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(54) PHOTOVOLTAIC CELL

(71) WE, PHOTON POWER INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, of 1820 Mills Avenue, El Paso, Texas 79910, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the manufacture of photovoltaic cells.

It is known to form photovoltaic cells by coating on a hot sheet of Nesa glass, or glass previously coated with SnO_x, a thin film of CdS by spraying a water solution o compounds which form a layer of CdS microcrystals on the SnO_x, and providing a Cu_2S heterojunction as a layer on the CdS layer, and forming electrodes on the film of Cu_2S. The Cu_2S layer has been formed by spraying a Cu_2S forming solution on the CdS film while the substrate was hot, but in accordance with the present application, the Cu_2S can be formed by dipping at or near room temperature or by electroplating, at or near room temperature. Cells so formed have heretofore utilized relatively thick films of CdS, or have resorted to other expedients to obviate the difficulty that CdS films generally permit permeation by Cu_2S, when Cu_2S is formed by dipping or electroplating, i.e., by ion exchange, which provides short circuits between the Cu_2S layer and the SnO_x, the latter constituting the negative electrode of the cell, rendering the cell inoperative. In order to convert solar energy to electrical energy on a large scale, square miles of solar cells may be required. Since Cd is a rare and expensive metal, it becomes important to form photovoltaic cells with minimum quantities of CdS and hence with extremely thin CdS films, yet that the cells be reliably fabricated and have long life. We have produced CdS photovoltaic cells in which the layer of CdS is about 2. or 4. microns thick, yet which show zero shorting permeation, the layers being highly impervious to Cu_2S or Cu containing solutions, in an ion exchange process. We have heretofore used the method of spraying a CdS forming solution on a glass coated with SnO_x, intermittently and at a slow rate, while maintaining the surface of the glass at uniform and constant temperature in the range between 500°F and 800°F.

According to the present invention there is provided a photovoltaic cell, comprising an electrically conductive substrate, a first layer containing CdS, a second layer of Cu_xS superposed on said first layer and forming a photovoltaic heterojunction therewith, and an electrode contacting said second layer, said first layer containing a selected metal in an amount effective to provide at least a portion of said CdS in said first layer with structure resistant to permeation by said Cu_xS through said first layer to said electrically conductive substrate.

Preferably, said compound of said selected metal is formed from a solution containing a cadmium compound and a salt of said selected metal. Said selected metal may advantageously be aluminium.

In one manner of making a photovoltaic cell according to the invention, plural spray applications are employed to form the CdS layer. All sprays employ the known materials, i.e., a solution containing essentially $CdCl_2$ and thiourea, but to one spray is added $AlCl_3 . 6 H_2O$, in proportion by weight equal to between 10% and 50% of Al, adding thiourea as required to combine with the Al, and in a superposed spray optionally a small quantity of HCl, but no $AlCl_3 . 6 H_2O$, or a very much reduced quantity of $AlCl_3 . 6 H_2O$; or, instead of applying two discrete films, one containing a large quantity of aluminium compound and the other containing none or very little, the coating may be

formed by gradually decreasing the concentration of aluminium in proceeding from the bottom of the layer adjacent to the SnO_x to the top of the layer, so that the top of the layer contains no aluminium or very little aluminium while the bottom of the layer may have as much as 50% aluminium. The quantity of the sulphur employed must be proportioned to the quantity of aluminium, forming a compound or crystal therewith.

It is then found that the portion of the eds layer which contains a large proportion of aluminium is extremely hard so that it can only with difficulty be removed by application of acid or by scraping, is highly adherent to the SnO_x layer, so that it can only with difficulty be removed, and is highly impervious to materials involved in forming a Cu_2S layer by ion exchange, or to Cu_2S, and inhibits diffusion of Cu through a CdS layer, where Cu_2S is formed by dipping or electroplating, i.e., by an ion exchange process. The inclusion of aluminium in CdS in the large quantities specified does not constitute a doping procedure, but is a new compound or alloy or a new crystalline form, having physical properties quite distinct from those of CdS, or CdS with small amounts of aluminium, in terms of hardness, toughness and imperviousness, but which remains photoconductive. For example, it is known that Al_2S_3 and CdS crystals are both hexagonal, and the Al may form Al_2S_3 crystals or a composite crystal or alloy, of Al, Cd, S or a tenary compound, through tests indicate the latter possibility to be unlikely. It has been found that if the entire film of CdS is heavily impreganted with Al the cell remains operative, but at reduced efficiency.

Techniques for manufacturing photovoltaic cells according to the invention will now be described in more detail with reference to specific examples.

One method of fabricating a photovoltaic cell according to the invention comprises spraying on a hot insulating transparent substrate coated with SnO_x a water solution of cadmium chloride, thiourea and an aluminium containing soluble compound in heavy concentration. On the latter may be superposed a further sprayed layer of cadmium chloride and thiourea, having little or no included aluminium. The aluminium concentration in the $CdCl_2$ layer may be concentrated most heavily in the underside of the CdS layer, i.e., be dispersed throughout the CdS layer with a much heavier concentration at the bottom of the layer than occurs at the top, whre no Al may occur or only little, or the Al may be dispersed equally throughout, the process being conducted while the sprayed surface of the substrate is maintained at a constant temperature in the range 500°F to 800°F, and thereafter heating the coated substrate to about 525°C, cooling to approximately room temperature, and thereafter coating with Cu_2S solution either by dipping or by electro-plating to form a heterojunction, and forming an electrode over the heterojunction.

A process as disclosed in our Patent Specification No. 1506158 is applied to a glass substrate as the glass substrate travels along a tank containing a molten salt or a molten metal. The sheet of glass may be supported solely by the molten liquid or partially by the molten liquid and partially by extraneous supports, so that its bottom surface is immersed in the liquid and the liquid continously supplies heat to the substrate. In the course of spraying the substrate with solutions, the upper exposed surface of the substrate is cooled by the spray. It is then necessary to conduct the spraying operation so slowly, and over so small a portion of the substrate surface at any instant of time, that the substrate surface can acquire from the molten material enough heat to recover the temperature of the exposed surface of the substrate between the sprays applied to any area. This process provides a uniform layer thickness, and also facilitates maintenance of constant temperature, or maintains the temperature more nearly constant than is otherwise feasible.

Subject to the considerations stated in the immediately preceding paragraph, the glass is assumed to be at approximately the temperature of the heated liquid, the temperature of which is such as to maintain the exposed surface of the glass at a temperature in the range 500°F to 800°F, and it is assumed for the purpose of the present process that the glass has been coated with SnO_x in a thin transparent layer. Spraying is advantageously accomplished under intense ultraviolet light, which is absorbed by CdS and enhances the internal energy of the CdS crystals.

EXAMPLE 1

In a first example of the invention, two solutions are prepared. The first solution may be in the proportion:

2 liters water
60. cc 1 Molar $CdCl_2$
60. cc 1 Molar thiourea
1.95 gm $AlCl_3 . 6H_2O$
(add sufficient thiourea to satisfy quantity of $AlCl_3$ used)

The second solution employed is in the proportion:

5 liters water
150. cc 1 Molar thiourea
150. cc 1 Molar $CdCl_2$
2 1/2 cc Hydrochloric acid

While thiourea is specified as a component, its function is to produce sulphur. Other compounds which are soluble in water, and which give up sulphur, can be substituted. Specifically, NN DMthiourea has been employed, but thiourea is the least ex-

pensive compound which has been found satisfactory. The specific quantity of $AlCl_3 . 6 H_2O$ may be varied over a wide range, provided that the quantity of sulphur available is proportionally varied. The purpose Al inclusion is to provide at least a stratum of CdS by combination of $CdCl_2$ with thiourea which is heavily impregnated with aluminium or Al_2S_3 microcrystals. During the coating the Cl and the H_2O are removed due to the temperature at which the process is carried out, and aluminium remains. This aluminium may be included at concentrations in any proportion from 10% to 50% by weight. Even higher percentages of aluminium may be employed, but higher percentages have not been found to produce superior performance. The layer of CdS, heavily impregnated with aluminium, is found to have physical properties quite different from CdS containing no aluminium or relatively small amounts. The layer is extremely hard, impervious to Cu_2S or Cu, and is highly adherent to the SnO_x. The reason for these physical properties is not known, but it appears that either aluminium is incorporated in the CdS crystal so that a new form of crystal is formed, or that a new tertiary compound is formed, or that Al_2S_3 microcrystals are formed.

The second solution contains no aluminium, in the example cited, but in fact some aluminium may be included in the form of $AlCl_3 . 6 H_2O$. Inclusion of HCl is optional, and for reasons unknown increases slightly the output of the cell, but so far as is known does not otherwise affect the operation of the cell.

EXAMPLE II

A single coating of water, $CdCl_2$, thiourea and $AlCl_3 . 6 H_2O$ is sprayed on glass coated with SnO_x, but as the spraying proceeds the proportion of $AlCl_3 . 6 H_2O$ to $CdCl_2$ is gradually decreased, for example, logarithmically, so that, for example, as much as 50% aluminium may be present in the lowermost part of the final layer, and zero or substantially zero aluminium at the upper surface of the layer. As the quantity of $AlCl_3$ is varied, the quantity of thiourea is varied proportionately, to satisfy both the Cd and the Al in forming the final compounds.

In either case, the preferred end result is that directly in contact with the SnO_x is a layer of CdS, and at the upper surface of the layer of CdS, on which is to be applied Cu_2S to form a heterojunction, there is no aluminium or very little aluminium. Two distinct layers may be employed, or a gradually decreasing percentage of aluminium, in proceeding from bottom to top of the layer.

The solutions are sprayed on the glass intermittently and slowly in successive passes over a considerable period of time, of the order of 10-40 minutes for the first coating and 10-40 minutes for the second coating, in Example I, and in the order of 20-60 minutes in the case of the graduated layer, and generally so slowly that the glass sheet always remains at the same average temperature, during the spraying, despite the heat abstracted from the glass in the spraying process. The total thickness of the layer formed in this way is 2. to 4. microns, or less. The coated plate is, after spraying is completed, heated to a temperature of 500°C to 550°C for 15 minutes.

After the CdS layer has been formed, the bath is slowly cooled, and the coated product may then be removed. The SnO_x layer employed is about .4 micron thick and has a resistivity per square of about 11-17 ohms.

To complete a photovoltaic cell, the CdS layer is coated with Cu_2S by dipping the previously cooled cell into an appropriate solution at room temperature or spraying with that solution at room temperature, or by forming the Cu_2S from solution by electroplating, in any case by ion exchange of Cu for Cd in CdS.

The solution employed to form a Cu_2S layer by dipping may be in proportions as follows:

100. cc	Water
7. cc	NHO_3 (5-1)
1.5 gm	(L+)-Tartaric Acid
1.5 gm	CuCl
1.5 gm	$G_4Ce(SO_4)_4$
1.5 gm	NaCl

The tartaric acid is a typical organic acid and for it may be substituted citric or lactic acid. The presence of $H_4Ce(SO_4)_4$ appears to add an increment of about 50. millivolts of voltage to the final cell, but the manner in which it functions in the process is not understood. For NaCl may be substituted another halide, as NH_4Cl. The HNO_3 is optional. Thereafter a deposit of copper is applied over the Cu_2S to a thickness of about 7,000. A, and aluminium is then coated over the copper to protect the copper from oxidation and from the effects of moisture and airborne impurities.

A preferred solution employed in plating is:

EXAMPLE I

700. cc	H_2O
3.9 gm	citric acid monohydrate
2.0 gm	NH_4Cl
7.5 gm	cupric acetate pentahydrate

The NH_4Cl may be omitted but improves the quality of the cells by a small factor. Plating is accomplished at a current density of .5 ma pr cm^2 for 2-5 minutes, with the CdS layer negative with respect to a copper anode.

EXAMPLE II

700. cc	H_2O
10.gm	cupric acetate pentahydrate
15. cc	acetic acid (20%)

The present method can be employed with Nesa glass as the starting material, obviating the need for coating with SnO_x, but Nesa glass has a resistivity per square of about 50.-75. ohms per square, whereas by our methods very low resistivity coatings may be produced, i.e., of the order of 8-17 ohms per square. The use of low resistivity coatings of SnO_x increases the efficiency of the cell by decreasing the amount of energy which is lost in the SnO_x.

Reference has been made hereinabove to the use of very intense ultraviolet light while spraying the cadmium sulphide forming solution. The precise intensity of the irradiation has not been measured, but four 150. watt ultraviolet lamps have been placed within a few inches of a small surface being sprayed, and the ultraviolet light is advantageous. If there is no irradiation during spraying, the cells sometimes have relatively lower outputs than occurs in the presence of intense ultraviolet light.

It also appears to be important to the process that the spraying occur by depositing droplets which are as uniform as possible. If the spray consists of many small and many large droplets, the very small droplets are evaporated by the intense heat, proximate to the exposed surface of the substrate, and only the larger droplets reach the substrate. This causes some wastage of CdS and it implies that the rate at which the spray is applied must take into account the non-uniformity of the droplets. While an air spray has been employed in the production of photovoltaic cells in accordance with the process, the use of electrostatic spraying is known to produce more uniform droplets than can be produced by an air spray and is therefore preferred. In accordance with the method of our parent application, supra, the glass substrate will be moving longitudinally along a trough or tank containing molten material, and the spray will occur by transverse passes across the substrate as the glass moves, so that the total quantity of spray reaching any given small area of the substrate will be uniform. The method allows for the fact that spray out of an air gun or out of an electrostatic spray gun does not have uniform pattern, the continuous motion of the spray gun and of the glass relative to the spray gun enforcing an averaging of the total spray deposited on any small unit area of the substrate, so that the final layer will be of uniform thickness.

It has been found that the cell remains operative if the entire CdS film is heavily impregnated with Al, say between 10% and 50% by weight of Cd.

After a cell is completed, including electrodes, it is heated to 400°F to 500°F.

The present cell is to be exposed to solar radiation via its glass substrate. The presence of Al in the CdS does not materially affect transparency of the CdS-Al layer, so that the heterojunction may be exposed via the latter.

Reference is directed to our patent specification no. 38426/75 (Serial No. 1528372) in which the same subject matter is disclosed and further aspects thereof are claimed.

WHAT WE CLAIM IS:—

1. A photovoltaic cell, comprising an electrically conductive substrate, a first layer containing CdS, a second layer of Cu_xS superposed on said first layer and forming a photovoltaic heterojunction therewith, and an electrode contacting said second layer, said first layer containing a selected metal in an amount effective to provide at least a portion of said CdS in said first layer with structure resistant to permeation by said Cu_xS through said first layer to said electrically conductive substrate.

2. A photovoltaic cell according to claim 1, whrein said compound of said selected metal is formed from a solution containing a cadmium compound and a salt of said selected metal.

3. A photovoltaic cell according to claim 1 or claim 2, wherein said first layer includes a first film component containing CdS and said selected metal, and a second film component containing almost pure CdS.

4. A photovoltaic cell according to claim 3, wherein said first and second film components together have a thickness of 4 microns or less.

5. A photovoltaic cell according to claim 4, wherein said selected metal is aluminium.

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