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PROCESS FOR PRODUCING PHOTOCONDUCTIVE CADMIUM SULFIDE

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This invention relates to a process for producing a sublimed layer of photoconductive cadmium sulfide. Other sulfides, such as zinc and magnesium sulfide are generally the known equivalents of cadmium sulfide which has been the specific material used in the course of various discoveries disclosed hereafter.

In the field of light amplification it is essential to obtain a layer of photoconductive material which will possess a high degree of reproducibility and uniformity. In achieving this end, it has been necessary to investigate the phenomena of photoconductivity, its mechanism, what causes it, and what influences its efficiency.

It has now been established that the photoconductivity which takes place within cadmium sulfide and similar materials is based upon the lattice structure of the cadmium sulfide material. At certain locations within the lattice work "vacancies" may occur which create a coulomb-like potential of positive or negative charge depending on whether it is a cation or anion which is missing. A vacant cation site will serve as a center of effective negative charge and conversely a vacant anion site will serve as a center of effective positive charge.

The same effect can be produced by infusion of impurities but the difficulty in this case lies in the control of extent, quality, and reproducibility of the photoconductivity so obtained. It has been discovered that certain impurity materials have valencies permitting the "capture" of an electron at the site wherein they are included, and these are referred to as "activators." Where cadmium sulfide is the photoconductive medium, group I metals and group V non-metals are "activator" ingredients; group III metals and group VII non-metallics have the opposite electrical effect and hence are called co-activators. The mechanism of photoconductivity depends upon the existence, in proper proportions of these "sites" of positive and negative charge whether the sites are created from "vacancies" or impurities. The present invention is based upon the creation of these charged sites through the presence of impurities.

Consideration such as ease of diffusion, temperature requirements, and reactivity make copper and indium the optimum ingredients for the activator and co-activator functions, respectively.

An important discovery underlying the uniformity and reproducibility of the photoconductive layer is that the ratio of activator to co-activator is very important whereas the total amount of each is of less relative importance. The value of the present invention lies in the means for achieving that proper proportion and infusing the ingredients into the cadmium sulfide layer which is formed in a uniform polycrystalline state.

Other methods of achieving this uniformity are set forth and claimed in separately filed patent applications including my copending application entitled Processes for Preparing Photoconductive Cadmium Sulfide, Serial No. 752,445, filed August 1, 1958.

Other objects and features of the present invention will become apparent from a consideration of the following description which proceeds with a detailed explanation of selected embodiments which have been chosen by way of examples of the invention.

The method followed in obtaining a photoconductive layer of cadmium sulfide is to first prepare a solution

having a desired proportion of activator and co-activator ingredients.

The solution is applied to the substrate surfaces prior to sublimation and allowed to dry giving a uniform layer of activating ingredients thereon. The substrate consists of a suitable backing of some inert ceramic or the like member. These ingredients are then diffused into the crystal lattice of the cadmium sulfide layer deposited on said substrate during the sublimation process.

The temperatures reached during sublimation of cadmium sulfide onto the substrates are such that diffusion of impurities into the host crystals occurs readily. The temperatures are in the order of 650° C. or above.

The activator, selected from group I, may consist of copper ion. The co-activator, selected from group III may consist of indium. Any of the other metals from these respective groups are their equivalents, but, these two materials are preferred since they have been found to disperse through the cadmium sulfide matrix quite readily.

It was discovered that optimum range in ratio of co-activator to activator lies between about 0.75 and 1.75. Satisfactory results may also be achieved within the range of about 0.50 to about 2.0. While the total amount of activator and co-activator was not found to be as critical as their relative proportions, it was established that for best results, the cadmium sulfide will contain from about 50 p.p.m. to about 500 p.p.m. of activator. This means that in the typical molal concentrations of solution a volume of about 0.5 ml. of solution is applied per square inch of substrate which consists of vitreous or inert ceramic. The concentration of both the activator and the co-activator is in the order of about 10^{-4} to about 10^{-3} moles per liter.

The following examples show the process of obtaining the proper proportion of activator to co-activator ingredients.

EXAMPLE 1

Group I, activator; group VII, co-activator

First, a solution of copper chloride (or other soluble coactivator) is prepared so that 1 ml. contains about 10^{-3} M of soluble co-activator, the chloride ion.

There is next prepared a solution of copper acetate so that 1 ml. contains about 3.5×10^{-4} M of soluble activator.

From these two solutions sufficient amounts are added to distilled water to adjust the ratio of activator to co-activator as desired. This solution is next added directly to the substrate and the impurities infused into the cadmium sulfide.

By following the above procedure it is possible to obtain a very fine degree of control of the ratio of activator and co-activator materials.

It is possible by means of this procedure to investigate the optimum ratio of activator to co-activator and to establish the optimum and workable proportions thereof.

EXAMPLE 2

Group I, activator; group III co-activator

In this example it is intended to prepare an aqueous solution of indium-copper equal to 1.5 molal. Assuming starting materials of copper acetate at a concentration of 2.5×10^{-5} mole/ml. there is added 1.5 parts thereof to 1.0 part indium chloride solution of a concentration 3.01×10^{-5} mole/ml. The resulting solution is:

$$\frac{(1.5)(2.5\times10^{-5})\ \text{In}}{(1.0)(3.01\times10^{-5})\ \text{Cu}}=1.25 \text{ volume of } 3.01\times10^{-5}\text{m./ml. sol.}$$

Tod 15 ml. of the indium solution there is added 12 ml. of the copper solution and about ½ ml. of HCl is

included to insure acidity which prevents precipitation. The resulting solution has a ratio of 1.505 parts indium to copper. The analysis per ml. figures to 1.64×10^{-5} M (In) and 1.09×10^{-5} M (copper).

The solution may be directly added to the substrate as in the previous embodiment. In this example, the advantages of the prepared solution lie in ease of preparation, ease of application, uniformity of results, and less need of critical technique.

EXAMPLE 3

Group I, activator; group III co-activator

In this example, samples of indium chloride solution and copper acetate were mixed together in various ratios of indium/copper viz., .5, 1.0, and 1.8. To obtain this, drops of the aqueous solution were added to 21 ml. of ethyl alcohol.

Single drops of solution were then added to the substrate. The advantage of using alcohol is that it is rapid drying. Cadmium sulfide sublimation is then carried on for about 3 minutes, at sublimation temperatures of 650° C. and above.

The impurity agent is of the order of 10^{-3} to 10^{-4} moles per liter and about 0.5 ml. of solution per square inch of substrate is applied.

The test results are summarized in the following chart:

Test Number	In/Cu	I_d Amperes	I_6 Amperes	Remarks
1	.5	5×10^{-10}	2.5×10^{-8}	This series firmly establishes the practicality of activating a sublimed layer of cadmium sulfide.
2	1.0	6×10^{-9}	1.5×10^{-7}	
3	1.8	8.5×10^{-6}	9.5×10^{-6}	
4	.5	5×10^{-10}	4.5×10^{-5}	
5	1.0	10^{-10}	4×10^{-9}	
6	1.8	3.5×10^{-6}	4.0×10^{-6}	
6a	0	$.5\times10^{-6}$	1.2×10^{-6}	
7	.5	740×10^{-6}	740×10^{-6}	
8	1.0	5×10^{-10}	3×10^{-7}	
9	1.8	2.5×10^{-9}	9.5×10^{-9}	
10	.5	1×10^{-8}	1.5×10^{-8}	
11	1.0	8.5×10^{-11}	1.4×10^{-8}	
12	1.8	1.3×10^{-6}	1.7×10^{-6}	
13	.5	5×10^{-10}	3.5×10^{-8}	
14	1.0	5×10^{-11}	1.3×10^{-8}	
15	1.8	(effective short circuit—current to high)		
16	.5	2×10^{-8}	1.5×10^{-7}	
16a	1.0			

In the chart:
I_d=cell current while the cell is in darkness.
I_6=cell current when illuminated with 6 foot candles.

There is some tendency, owing to surface tension, for the liquid to collect in pools and leave localized concentrations of the impurity across the surface of the substratum. To avoid this, the use of a wetting agent and etched substrate surface is recommended.

All of the described solutions in the chart are of a concentration in the order of 10^{-6} M/ml.

While I have described above the principles of my invention in connection with specific apparatus, it is to be clearly understood that this description is made only by way of example and not as a limitation to the scope of my invention.

What is claimed is:

1. A process for producing a photosensitive layer of sublimed cadmium sulfide, comprising the steps of: preparing a solution of activator and co-activator consisting of copper acetate and copper chloride, said activator and co-activator being in the ratio of not substantially less than 0.5 nor substantially more than 2.0, depositing said activator and co-activator over an inert substrate medium by evaporating the solvent of said activator and co-activator solute, and sublimating a quantity of cadmium sulfide which is formed over said substrate and is thereby made photoconductive by infusion of said activator and co-activator ingredient therein as the sublimation proceeds.

2. The process of claim 1 in which the activator and co-activator materials consist of copper acetate and indium chloride, respectively.

3. The process of claim 1 in which said activator is copper acetate, and said co-activator is selected from the class consisting of copper chloride and indium chloride.

4. The process of claim 3 in which photoconductivity developed in the supernatant layer of sublimed material is controlled by the ratio of co-activator to activator ingredients.

5. The process of claim 4 in which the amount of activator and co-activator is determined from the concentration and quantity of solution which is initially formed over the inert ceramic as a substratum.

6. The process of claim 5 in which the substratum is formed from about .5 ml. of solution containing 10^{-4} to 10^{-3} moles of activator and co-activator so as to produce from about 50 to 500 parts per million in the cadmium sulfide layer.

7. The process of claim 6 in which cadmium sulfide is sublimed at a temperature not substantially less than 650° C. for a time of approximately 5 minutes.

8. A process for producing a photoconductive layer of cadmium sulfide comprising the steps of: preparing a solution of dissolved activator and co-activator ingredients in the desired proportion, applying a quantity of said solution to an inert surface serving as the backing for said photoconductive layer, evaporating the solvent of said solution to precipitate said activator and co-activator, which form a substratum on said backing, and sublimating cadmium sulfide to form a layer over said substratum which becomes dispelled through the cadmium sulfide during sublimation to render the cadmium sulfide photoconductive.

9. The process of claim 8 in which the vapor phase deposition of the cadmium sulfide is carried out under a thermal gradient in which the deposit is formed as a thin polycrystalline layer having a molecular array characterized by a high degree of order therein.

10. The process of claim 9 in which the deposited layer of cadmium sulfide exhibits properties of photoconductivity in accordance with the crystalline defects produced therein, and controlling atmospheric conditions surrounding said deposition by regulating the partial pressures of cadmium and sulphur which are dissociation products of said cadmium uslfide.

11. The process of claim 10 in which said substratum is controllably heated and thereafter covered with sublimed cadmium sulfide, said substratum being thereby used to control the amount of free cadmium from the sublimed vapor phase deposition.

12. The process of claim 11 in which the cadmium sulfide is heated to about 1,000° C. and thereafter carried in vapor form to the substrate where it is deposited in a form dependent upon the established thermal gradient.

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