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(54) Production of semiconductor bodies made of amorphous silicon

(57) The invention relates to a process for the production of semiconductor bodies consisting of amorphous silicon, in which the amorphous silicon (9) is deposited on a heat resistant substrate (5) by a glow discharge process in a silicon halide atmosphere at low pressure and at a low substrate temperature, in a quartz glass reactor (2), the deposition being carried out to form discrete layers, and hydrogenation employing atomic hydrogen being carried out between the formation of the individual layers. The amorphous silicon produced in this way can be used as basic material for solar cells.

FIG 1

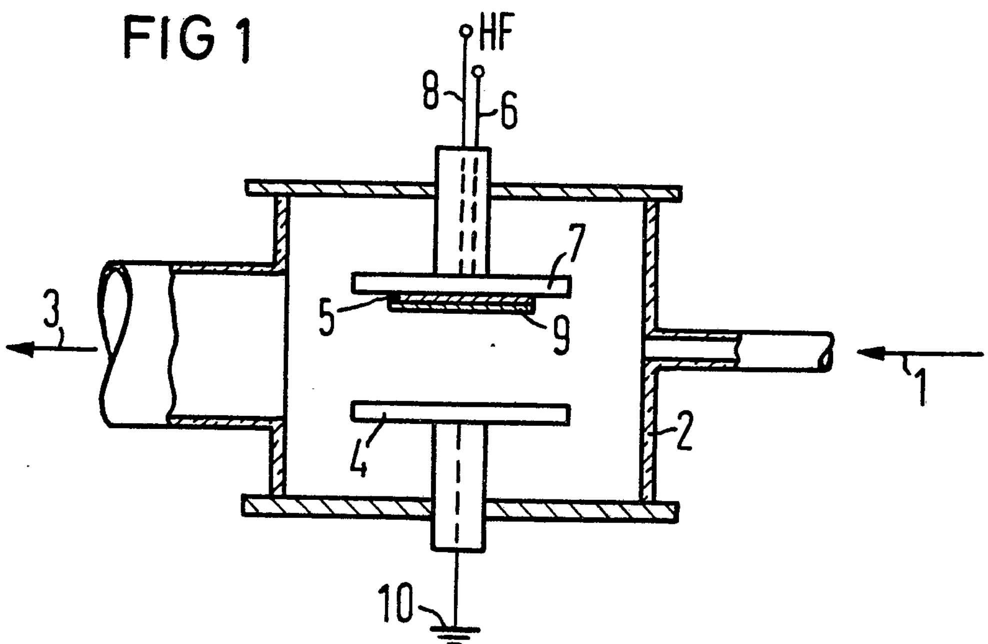

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FIG 1

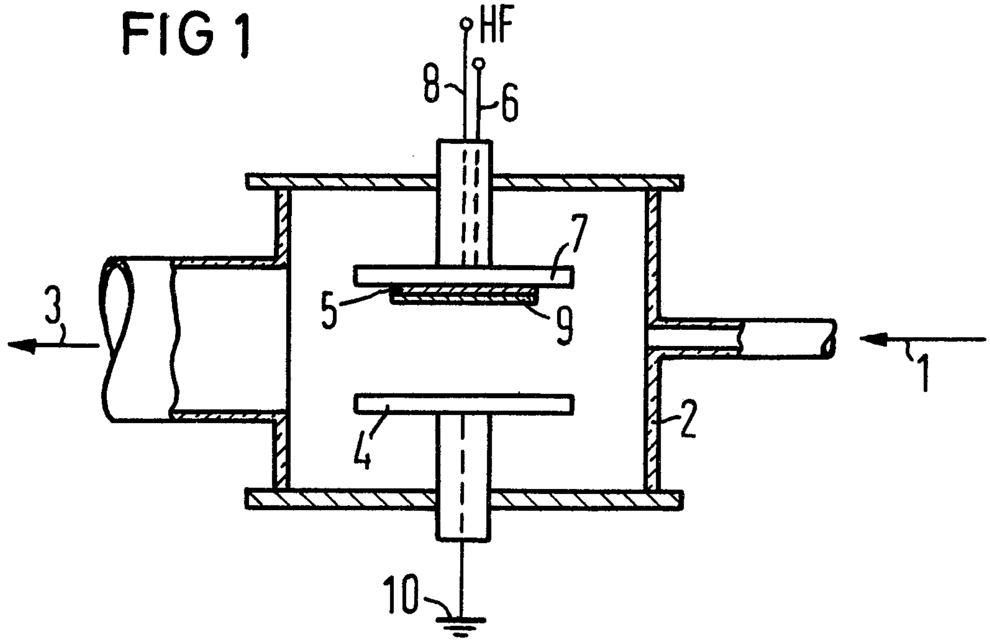
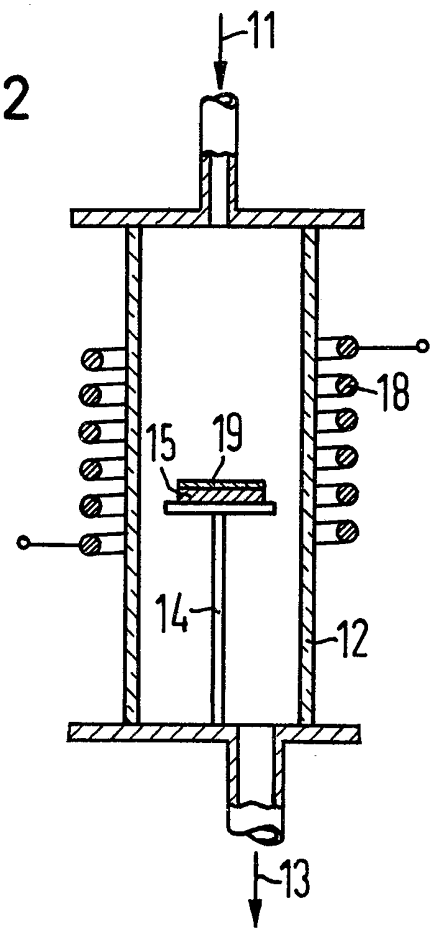


FIG 2



SPECIFICATION

Production of semiconductor bodies made of amorphous silicon

The present invention relates to a process for the production of semiconductor bodies made of amorphous silicon, in particular for further processing to form solar cells in which the amorphous silicon is deposited onto a substrate which is heat resistant and inert to the reaction gases used, by a glow discharge process in an atmosphere containing a gaseous silicon compound at low pressure and at a low substrate temperature.

Some electrical components made of silicon, such as solar cells, can be produced using a form of silicon which need not meet such high requirements in respect of its crystal quality and purity, as in the case of integrated semiconductor circuits. Since solar cells must be very cheap in comparison with integrated semiconductor circuits, in order to find a wide range of use (e.g. for miniature equipment in the watt-range which is not dependent on a mains supply or for generators in the KW-range which are similarly not dependent on a mains supply) the production of the silicon bodies which are used as starting materials for such solar cells must also be as simple and cheap as possible.

A material which is of interest for the production of solar cells and appears promising as regards simplicity and cost of production is amorphous silicon (so-called a-Si). Solar cells made of this material are described in U.S. Patent Specification No. 4,064,521 and German Patent Specification No. 27 43 141.

U.S. Patent Specification No. 4,064,521 discloses a process for producing solar cells in which an amorphous silicon layer having a thickness of about 1 μm is deposited onto a steel plate by decomposing silane (SiH_4) in a low pressure plasma unit. A Schottky contact is subsequently established by vapour depositing a very thin platinum layer on the silicon layer. An important condition for the efficiency of the solar cell formed (5.5 %) is the incorporation of atomic hydrogen which saturates the free valences in the amorphous silicon so that these cannot act as recombination centres for the charge carriers released in the presence of light. The incorporation of hydrogen takes place when using silane, simultaneously with the decomposition process in the plasma reactor.

In the process described in German Patent Specification No. 27 43 141, a chlorinated or brominated silane is used in place of the expensive pure silane (SiH_4) containing only hydrogen, for depositing the amorphous silicon, and the deposition process is controlled in such a way that the amorpous silicon layer produced contains up to 7 atom-% of a halogen of the group comprising chlorine, bromine and iodine, and also hydrogen in order to compensate for the free valences in the amorphous silicon. A disadvantage of this process is that, if the halogen content is too high, the electrical properties of the amorphous silicon are disadvantageously affected and consequently the efficiency is reduced.

It is an object of the present invention to provide a process for the production of amorphous silicon by means of which a product can be simply obtained which is suitable for use to form solar cells of high efficiency, but at the same time is cheap to produce.

According to the invention, there is provided a process for the production of a semiconductor body made of amorphous silicon, comprising the step of depositing amorphous silicon onto a heat resistant substrate by a glow discharge in an atmosphere containing a gaseous silicon halide and hydrogen at a sub-atmospheric pressure, said substrate being inert to said atmosphere and being heated only to a relatively low temperature such that amorphous silicon is deposited, the deposition of said amorphous silicon being effected in a plurality of discrete layers and hydrogenation of the deposited material being carried out between the deposition of the individual layers with atomic hydrogen, in the same reactor, at the same substrate temperature, and at the same pressure as during the deposition of the amorphous silicon.

The silicon halide used is preferably silicochloroform ($SiHCl_3$), or silicon tetrachloride ($SiCl_4$), which are cheaper than silane by a factor of 10. When silane dichloride (SiH_2Cl_2) and silane monochloride (SiH_3Cl) are produced on a large scale, a favourable price and thus a deposition process which is favourable from the point of view of cost can also be achieved using these materials. However, the corresponding bromine and fluorine compounds of silicon can also be used in the same way.

The deposition is preferably carried out stepwise in at least three layers, with an overall thickness of the amorphous silicon layer of 0.5 to 2 μm, preferably about 1 μm. Cheap substrate wafers, preferably consisting of high grade steel, glass or polymide foil (e.g. that sold under the Trade Mark "KAPTON") may be used. However it is equally possible to use a substrate, a metal strip which will subsequently form the contact terminal (rear contact) of a solar cell and may consist, for example, of nickel or molydenum.

The ratio of silicon compound to hydrogen used in the deposition reaction preferably has a value greater than 1 : 1 (i.e. the stochiometric ratio).

In the process of the invention, the hydrogenation carried out after the deposition of each amorphous silicon layer causes the free valences (so-called "dangling bonds") to be satisfied by atomic hydrogen. This takes place particularly intensively at the surface of each layer so that in the case of a layer sequence a higher hydrogen content is achieved within the overall body formed. This results in a more homogeneous distribution of the hydrogen over the total layer thickness. Both factors result in an improvement in the efficiency of a solar cell formed from the amorphous silicon body.

The invention will now be further described with reference to the drawing, in which:—

Figure 1 is a schematic side sectional view of a capacitive HF glow discharge reactor arrangement for carrying out the invention; and

Figure 2 is a similar view to that of Figure 1 of an inductive HF glow discharge reactor arrangement for carrying out the invention.

Referring to Figure 1, a reaction gas consisting of a gaseous silicon compound, (for example, silicochloroform, $SiHCl_3$) and hydrogen, which is to be used to produce the amorphous silicon layer by a glow discharge is introduced into a quartz reactor 2 through an inlet tube as indicated by the arrow 1, the reactor having previously been evacuated to a pressure of 10^{-6} torr through an outlet in the direction of the arrow 3. This is achieved by pumping with the heater unit of the reactor switched on. When the reaction gas which consists of silicochloroform and hydrogen in a mixture ratio of $SiHCl_3:H_2$ of 1 : 2 has a flow speed of 5 l/h, a substrate 5 which is mounted on an electrode 7 and which substrate consists of galvanised high grade steel plate, is heated to a temperature of 200 to 300°C by means of an electrode heating means 6. When HF energy is fed in through a line 8, connected to the electrode 7 a glow discharge between a counter-electrode 4 and the substrate 5 and electrode 7 is set up and deposition of an amorphous silicon layer 9 onto the substrate 5 commences. The two electrodes are spaced from one another by a distance of at least 1 cm.

A HF power of 10 watts and a plasma gas pressure of 0.5 mbar may, for example, be used. The counter-electrode 4 is earthed as indicated at 10. After about 10 minutes, the deposition is interrupted by discontinuing the supply of the gaseous silicon compound, the reactor merely being flushed with hydrogen, so that hydrogenation of the amorphous silicon layer 9 which has been deposited by the atomic hydrogen formed now takes place. After a further 10 minutes, the valve controlling the supply of the silicon halide is re-opened and a further amorphous silicon layer is deposited on the layer 9 already deposited on the substrate 5. This procedure is then repeated a further three times, the free valences of the amorphous silicon being saturated with atomic hydrogen after each deposition step. Following a fifth sequence of deposition and hydrogenisation, the amorphous silicon layer present on the substrate 5 has reached a total layer thickness of about 1 μm and can be further processed together with the substrate 5 itself to form a solar cell by the use of known production steps, such as the production of pn-junctions, Schottky contacts or inversion layers, the production of anti-reflex layers, and the use of vapour deposition and masking techniques.

In the inductive reactor arrangement shown in Figure 2, the reaction gas ($SiHCl_3 + H_2$) is introduced into a reactor in the form of a quartz tube 12 through a gas supply pipe in the direction indicated by an arrow 11 and leaves through a gas outflow pipe in the direction of the arrow 13, the gas discharge pipe simultaneously serving as a connection to a vacuum pump. The reaction gas is decomposed by a glow discharge produced by means of a multi-winding induction coil 18 which is arranged outside the quartz tube 12, and amorphous silicon is deposited on a substrate 15 which is arranged on a heated substrate holder 14 and may consist of a contact metal or a polyimide foil provided with a conductive coating. The conditions to be observed during the deposition of this layer 19 are the same as in the case of the embodiment illustrated in Figure 1. Here again a layered deposition and intermediate hydrogenation of the free valences present in the amorphous silicon is carried out in at least three stages.

CLAIMS

1. A process for the production of a semiconductor body made of amorphous silicon, comprising the step of depositing amorphous silicon onto a heat resistant substrate by a glow discharge in an atmosphere containing a gaseous silicon halide and hydrogen at a sub-atmospheric pressure, said substrate being inert to said atmosphere and being heated only to a relatively low temperature such that amorphous silicon is deposited, the deposition of said amorphous silicon being effected in a plurality of discrete layers and hydrogenation of the deposited material being carried out between the deposition of the individual layers with atomic hydrogen, in the same reactor, at the same substrate temperature, and at the same pressure as during the deposition of the amorphous silicon.

2. A process as claimed in Claim 1, wherein a chlorine-substituted silane is used as silicon halide.

3. A process as claimed in Claim 1 or Claim 2, wherein the deposition is effected in at least three discrete layers, to provide an overall layer thickness in the range of from 0.5 to 2 μm.

4. A process as claimed in Claim 3, wherein the total layer thickness as 1 μm.

5. A process as claimed in any one of the preceding Claims, wherein said substrate is a high grade steel plate, or a glass plate provided with a conductive layer, or a polyimide foil.

6. A process as claimed in any one of Claims 1 to 4, wherein a metal strip is used as said substrate and later serves as a contact terminal for said body.

7. A process as claimed in any one of the preceding Claims, wherein the ratio of silicon compound : hydrogen in the deposition process is set at a value of greater than 1 : 1 (the stochiometric ratio).

8. A process as claimed in any one of the preceding Claims, wherein the gas pressure during deposition and hydrogenation is in the range of from 0.06 to 5 mbar.

9. A method as claimed in any one of Claims 1 to 8, wherein the deposition and hydrogenation steps are carried out in a quartz glass reactor

provided with a gas supply pipe and a gas outflow pipe connected to a vacuum pump, said reactor having a pair of electrodes therein arranged opposite to and spaced from one another by a distance of at least 1 cm and which electrodes are connected to a HF generator, said substrate being mounted on one of said electrodes, and at least that electrode being designed to be heatable.

10. A method as claimed in any one of Claims 1 to 8, wherein the deposition and hydrogenation steps are carried out in a quartz glass reactor provided with a gas supply pipe and a gas outflow pipe connected to a vacuum pump, an annular multi-winding induction heating foil arranged outside of and surrounding said reactor, said coil being connected to a HF generator, said substrate being mounted on a holder located in said reactor in the operating region of said coil.

11. A process for the production of a semiconductor body made of amorphous silicon substantially as hereinbefore described with reference to Figure 1, or Figure 2, of the drawing.

12. A semiconductor body made of amorphous silicon produced by a process as claimed in any one of Claims 1 to 11.

13. A solar cell formed from a semiconductor body as claimed in Claim 12.

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