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IMPROVEMENTS IN OR RELATING TO DEPOSITION OF PHOTOSENSITIVE THIN FILMS OF THALLIUM SULPHIDE LAYERS.

PROVISIONAL 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, KRISHNAMOORTHY NAGARAJA RAO, Senior Scientific Assistant and MARY JULLANA MANGALAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-3, all Indian citizens.

The following specification describes the nature of this invention.

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

Hitherto it has been proposed to deposit these thin films only by vacuum evaporation. Cells prepared by such a method have been known to become photosensitive after a special process of sensitization responding to radiation in the region 0.5 micron to 1.5 microns with a maximum at 1.0 micron. It has been reported that such cells are even better than the well known selenium cells.

This method of preparation is open to the objection that conditions of deposition are governed by several critical factors and apart from involving costly apparatus, reproducibility is difficult.

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 taken a mixture of a soluble thallous salt and organic sulphur compounds like thiols, thiourea, substituted alkyl thioureas and some inorganic thiocompounds in solution and then adjusting the pH to be on the alkaline side around 12 to get the desired film thickness of about 2 microns of thallium sulphide on the substrate (glass).

The following typical Examples are given to illustrate the invention :

Example 1

Deposition bath consists of an aliquot amount of saturated solution of thallous chloride, about equal volume of 1.5M thiourea diluted to about twice the volume. The ground glass plates of 1 c.m.×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. 50% alkali is gradually added until a mirrory deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for 20-30 minutes. They are then taken out and dried. Fairly good and adherent deposits are obtained there. The photosensitivity of these plates, without any further treatment, is of the same order as that reported for the vacuum evaporated thallium sulphide cells treated specially subsequently. Plates prepared by this chemical deposition actually showed satisfactory response in the visible. The reported sensitivity in the visible is of the order of 1.0 for the vacuum evaporated cells. Our values claimed herein are also of the same order.

Example 2

Deposition bath consists of an aliquot amount of saturated solution of thallous chloride about three times the volume of 3M thiourea. The ground glass plates affixed to a perspex holder are immersed in the bath and then the contents are stirred. About 30% alkali is added gradually until the mirrory deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for 10-20 minutes. Then they are taken out and dried. Good adherent deposits are obtained which are as photosensitive as those mentioned in Example 1.

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. Further these plates even when freshly deposited without further treatment are as sensitive as those reported in literature.

(3) 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.

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Dated this 26th day of May 1967.

COMPLETE SPECIFICATION.

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

Chemical deposition of thin films of photosensitive thallium sulphide layers useful as a solid state device for measuring signals in infra red communication systems around maxium sensitivity peak of 0.9 microns and also for measuring levels of illumination in a wide spectral range from 0.4 microns to 1.3 microns.

Hitherto these photosensitive thin films of thallium sulphide are being deposited by the method of vacuum evaporation.

Drawbacks connected with hitherto known processes|devices

This method of vacuum evaporation is governed by several critical factors and is also costly. Further, reproducibility and the uniformity of deposition are difficult to achieve by vacuum evaporation.

The main object of the invention is to simplify the method of deposition by minimising the number of critical factors, making it less expensive and getting uniform deposits of thin films of thallium sulphide.

The main principle underlying the invention is to deposit thallium sulphide films by a chemical method. The basis of the chemical method consists in making use of the reaction

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between a soluble thallous salt and an organic sulpher compound like a thiol or thiourea or substituted alkyl thiourea or some inorganic thiocompounds in solution and then adjusting the pH to be on the alkaline side around 12 to get the desired film thickness of about 3 microns.

The new result flowing from the new finding defined in quantitative terms

By this new method of chemical deposition, we obtained the desired thallium sulphide films of thickness ranging from 3-6 microns 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 films thus deposited are photosensitive.

A statement (definition) of invention

Thin films of photosensitive thallium sulphide layers have been obtained hitherto only by the vacuum evaporation method with all the disadvantages mentioned earlier.

According to the present invention, the method for deposition of thin films of photosensitive thallium sulphide layers consists in deposition of the films by a chemical method making use of the reaction between a soluble thallous salt and an organic sulpher compound like a thiol or thiourea or substituted alkyl thiourea or some inorganic thiocompounds in solution and then adjusting the pH to be on the alkaline side around 12 to get the desired film thickness of about 3 microns. The invented method not only gives photosensitive thin films of thallium sulphide by chemical method of deposition but also obviates the difficulties and the disadvantages associated with the method of vacuum evaporation.

Other novel features

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 the 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.

Detailed description with reference to drawings

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

The plate holder consists of 5 c. m. square perspex sheet of about 0.5 c.m. 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 c.m.×0.5 c.m. These plates are ground with emery grade No. 520. These ground plates are attached with quick fix to the perspex holder with the ground surface facing downwards (the deposition side).

The deposition bath consists of a mixture of soluble thallous salt solution and one of the organic compounds mentioned above. 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 between 3 and 6 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 increases the sensitivity.

A few typical Examples

EXAMPLE 1

Deposition bath consists of 10 ml of 0.5 M thallous nitrate solution and 12.0 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 the contents stirred with a magnetic stirrer. 50% sodium hydroxide is gradually added until the pH reached 12 when a bright mirrory deposit is obtained on the wall of the container. The plates are allowed to remain inside the beaker for about 30 minutes. The holder is then removed, washed with distilled water and the plates are wiped with cotton-wool soaked in distilled water. The plates are removed and good adherent deposits are obtained which are photosensitive.

EXAMPLE 2

The deposition bath consists of 50 ml of saturated thallous chloride solution, 15 ml of 2.0 M N-N′ diethyl thiourea diluted to about 100 ml. The ground glass plates affixed to a perspex holder are immersed in the bath and then the contents are stirred. 2 M sodium hydroxide is gradually added until the mirrory deposit is obtained on the walls of the container. The plates are allowed to remain inside the solution for 10-20 minutes. Then they are taken out and dried. Good adherent deposits are obtained which are photosensitive.

The main advantages of the invention

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 concentrations can be done easily by adding dopants to the depositing bath.

Summary (critical discussion)

This films of thallium sulphide cells have been used in infra red communication systems during night. Further they have high photosensitivity in the region from 0.4 micron to 1.3 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 of 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 be only done with doubtful reproducibility. We have evolved for the first time successfully a method of chemical deposition to get equally photosensitive layers of thallous sulphide 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.

We claim :

1. A method for deposition of thin films of photosensitive thallium sulphide layers which consists in deposition of the films by a chemical method making use of the reaction between a soluble thallous salt and an organaic sulpher compound like a thiol or thiourea or substituted alkyl thiourea or some inorganic thiocompounds in solution and then adjusting the pH to be on the alkaline side around 12 to get the desired film thickness of about 3 microns.

2. A method as claimed in Claim 1 wherein thallium sulphide films of thickness ranging from 3-6 microns are obtained on the glass substrates.

3. A method for obtaining photosensitive thin films of thallium sulphide layers substantially as hereinbefore described.

4. Photosensitive thin films of thallium sulphide layers whenever obtained accordingly to a method substantially as hereinbefore described.

5. A method as claimed in any of the preceding claims wherein the essential steps of the process consist of the chemical deposition of thallium sulphide layers by which when the ground glass substrates on which the layers are to be deposited are kept immersed in a beaker, in a solution containing a mixture of a soluble salt of thallium and thiourea, to which alkali solution is added such that the contents of the bath acquire a pH of about 12 adherent fine photosensitive deposits of thallium sulphide are obtained.

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