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

Hitherto it has been proposed to deposit these thin films only by vacuum deposition. This 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 very inexpensive 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 silver salt and organic sulphur compounds like thiols, thiourea, substituted alkyl thioureas and some inorganic thiocompounds along with a complexing agent in solution and then adjusting the pH to be on the alkaline side in the range 6-10 to get the desired film thickness of 3-6 microns of silver sulphide on the substrate.

The following typical examples are given to illustrate the invention:

Example 1
Deposition bath consists of an aliquot amount of approximately 0.5 M aqueous solution of silver nitrate, about three times by volume of 2x10^{-3} M thiourea diluted to about three times. The ground glass plates affixed to a perspex holder are immersed in the bath and then the contents are stirred.

Fairly concentrated ammonia or any alkali gradually added until a mirror deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for 10 to 20 minutes. Then they are taken out and dried. Fairly good adherent deposits are obtained which are photosensitive.

Example 2
Deposition bath consists of an aliquot amount of approximately 0.5 M aqueous solution of a soluble silver salt, about three times by volume of 2x10^{-3} M of N,N'-diethyl thiourea diluted to about two and half times. The ground glass plates affixed to a perspex holder are immersed in the bath and then the contents are stirred. Fairly concentrated ammonia or any alkali is gradually added until the mirror deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for 10 to 20 minutes. Then they are taken out and dried. Fairly good adherent deposits are obtained which are photosensitive.

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. 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 20th day of March, 1967.

Sd/-

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Price: TWO RUPEES.
COMPLETE SPECIFICATION

"IMPROVEMENTS IN OR RELATING TO DEPOSITION OF PHOTOSensitive FILMS OF SILVER SULPHIDE LAYERS"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAiF MARQ, 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 VEN-KATA SURYANARAYANA, Scientist, NARA-SIMHAN RANGARAJAN, Senior Scientific Assistant, KRISHNAMOORTHY NAGARAJA RAO, Senior Scientific Assistant and MARY JULIANA MANGALAM, Senior Scientific Assistant, all of the Chemical Physics Division, Central Electrochemical Research Institute, Karakudi-3, Madras c, India, all Indian citizens.

Chemical deposition of thin films of photosensitive silver sulphide layers useful as a solid state device for measuring low levels of illumination (100 to 1000 lux) in the spectral range of 0.4 to 1.4 microns.

Prior knowledge:

Hitherto these photosensitive thin films of silver sulphide were 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 (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 elements which in turn depends upon the length of the heating elements (wire), the disposition of the glass plates on which the material is to be evaporated etc.) and is also costly. Further, reproducibility and the uniformity of deposition are difficult to achieve by vacuum evaporation.

The main object of the invention:

The main object of this invention is to simplify the method of deposition by minimising the number of critical factors (mentioned above) making it less expensive and getting uniform deposits of thin films of silver sulphide.

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

The main principle underlying the invention is to deposit silver sulphide films by a chemical method. The basis of the chemical method consists in making use of the reaction between a soluble silver salt and an organic sulphur compound like a thiol or thiourea or substituted alkyl thiourea or some alkali thiosulphates in presence of complexing agents like ammonia, amines and substituted alkyl and aryl amines in solution at an optimum pH, which is on the alkaline side in the range of 8-10.

The new result flowing from the new finding (define in quantitative terms):

By this new method of chemical deposition we obtained the desired silver sulphide films of thickness ranging from 3-6 microns of silver sulphide 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.

A statement of invention:

According to the present invention, the process for the deposition of photosensitive layer of silver sulphide on a substrate like glass for use as semi-conductor devices for measuring low levels of illumination (100-1000 lux) in the spectral range from 0.4 microns to 1.4 microns consists in reacting an aqueous solution of a soluble silver compound like silver nitrate and a soluble organic sulphur compound like alkyl thiourea, thiosulphimide, thioles, in presence of a substance like ammonia which keeps the silver ions in a complex form, wherein the reaction is conducted in an optimum pH in the range of 8-10 whereby silver sulphide is formed which deposits as a thin layer on the glass substrates having photosensitive properties.

Thus, an organic sulphur compound consisting of a substituted alkyl thiourea or alkali thioureas and a complexing agent for silver ions such as ammonia amines or substituted alkyl or aryl amines may be used.

Silver sulphide films of thickness ranging from 3-6 microns of silver sulphide are obtained on glass substrates. The deposition is done at laboratory temperature (30-35°C).

Cations and anions called dopants (as known in the art) like group IIb metal ions in the periodic table and halide ions may be introduced into the deposited layers by adding the dopants to the solution.

The present invention thus provides a process for chemical deposition of films of silver sulphide which comprises the active elements in one of the photosensitive devices for measuring low levels of illumination. This chemical method is efficient from the point of view of reproducibility, uniformity of deposition and handling and incorporation of dopants. These thin films were previously deposited by a vacuum evaporation method, the disadvantages of which have been mentioned earlier. The difficulties and disadvantages inherent in vacuum evaporation method are not only obviated by this invention of chemical deposition, but in addition this new method is not only simple but is quite cheap and no sophisticated equipment is necessary here.
Subsidiary 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 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.

Detailed description:

The experimental set up consists of two parts—
(1) The Plate holder (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. thick 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 glass plate is 1 cm. x 0.5 cm. 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 silver salt solution and one of the organic sulphur compounds like thiourea mentioned above along with one of the complexing agents. 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 in the range 8-10. 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 then 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 and heat treatment in oxygen has been found to increase the sensitivity.

A few typical examples:

Example 1

Deposition bath consists of 10 ml of 0.5 M silver nitrate solution and 35ml of 0.5 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. A mixture of 5 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 adherent deposits are obtained which are photosensitive.

Example 2

The deposition bath consists of 15 ml of 0.5 M aqueous solution of silver nitrate, 45 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 content of the stirred 2 M sodium borohydride is gradually added until the mirrorry deposit is obtained on the wall of the container. The plates are allowed to remain inside the solution for 10 to 20 minutes. Then they are taken out and dried. 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 (30-35°C) 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):

Thin films of silver sulphide have been used as semiconductor devices for measuring low levels of illumination in the spectral range from 0.4 micron to 1.4 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 films layers. Also in several other semiconductor devices, the doping of these films, which is a process well known for increasing 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 silver 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 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.

Noteworthy features:

A process for chemical deposition of thin films of silver sulphide which comprises the active elements in one of the photosensitive devices for measuring low levels of illumination. This method is efficient from the point of view of reproducibility, uniformity of deposition and handling and incorporation of dopants. These thin films were previously deposited by a vacuum evaporation method, the disadvantages of which have been mentioned earlier. The difficulties and disadvantages inherent in vacuum evaporation method are not only obviated by this invention of chemical deposition, but in addition this new method is not only simple but is quite cheap and no sophisticated equipment is necessary here.

WE CLAIM:

1. A process for the deposition of photosensitive layers of silver sulphide on a substrate like glass for use as semiconductor devices for measuring low levels of illumination (100-1000 lux) in the
spectral range from 0.4 micron to 1.4 microns which consists in reacting an aqueous solution of a salable silver compound like silver nitrate and a soluble organic sulphur compound like thiourea, thiosaccharimide, thials, in presence of a substance like ammonia which keeps the silver ions in a complex form, wherein the reaction is conducted in an optimum pH in the range of 8—10 whereby silver sulphide is formed which deposits as a thin layer on the glass substrates having photosensitive properties.

2. A process as claimed in claim 1 wherein are used an organic sulphur compound consisting of a substituted alkyl thioureas or alkali thiosulphates, and a complexing agent for silver ions such as ammonia amines or substituted alkyl or aryl amines.

3. A process as claimed in claim 1 or 2 wherein silver sulphide films of thickness ranging from 3-6 microns of silver sulphide are obtained on glass substrates.

4. A process as claimed in any of the preceding claims wherein the deposition is done at laboratory temperature (30-35°C).

5. A process as claimed in any of the preceding claims wherein cations and anions called dopants (as known in the art) like group II B metal ions in the periodic table and halide ions, are introduced into the deposited layers by adding the dopants to the solution.

6. A process for the deposition of photosensitive films of silver sulphide layers substantially as hereinbefore described with reference to the experimental set up and example.

7. Photosensitive layers of silver sulphide on a substrate like glass suitable for use as semiconductor devices for measuring low levels of illumination (100—1000 lux) in the spectral range from 0.4 micron to 1.4 microns wherever obtained according to a process substantially as hereinbefore described.

Dated this 15th day of December, 1967.

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