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PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO PHOTSENSITIVE THIN FILMS OF THALLIUM SELENIDE LAYERS"

COUNCIL OF SCIENTIFIC & 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 describes the nature of this inventions:—

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.
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This invention relates to improvements in or relating to photosensitive thin films of thallium selenide layers.

Since 1958, the Russian Workers have been developing photosensitive thin films of thallium selenide cells having the peak response at 1.1 microns with a band gap of 0.8 e.v. It is reported that on prolonged heating for about 200 hours around 100°C the peak response even shifts to 1.7 microns. These layers have been shown to have a bright potentiality for detection in the near infra-red the entire range of response being between 0.75 microns and 2 microns. These cells have so far been prepared only by vacuum evaporation.

The method of vacuum evaporation is open to the objection that conditions of deposition are controlled by several critical factors and apart from involving costly apparatus, reproducibility is rather difficult. Further the vacuum evaporated layers rarely give uniform sensitivity in the entire area of the film.

The object of this invention is to obviate these disadvantages by simplifying the method by using a chemical method of deposition wherein no sophisticated equipment is necessary at all.

To these ends, the invention broadly consists in taking a mixture of a soluble thalious salt and sodium seleno sulphate and adjusting the pH of the solution to be on the alkaline side around 12 and adding a reducing agent to get the desired film thickness of thallium selenide on the glass substrates.

The following typical examples are given to illustrate the invention:

Example 1

Deposition bath consists of an aliquot amount of saturated solution of thalious chloride with 1/6th the volume of sodium seleno sulphate containing an equivalent of 0.5% of selenium metal. The ground glass plates of 1 c.m. x 0.5 c.m. (cut from slide glass) affixed to a perspex holder are immersed in the bath and then the contents are stirred, with a magnetic stirrer. A solution containing alkali and hydrazine, 30% with respect to the former and 20% with respect to the latter is added gradually until a mirrory deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for about half an hour. To get the film thickness around 2 microns, it has been necessary to deposit for a second time. After the second deposition, the plates are taken out and dried. The characteristics of these plates without any further treatment are as follows:—

The peak response is at 1.05 microns, the band gap is around 0.8 e.v. and the response starts from 0.65 microns and goes around 1.45 microns. They are of a slightly p-type and are intrinsic. These characteristics tally quite well with the vacuum evaporated thin films.

Example 2

Deposition bath consists of an aliquot amount of saturated solution of thalious chloride and a mixture of sodium hydroxide and hydrazine, 30% with respect to the former and 20% with respect to the latter. To this solution, sodium seleno sulphate is added by small instalments keeping the bath stirred by a magnetic stirrer. As the mirrory deposit is formed, the plates are allowed to be in

the bath well around half an hour. To get a thickness of 2 microns, a second deposition is done over it. Then they are taken out and dried. Good adherent deposits with characteristics given in the example 1 are obtained.

The following are among the main advantages of the invention:

- (1) No costly equipment is needed.
- (2) Method of deposition is very easy and reproducible and can be done at laboratory temperature.
- (3) This method has the advantage that much of the after treatment can be mini-

mised by adding proper oxidising agent to the bath itself bringing about sensitization of the plates.

- (4) Introduction of dopants into the deposited layers and control of their concentration can be done easily by adding the dopants to the depositing bath itself.

Dated this 22nd day of June, 1967.

Sd./-
(R. BHASKAR PAI),
PATENTS OFFICER,
Council for Scientific and Industrial Research.

COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO PHOTOSENSITIVE THIN FILMS OF THALLIUM SELENIDE LAYERS"

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES (ACT [XX] 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, Madras, India, all Indian citizens.

This invention relates to improvements in or relating to deposition of photosensitive thin films of thallium selenide layers.

Chemical deposition of thin films of photosensitive thallium selenide layers useful as a solid state device for measuring low levels of illumination in the spectral range of 0.65 to 1.45 microns.

Since 1958, the Russian Workers have been developing photosensitive thin films of thallium selenide cells having the peak response at 1.1 microns with a band gap of 0.8 e.v. It is reported that on prolonged heating for about 200 hours around 100°C the peak response even shifts to 1.7 microns. These layers have been shown to have a bright potentiality for detection in the near infra-red, the entire range of response being between 0.75 microns and 2 microns. These cells have so far been prepared only by vacuum evaporation. Hitherto these photosensitive thin films of thallium selenide were being deposited by the method of vacuum evaporation.

This method of vacuum evaporation is governed by several critical factors (as for example, inside pressure disposition and temperature of the substrate on which deposition is to be made, and the purity of the thallium selenide compound or if thallium and selenium are taken, then their composition) and is also costly. Further, reproducibility and the uniformity of deposition are difficult to achieve by vacuum evaporation.

The main object of this invention is to simplify the method of deposition by minimising the number of critical factors, as for example, those enumerated above, making it less expensive and getting uniform deposits of thin films of thallium selenide.

The main principle underlying the invention is to deposit thallium selenide films by a chemical

method. The basis of the chemical method consists in making use of the reaction between a soluble thallium salt and sodium selenosulphate at an optimum pH, which is on the alkaline side around 12.

By this new method of chemical deposition, we obtained the desired thallium selenide films of thickness ranging from 3-6 microns of thallium selenide on the glass substrates. This method of chemical deposition, which has not been done by others so far, has the advantage that the experimental procedure is quite simple, the deposits obtained are uniform and the film thus deposited is photosensitive.

According to the present invention, the process for the production of photosensitive thin films of thallium selenide which comprises (i) immersing ground glass plates in a solution of a soluble salt of thallium to which has been added an aqueous solution of sodium selenosulphate, keeping the contents stirred, (ii) bringing the pH of the solution to around 12 by adding a concentrated solution of sodium hydroxide and (iii) repeating the steps (i) and (ii) to make a second deposit of thallium selenide on the first.

Thus, ground glass plates of size 1 cm. × 0.5 cm. are attached to a plain rectangular perspex holder attached to a central vertical rod, the holder is suspended with a clamp and kept immersed in a solution of soluble salt of thallium.

A solution of soluble salt of thallium as for example, thallos chloride, thallos acetate, thallos nitrate or the like may be used.

To the solution of soluble salt of thallium is added an aqueous solution of sodium selenosulphate obtained by dissolving selenium in sodium sulphite solution and the contents are kept stirred.

A concentrated solution of sodium hydroxide is added to bring the pH around 12, and after about 20-30 minutes, a good but thin deposit of thallium selenide is obtained.

Thallium selenide films of thickness ranging from 3-6 microns of thallium selenide are obtained on the glass substrates.

Thin films of photosensitive thallium selenide layers have been obtained hitherto only by the vacuum evaporation method with all the disadvantages mentioned earlier. The present invention not only gives photosensitive thin films of thallium selenide by chemical method of deposition but also obviates the difficulties and the disadvantages associated with the method of vacuum evaporation.

Doping of these layers with small quantities of other ions which will modify the characteristics of the photosensitive layers could be done under controlled conditions and in a manner more reproducible than in vacuum evaporation. In the method of vacuum evaporation, it is very difficult to reproduce the conditions and concentrations of the dopants whereas by this new method of chemical deposition, it is possible to control the level of doping in the thin film by incorporating the dopants in the bath itself.

The experimental set up consists of two parts—(1) the plate holder and (2) the deposition bath in which the plate holder is dipped.

The plate holder consists of 5 cm square perspex sheet of about 0.5 cm thickness firmly attached at its centre to a vertical rod of stainless steel. The substrate on which these thin films have been deposited is made of slide glass. The area of each plate is 1 cm × 0.5 cm. These plates are ground with emery grade No. 520. These ground plates are attached with quickfix to the perspex holder with the ground surface facing downwards (the deposition side).

The deposition bath consists of a mixture of soluble thallium salt solution and sodium selenosulphate. The selenosulphate solution was prepared by dissolving selenium metal in a concentrated solution of sodium sulphite. The perspex holder is dipped in the solution such that the plates are well within the solution. The solution is kept stirred using a magnetic stirrer. After sufficient stirring, an alkali is added to raise the pH to an optimum value around 12. The plates are kept for about 30 minutes by which time it has been observed that the deposition is almost complete and the thickness of the layer obtained is an optimum lying around 2 microns. The operations were repeated over again. Double deposition yielded a total thickness around 4 microns. After the deposition is completed, the perspex holder is taken out and the plates are washed with a jet of distilled water and taken out from the perspex holder. The surface of the plates is cleaned physically with a piece of wet cotton and dried. These plates have been found to be photosensitive though heat treatment in oxygen has been found to increase the sensitivity.

Example 1

Deposition bath consists of 50 ml of saturated solution of thallos chloride with 1/6th the volume of sodium selenosulphate containing equivalent of 0.5% of selenium metal. The ground glass plates of 1 cm × 0.5 cm (cut from slide glass) affixed to a perspex holder are immersed in the bath and then the contents are stirred, with a magnetic stirrer. 25 ml of a solution containing alkali and hydrazine, 30% with respect to the former and 20% with respect to the latter is added gradually until a mirrory deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for about half an hour. To get the film thickness around 4 microns,

it has been necessary to deposit for a second time. After the second deposition, the plates are taken out and dried. The characteristics of these plates without any further treatment are as follows:—

The peak response is at 1.05 microns, the band gap is around 0.8 e.v. and the response starts from 0.65 microns and goes around 1.45 microns. They are of a slightly p-type and are intrinsic. These characteristics tally quite well with the vacuum evaporated thin films.

Example 2

Deposition bath consists of 30 ml of concentrated solution of thallos acetate and a 25 ml mixture of sodium hydroxide and hydrazine, 30% with respect to the former and 20% with respect to the latter. To this solution, sodium selenosulphate is added in small instalments keeping the bath stirred by a magnetic stirrer. As the mirrory deposit is formed, the plates are allowed to be in the bath well around half an hour. To get a thickness of 4 microns, a second deposition is done over it. Then they are taken out and dried. Good adherent deposits with characteristics given in the example 1 are obtained.

The main advantages of this invention are (1) no costly equipment is needed, (2) the method of deposition is very easy and reproducible and can be done at laboratory temperature and (3) introduction of dopants into the deposited layers and control of their concentration can be done easily by adding dopants to the depositing bath.

Thin films of thallium selenide have been used as semi-conductor devices for measuring low levels of illumination in the spectral range from 0.65 micron to 1.45 microns. The method of making these thin films was by vacuum evaporation and there was no other simplified method. This well known method has been rather difficult in the sense that it required a sophisticated system comprising a vacuum unit for depositing these thin film layers. Also in several other semiconductor devices, the doping of these films, which is a process well known for augmenting the photosensitivity of these layers could only be done with doubtful reproducibility. We have evolved for the first time successfully a method of chemical deposition to get equally photosensitive layers of thallium selenide adherent as well as of the required thickness. The chemically deposited layers are quite uniform whereas the vacuum evaporated ones are known to be not so uniform. The handling and incorporation of dopants is quite easy by the method of chemical deposition whereas it is not so with vacuum evaporation. Above all, the chemical method is quite cheap compared with the costly equipment needed for vacuum evaporation.

Photosensitive thin films of thallium layers which are highly sensitive in the spectral range between 0.65 micron and 1.45 microns were prepared only by vacuum evaporation method. By this invention, we have, for the first time, achieved the same by chemical deposition, which is simple, cheap and more efficient from the point of view of reproducibility, uniformity of deposition and handling and incorporation of dopants.

WE CLAIM:

1. A process for the production of photosensitive thin films of thallium selenide which comprises (i) immersing ground glass plates in a

solution of a soluble salt of thallium to which has been added an aqueous solution of sodium selenosulphate, keeping the contents stirred, (ii) bringing the pH of the solution to around 12 by adding a concentrated solution of sodium hydroxide and (iii) repeating the steps (i) and (ii) to make a second deposit of thallium selenide on the first.

2. A process as claimed in claim 1 wherein ground glass plates of size 1 cm × 0.5 cm are attached to a plain rectangular perspex holder attached to a central vertical rod, the holder is suspended with a clamp and kept immersed in a solution of soluble salt of thallium.

3. A process as claimed in any of the preceding claims 1 or 2 wherein is used a solution of soluble salt of thallium as for example, thalious chloride, thalious acetate, thalious nitrate or the like.

4. A process as claimed in any of the preceding claims wherein to the solution of soluble salt of thallium is added an aqueous solution of sodium selenosulphate obtained by dissolving metal selenium in sodium sulphite solution and the contents are kept stirred.

5. A process as claimed in any of the preceding claims wherein a concentrated solution of sodium hydroxide is added to bring the pH around 12, and after about 20-30 minutes, a good but thin deposition of thallium selenide is obtained.

6. A process as claimed in any of the preceding claims wherein thallium selenide films of thickness ranging from 3-6 microns of thallium selenide are obtained on the glass substrates.

7. A process for the production of thin films of thallium selenide substantially as herein before described.

8. Thin films of thallium selenide whenever produced according to a process substantially as herein before described.

Dated this 25th March, 1968.

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