate as flux.

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Dated this 21st day of Aprils, 1969.

Prabhat Press, Meerut/Patent/73-150.