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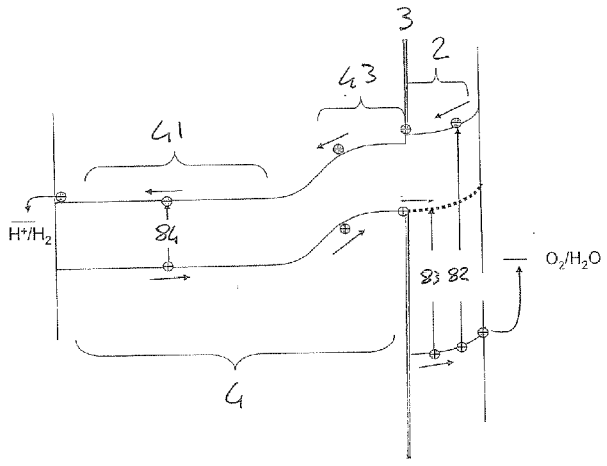


Fig. 3

(57) Abstract: The present invention concerns a semiconductor photoelectrode (1) comprising an upper layer (2) made of a photoactive material, an interface layer (3), at least in part adjacent to the upper layer (2), a semiconductor layer (4), at least in part adjacent to the interface layer (3); wherein theinterface layer (3) is at least in part interposed between the upper layer (2) and the semiconductor layer (4), such that there is at least one path, for an electron created in the upper layer (2), for moving from the upper layer (2) to the semiconductor layer (4) passing through the interface layer (3), where the interface layer (3) has a thickness such that it can be crossed, due to tunnelling, by the electrons which move from the upper layer (2) to the semiconductor layer (4) passing through the interface layer (3).

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Title: "ELECTROCHEMICAL PHOTOELECTRODE"

The present invention refers to an electrochemical photoelectrode for the transformation of the electromagnetic energy produced by a light source.

Electrochemical photoelectrodes or photoelectrochemical devices (PEC) are devices capable of directly using solar energy to drive a chemical reaction, for example for separating water into gaseous hydrogen and oxygen.

PECs are thus considered a promising technology for being able to satisfy future needs of gaseous hydrogen, linked to the increasing diffusion of fuel cells.

An important parameter for evaluating the quality of a PEC is the quantity of gas produced per unit of energy received.

In the art, photoelectrodes are known that are composed of a single photoactive layer which, absorbing solar radiation with sufficient energy, creates electron-hole pairs capable of directly causing the splitting of the water molecule and the formation of hydrogen and oxygen.

Nevertheless, the fraction of solar radiation provided with sufficient energy for the direct conversion is quite small; thus the efficiency of the PEC cannot be high.

In order to be able to utilise a greater fraction of the solar energy, photoelectrodes have been developed with several layers (or hybrid photoelectrodes) in which electrons and holes can undergo multiple excitations, also exploiting the solar radiation provided with lower energy than that required for the direct conversion so as to increase the conversion efficiency of the photoelectrode.

Turner et al. (Science 280, 425 (1998)) describe a hybrid photoelectrode made with semiconductors of III-V type. This photoelectrode has a good efficiency but is costly and is sensitive to photocorrosion, that is the corrosion generated by the electrolytes in which the photoelectrode is immersed.

US 7,122,873 describes a hybrid photoelectrode which has a

photoactive oxide layer for protecting the underlying layers from photocorrosion.

Another problem present in the hybrid photoelectrodes is related to the interface between two adjacent layers: in order to not decrease the overall efficiency of the photoelectrode, such interface must permit the transport of electrons and holes between the two adjacent layers, and at the same time prevent the recombination of the same.

Such problem is resolved in US 7,122,873 by interposing a layer of conductive oxide between the layer of photoactive oxide and the semiconductor layer.

Nevertheless, the electron-hole pairs can recombine with each other within the intermediate conductive layer. When such recombination occurs heat is produced, decreasing the efficiency of the photoelectrode; the recombinaton is also favoured by the presence of the electronically active defects present at the interface between the intermediate layer and the semiconductor layer.

In light of the state of the art described above, the object of the present invention to make an electrochemical photoelectrode having a greater conversion efficiency than that known in the art up to now, resolving at least in part the abovementioned problems.

In accordance with the present invention, such object is attained by means of a photoelectrode in accordance with claim 1.

Thanks to the present invention, it is possible to make a hybrid electrochemical photoelectrode which combines a good resistance to photocorrosion with a greater conversion efficiency than known in the art.

The characteristics and advantages of the present invention will be clear from the following detailed description of a practical embodiment, given as a non-limiting example with reference to the drawing set, in which:

-Figure 1 shows an electrochemical photoelectrode in accordance with a first preferred embodiment of the present invention;

-Figure 2 shows an electrochemical photoelectrode in accordance with a second preferred embodiment of the present invention;

-Figure 3 shows a schematic view, not in scale, of the energy levels encountered inside the device according to a preferred embodiment of the present invention.

With reference to the attached drawings, a semiconductor photoelectrode, indicated with 1 in its entirety, comprises an upper layer 2, an interface layer 3, at least in part adjacent to the upper layer 2 and a semiconductor layer 4, at least in part adjacent to the interface layer 3.

The interface layer 3 is at least in part interposed between the upper layer 2 and the semiconductor layer 4, so that there is at least one path, for an electron created in the upper layer 2, for moving into the semiconductor layer 4 passing through the interface layer 3.

Preferably, any possible path for an electron generated in the upper layer 2 crosses the interface layer 3 before arriving in the semiconductor layer 4.

Similarly, for a hole, the opposite holds true: the interface layer 3 is such that it can, or advantageously must, be crossed by a hole which moves from the semiconductor 4 to the upper layer 2.

According to the invention, the interface layer 3 is an insulator, has a thickness such that it can be crossed by the electrons and by the holes due to tunnelling, and is arranged in a manner such that it passivates (that is, it is capable of passivating) the semiconductor layer 4 in the zones where they are in contact.

The semiconductor layer 4 can comprise one or more zones of p-i-n type, each comprising an n-type semiconductor 41, an intrinsic semiconductor 42 and a p-type semiconductor 43, so to

separate the electric charges which are found at its interior.

The semiconductor layer 4 can be made with monocrystalline silicon; alternatively, it is possible to use amorphous silicon, amorphous germanium, amorphous silicon-germanium, monocrystalline silicon, monocrystalline germanium, monocrystalline silicon-germanium, copper-indium-gallium diselenide (CIGS) or the like, or a combination of these.

Advantageously, it has a band gap in the range of 1 eV - 2 eV.

The interface layer 3 must be capable of passivating the semiconductor layer 4 in order to prevent the recombination of the photoexcited electrons with the photoexcited holes, so to raise the conversion efficiency of the photons. This means that the interface layer 4 contains a low density of electronically active defects (whether bulk or interface).

The density of electronically active defects can be defined and measured by means of the method described by A. J. Sabbah and D. M. Riffe in JOURNAL OF APPLIED PHYSICS, VOLUME 88, NUMBER 11, 1 DECEMBER 2000.

Measured according to such method, with "low density" it is intended a recombination velocity of less than 1,000 cm/s, preferably less than 100 cm/s.

The interface layer 3 can be advantageously made with an insulating material, for example having a band gap greater than 3 eV. Clearly, since the precise value of the band gap of a thin layer can be affected by factors outside the material itself, reference is made to the band gap which the base material would have without outside influences (bulk material).

In order to allow the electrons and holes to easily pass from the upper layer 2 to the semiconductor layer 4 due to tunnelling, the thickness of the intermediate layer can be less than 2 nm, preferably less than 1 nm, still more preferably less than 0.5 nm, for example it can be a monatomic layer.

The interface layer 3 can be amorphous or crystalline; for

example, there can be a single crystalline layer of $SrTiO_3$ deposited on Si (100) using an interface layer consisting of precisely one monolayer of oxygen and ½ monolayer of Sr.

Alternatively, the interface layer 3 can be a thermal SiO_2 layer.

The upper layer 2 is composed of a photoactive material, advantageously a photoactive oxide, i.e. such to permit the creation of an electron-hole pair when excited by high energy electromagnetic radiation; the band gap of the upper layer 2 is preferably greater than 1.7 eV, for example about 3.4 eV ($SrTiO_3$) and advantageously it is less than 5 eV.

Advantageously, the material of the upper layer 2 is selected such that there is a relatively small energy difference (preferably less than 0.1 eV) between its conduction band and the conduction band of the semiconductor layer 4.

Such small energy difference facilitates the transport of the electrons in the conduction band from the upper layer 2 to the semiconductor layer 4, through the interface layer 3, such that this is substantially without energy losses due to the energy level difference.

The upper layer 2 can be a doped oxide or an oxide with a controlled oxygen vacancy content, so to increase its absorption efficiency, and can be epitaxial, polycrystalline or amorphous; for example, it can be $SrTiO_3$, tungsten trioxide (WO_3), iron oxide (Fe_2O_3), titanium dioxide (TiO_2), or the like, or a combination of these.

The three upper 2, interface 3 and semiconductor 4 layers are advantageously made atop a substrate 5, which is situated on the side of the semiconductor 4, as is visible in figures 1 and 2.

The substrate 5 can be a semiconductor material and comprise for example a single silicon crystal, it can be metal and comprise for example steel, titanium or nickel; or it can be insulating, for example made of glass or plastic.

Optionally, it is possible to arrange a reflecting layer 6 between the substrate 5 and the semiconductor layer 4, so to reflect the electromagnetic radiation into the active part of the photoelectrode 1, or into the semiconductor layer 4 and/or upper layer 2, increasing its conversion efficiency.

The reflecting layer 6 can be made of any material which has a refraction index less than that of the semiconductor 4, for example zinc oxide (ZnO) or the like.

With reference to figures 1 and 2, the photoelectrode 1 according to the present invention is capable of producing one or more gases 71, 72 when at least partially immersed in a suitable material 7, comprising the constituents of the gas or gases 71, 72, and stimulated by electromagnetic radiation 81 emitted by a suitable source 8.

Advantageously, the material 7 can comprise an aqueous electrolyte, such as for example solutions of potassium hydroxide, sodium hydroxide, sulphuric acid, phosphoric acid (for example 1-normal), hydrochloric acid, or it can be water.

In a preferred embodiment, the gases 71, 72 are oxygen and hydrogen and the light source 8 is the sun.

The photoelectrode 1 of the present invention is therefore suitable for producing hydrogen gas and oxygen gas when immersed in aqueous solution and stimulated by solar radiation.

With reference to figure 3, the functioning of the photoelectrode 1 according to the present invention is schematised with the energy levels of the electrons and holes in the conduction bands illustrated on the y-axis, and the spatial coordinate of the path the electrons (and holes) follow inside the photoelectrode 1 illustrated on the x-axis.

With 82, 83 and 84, the energy levels are indicated which the electrons (or the holes) can have when excited by the radiation 81.

The amplitude of the height difference is representative of the energy which must be provided for creating the electron-hole

pair inside a given material, and thus is representative of the absorbable wavelength.

In such diagram, the electrons, represented with a (-), tend by nature to move downwards, while the holes, represented with (+), tend by nature to move upwards.

Starting from the upper layer 2, this is capable of absorbing radiation 81 capable of providing sufficient energy for creating the electron-hole pair separated by the energy gap 82.

The hole can immediately act on the material 7, oxidising it in order to create the gas 72, in the specific case oxygen; the electron, on the other hand, migrates through the interface layer 3 and through the semiconductor layer 4 in order to reduce the material 7 so to create the gas 71, in the specific case hydrogen.

The leftward movement of the electron, in figure 3, is favoured by the energy levels of the layers p 43, i 42 and n 41 of the semiconductor layer 4.

The arrow 84 schematises the absorption of the semiconductor layer 4, which occurs on a wavelength different from those absorbed in the upper layer 2.

Due to the properties of the layers n 41, i 42 and p 43 of the semiconductor layer 4, the holes can migrate (towards the right in figure 3) through the interface layer 3 until they occupy layers in the gap of the upper layer 2, where, stimulated by a further absorption, represented by the gap 83, they can reach the valence band.

Analogous to the p-i-n junction of the semiconductor layer 4, in the upper layer 2 the liquid in which the photoelectrode is immersed creates a spatial variation of the energy level of the bands, which has the same effect of the p-i-n junction. This phenomenon, known as “band-bending”, permits the separation of the charges inside the upper layer 2.

Once they have entered into the valence band of the upper

layer 2, the holes can feed the chemical reduction reaction for the production of the gas 72.

The scheme of figure 3 well describes the embodiment of figure 1: the spatial coordinate representative of the movement of the electrons (or holes), arranged on the y-axis, is arranged in the direction of the width (from left to right) of the embodiment of figure 1.

In the embodiment of figure 1, the photoelectrode 1 comprises, from left to right:

-a catalyst 51 for the production of the gas 71,

-a conductor substrate 5 which permits the transfer of the electrons from the semiconductor layer 4 to the material 7,

-a reflecting layer 6 for reflecting the useful radiation (which can be absorbed in the gaps 82, 83 or 84) inside the active portion of the photoelectrode 1,

-a semiconductor layer 4 comprising, in order, an n-layer 41, an i-layer 42 and a p-layer 43,

-the interface layer 3,

-the upper layer 2, which covers the entire p-layer 43 of the semiconductor layer 4,

-a catalyst 21 for the production of the gas 72.

Advantageously, a protective layer 9 can be used for protecting the sides of the photoelectrode 1 from external aggression, due for example to the material 7.

This embodiment allows that which is deemed to be the maximum conversion efficiency of the photoelectrode, but it is also possible to omit one or more of these elements, in alternative embodiments.

The catalysts can be made with materials and methods known in the art; in a preferred embodiment they are a coating of platinum, of mixed metals such as cobalt-molybdenum or the like.

The upper layer 2 can be monocrystalline $SrTiO_3$, obtained via epitaxial growth atop the face (100) of a monocrystalline silicon wafer which comprises a p-i-n junction.

According to the preferred embodiment of figure 2, the substrate 5 is an insulating material; in this case, it is not possible to have electron movement (or hole movement) inside. The p- and n- doped areas 43, 41 of the semiconductor layer 4 are thus side by side, while the upper layer 2 substantially covers the p-doped regions 41 and leaves the n-doped regions 43 substantially free. Generally speaking, the photoactive layer 2 covers at least the p-doped regions 43, extending as much as possible over part of the n-doped regions 41.

The production methods of doped semiconductors for forming p-i-n junctions arranged in layers, as in figure 1, or arranged side by side, as in figure 2, are known in the art and will thus not be further described.

The upper layer 2 can be made by means of methods known in the art, for example MBE, CVD or sputtering.

Advantageously, during the growth of the upper layer 2, every time that the partial pressure of oxygen exceeds the value of 5×10^{-7} Torr in order to ensure a complete oxidation of the oxygen constituents, the deposition temperature is maintained lower than 350°C.

In this manner, one prevents the formation, between the semiconductor layer 4 and the upper layer 2, of an interface layer 3 which has a thickness greater than 2 nm. Preferably, the deposition pressure and temperature are selected so that an interface layer is formed with thickness less than 0.5 nm.

As is visible in figure 2, in such embodiment the spatial coordinate representative of the movement of the electrons, arranged on the x-axis in figure 3, thus corresponds with a curved line, such as for example that indicated with P in figure 2.

Of course, a man skilled in the art, in order to satisfy contingent and specific needs, can make numerous modifications and variations to the above-described configurations, all moreover contained in the protective scope of the invention as

defined by the following claims.

CLAIMS

1. A semiconductor photoelectrode (1) comprising:

- an upper layer (2), made of a photoactive material;
- an interface layer (3), at least in part adjacent to said upper layer (2);
- a semiconductor layer (4), at least in part adjacent to said interface layer (3);

wherein said interface layer (3) is at least in part interposed between said upper layer (2) and said semiconductor layer (4), so that there is at least one path, for an electron created in said upper layer (2), for moving from said upper layer (2) to said semiconductor layer (4) passing through said interface layer (3);

characterised in that

said interface layer (3 has a thickness such that it can be crossed, due to tunnelling, by the electrons which move from said upper layer (2) to said semiconductor layer (4) passing through said interface layer (3).

2. Photoelectrode (1) according to the preceding claim, wherein said interface layer (3) has a thickness of less than 2 nm.

3. Photoelectrode (1) according to claim 1, wherein said interface layer (3) passivates said semiconductor layer (2) in the zones where they are in contact.

4. Photoelectrode (1) according to any one of the preceding claims, wherein said interface layer (3) passivates said semiconductor layer in a manner such that the surface recombination velocity (SRV) is less than 1,000 cm/s.

5. Photoelectrode (1) according to any one of the preceding claims, wherein said upper layer (2) is an oxide.

6. Photoelectrode (1) according to the preceding claim, wherein said upper layer (2) is composed of a material selected from the group comprising $SrTiO_3$, WO_3, Fe_2O_3, TiO_2 or a combination of these.

7. Photoelectrode (1) according to any one of the preceding

claims, wherein said interface layer (3) is an insulator.

8. Photoelectrode (1) according to any one of the preceding claims, wherein said interface layer (3) is crystalline.

9. Photoelectrode (1) according to any one of the claims 1 to 7, wherein said interface layer (3) is amorphous.

10. Photoelectrode (1) according to any one of the preceding claims, wherein said interface layer (3) is a thermal SiO_2 layer.

11. Photoelectrode (1) according to any one of the preceding claims, wherein there is an energy difference between the conduction band of said interface layer (3) and the conduction band of the semiconductor layer (4) of less than 0.1 eV.

12. Photoelectrode (1) according to any one of the preceding claims, wherein said semiconductor layer (4) comprises a p-i-n junction where the layer n (43) is adjacent to said interface layer (3).

13. Photoelectrode (1) according to any one of the preceding claims, comprising a substrate (5) substantially adjacent to said semiconductor layer (4).

14. Photoelectrode (1) according to claim 13, wherein said substrate (5) is insulating and said semiconductor layer (4) comprises p-i-n junctions arranged side by side.

15. Photoelectrode (1) according to any one of the preceding claims, wherein said upper layer (2) is made with a material having a band gap in the range of 1.7 eV - 5 eV.

16. Photoelectrode (1) according to claim 13, wherein said substrate (5) is conductive and said upper layer (2), interface layer (3) and semiconductor layer (4) are substantially parallel and opposite each other.

17. Photoelectrode (1) according to any one of the preceding claims, comprising a reflecting layer (6) adjacent to said semiconductor layer (4).

18. Photoelectrode (1) according to any one of the preceding claims, comprising a catalyst layer (51, 71) for the chemical reactions for which said photoelectrode (1) is conceived.

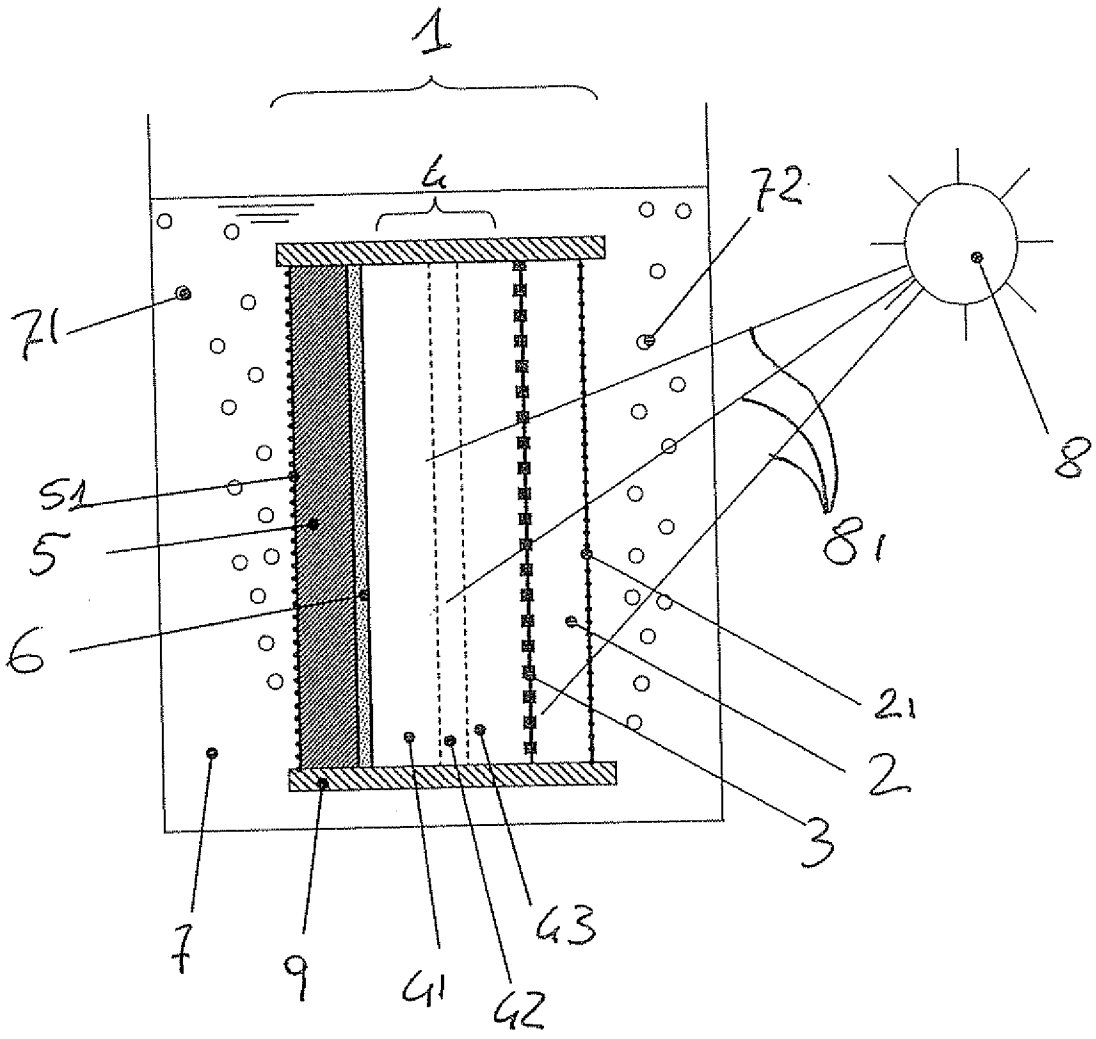


Fig. 1

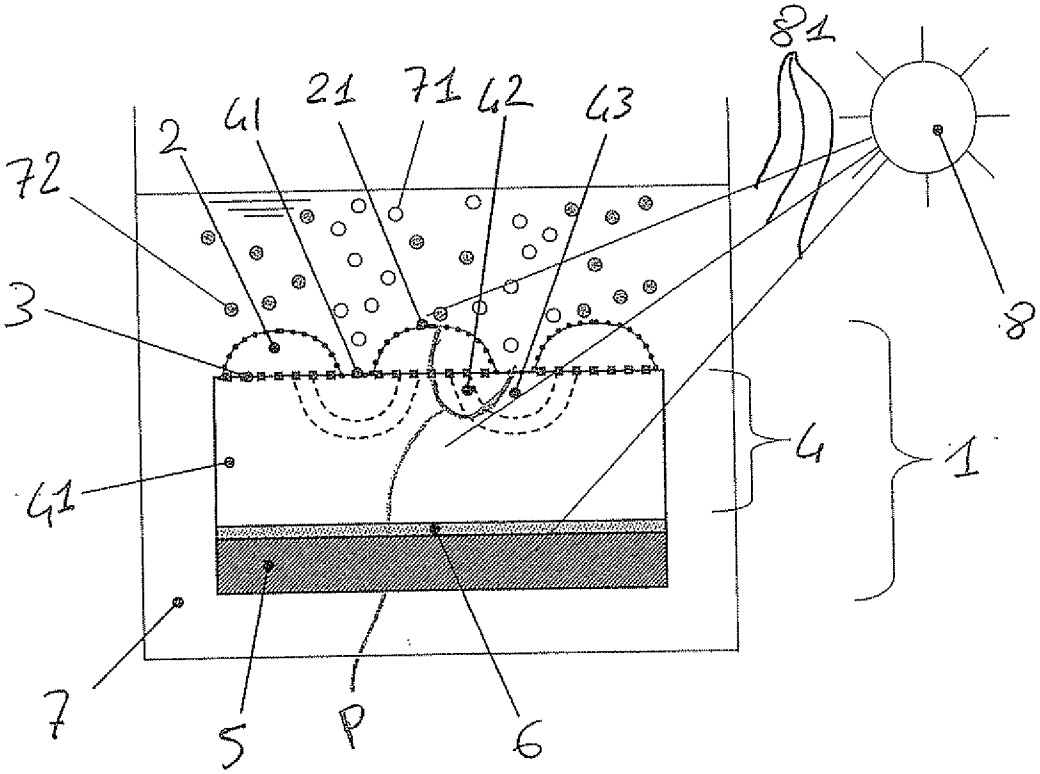


Fig. 2

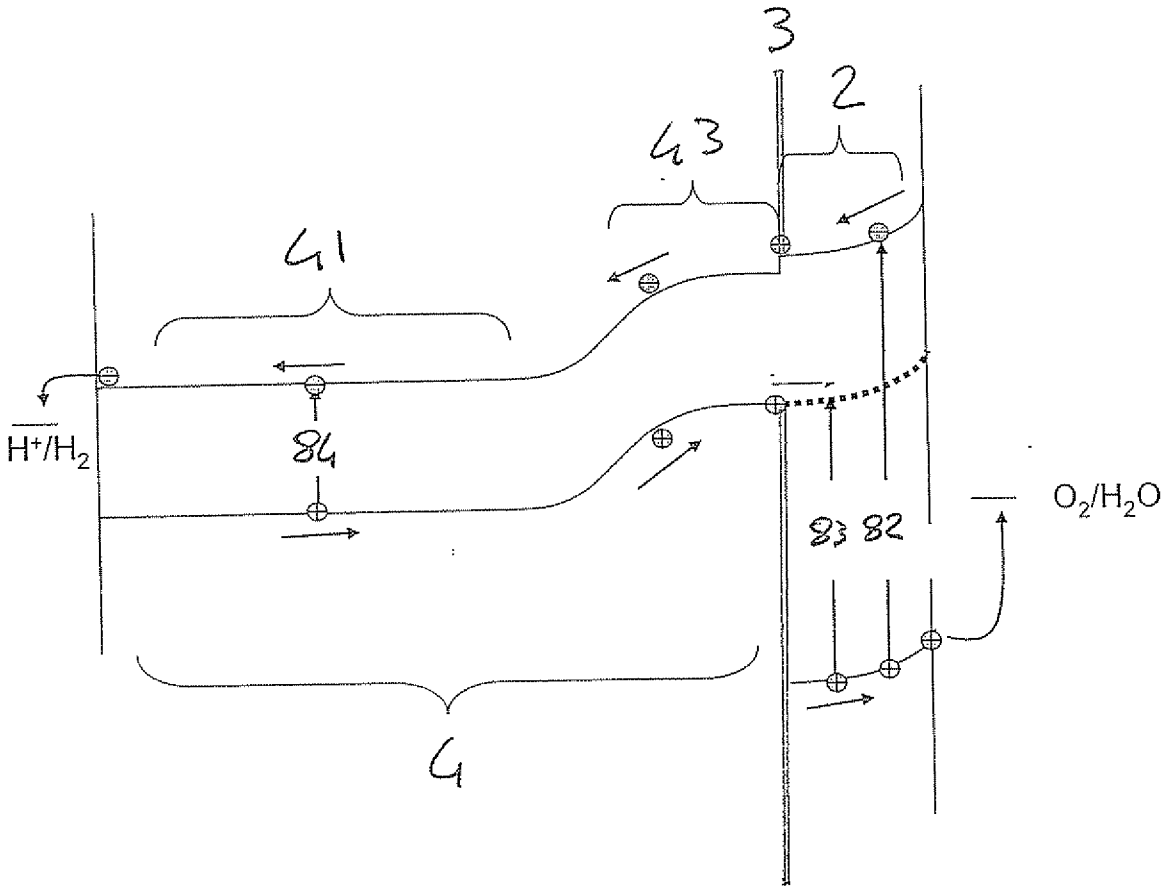


Fig. 3