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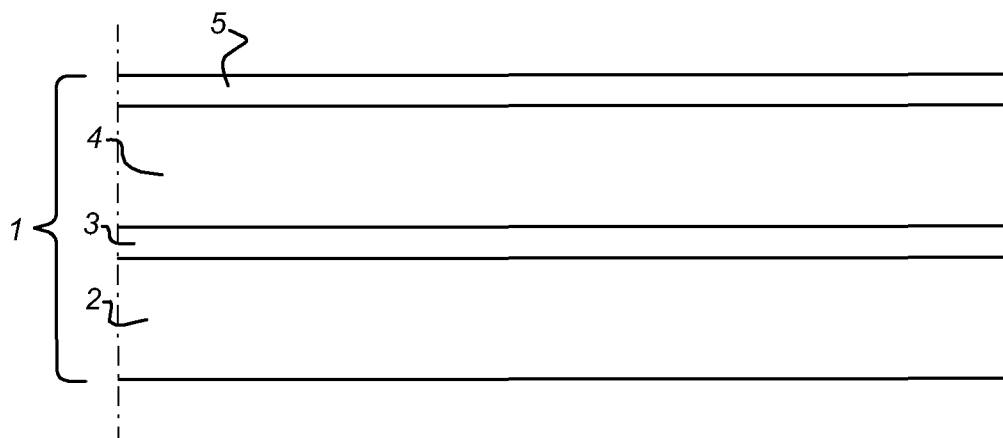
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(54) Title: OPTICAL SWITCHING DEVICE



(57) Abstract: A hydrogen permeable optical reflective layer (4) of a transition metal is deposited on transition metal (hydride) layer (3) which can switch from a black absorbing state. A hydrogen permeable catalytic layer (5) of a transition metal is deposited on top of the reflective layer (4). Ti and/or Pd may be used as transition metal(s) in all of the three layers (3,4,5). Co-sputtering may be used to deposit a transition metal (hydride) switching layer (3) with a maximum thickness of 100 nm on a substrate (2) which can be of any material. The thickness of the optical reflective layer (4), which is larger than the thickness of the switching layer (3), is more than 10 nm (but preferably 50-200 nm) so that there is (no or) little transmission. The thickness of the catalytic layer (5) is about 10 nm. If a detector (11) is included one can produce a hydrogen sensor. Alternatively, one can produce a temperature controlled solar energy converter (17) by including a fluid heater (18).

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

Optical switching device.

The present invention relates to an optical switching device comprising a substrate, an active metal layer provided on said substrate having different optical properties at loading/unloading with/of hydrogen and a catalytic layer. Such a device is generally known in the art. As active metal a magnesium transition metal alloy is for example used. It has been found that a magnesium nickel layer being provided on a substrate and on top of which a catalyst such as palladium is provided will turn into a magnesium nickel hydride layer near the substrate when hydrogen is added to such layer. This means that although hydrogen enters the device through the catalyst the hydride phase nucleates first at the magnesium nickel layer/substrate interface. This leads to a self-organized layering of the sample. With increasing hydrogen absorption the hydride layer grows until the whole magnesium nickel layer is converted to a hydride. Such layers are also known as VARIable REFlection Metal hydrides (VAREM) or metal-hydride switchable mirrors.

Depending on the conversion such a layer can have properties ranging from reflective through black to transparent. The transparent and reflective modes are relatively stable and easy to obtain and maintain. However a stable black situation in which the light entering through the substrate is absorbed, is difficult to maintain. It depends sensitively on external parameters such as temperature and H<sub>2</sub> gas pressure.

The different physical appearances are preferably obtained by loading with hydrogen or unloading hydrogen for example by using oxygen. Electrochemical hydrogenation/dehydrogenation can also be used. The hydrogen concentration in which the black condition is obtained is very critical.

US 2002/101413 discloses a light switching device wherein a switching film is provided with a catalyst Pd-layer on which a hydrogen ion conducting electrolyte layer is provided. On this hydrogen ion conducting electrolyte layer a hydrogen storage layer is present. With this device one actively controls the amount of hydrogen and thereby the optical state of the active layer.

The invention aims to provide an optical switching device in which the black condition is both easily obtained and on the other hand can easily be maintained.

According to the invention this is realized in that, between said active metal layer and said catalytic layer an auxiliary layer comprising a transition metal layer is

provided having a thickness larger than the thickness of said active metal layer and being hydrogen permeable.

According to the invention there is no longer a “self-organized” double layer needed to provide for the large change in optical behavior. The self organized double layer is according to the invention replaced by an auxiliary layer which has been  
5 separately provided and comprises a transition metal layer. In contrast to the prior art an auxiliary layer is provided between the metal layer and the catalytic layer.

It has been found that by using an artificially provided auxiliary layer a stable black condition is obtained of the magnesium transition metal (hydride) layer. It has  
10 also been found that after unloading the hydrogen and reloading with hydrogen reproducible results are obtained which means that switching can be obtained in a reproducible way making the optical switching device suitable for all kinds of applications.

Furthermore it has been found that a better contrast can be obtained and oxidation  
15 protection is further improved.

The thickness of the transition metal layer should be such that there is no or little transmission.

The active metal layer can comprise any metal which has changing optical properties at loading or unloading with hydrogen. As example magnesium or  
20 magnesium based transition metals are mentioned. Also combination of several elemental metals can be used or metal hydrides such as yttrium hydride being in the metallic phase. Further possibilities for the active layer can be rare earths including yttrium, possibly in combination with a transition metal, magnesium and so on. Another preferred option is the use of  $Mg_2Ni$  as active layer.

25 According to a preferred embodiment of the invention the active layer has a thickness of 100 nm at maximum. The transition metal layer or auxiliary layer has a thickness starting from 10 nm and is preferably not more than 1  $\mu m$ .

The auxiliary layer can comprise layers being positioned on top of each other and comprising a different transition metal for example titanium, nickel and/or niobium. It  
30 is also possible that different layers are stacked on each other having a different structure, as long as the layer stack allows for hydrogen diffusion and is optically reflective.

The substrate according to the invention can comprise any material such as glass.

The transition metal of the transition metal layer can comprise any transition metal known from the periodic system and in more particular titanium and/or palladium.

The same applies to the transition metal in the magnesium transition metal active  
5 layer which preferably comprises nickel.

According to an advantageous embodiment the optical switching device is passive. This means that switching is only obtained by gas pressure and not to the use of electrical tension. However, an embodiment being electrolytically switched is within the range of the subject application.

10 The optical switching device according to the invention can be prepared by deposition of the several layers mentioned above on a substrate. This deposition can comprise sputtering such as co-sputtering of the several metals to obtain for example the magnesium transition metal layer.

As indicated above there are many applications for the optical switching device  
15 according to the invention. The most simple one is the use as a mirror which can switch from the black absorbing phase to the reflective phase.

Because optical switching is obtained depending on the presence of hydrogen according to a further embodiment of the invention it is possible to provide a hydrogen sensor having an optical switch as described above. Through a sensor the optical  
20 properties of an optical switching device according to the invention can be monitored. It is possible that there is a distance between the optical switching device and the optical sensor which can be bridged by fibre optics. Furthermore it is possible to monitor a large number of optical switching devices with a single optical sensor.

The optical switching device can be embodied to have the optical properties  
25 reversible or non-reversible. An example for the last possibility is the use of a tag which shows exposure of an article or person in an environment in which hydrogen might be present. Such a tag can be disposable.

The invention can also be used in an energy conversion assembly comprising a photovoltaic element and a water heater. Such an assembly can for example be  
30 arranged on a roof wherein the incident light first hits the photovoltaic element. Under some conditions it might be desirable that radiation is not transferred to the water heater whilst in other conditions it is desirable to heat the water. These different

conditions can be switched by placing an optical switching device according to the invention between such photovoltaic element and a water heater.

The invention will be further elucidated referring to embodiments shown in the drawing wherein:

5 Fig. 1 schematically shows the layer structure of an optical switching device according to the invention;

Fig. 2 schematically shows the application of the optical switching device as a hydrogen sensor; and

Fig. 3 shows the use in an energy conversion assembly.

10 In fig. 1 an example for an optical switching device according to the invention is generally referred to by 1. A substrate 2 is present which can be any material. However, preferably glass is used as is usual in optical devices. On top of the glass a 30 nm magnesium transition metal layer as active layer is provided such as an  $Mg_2Ni$  layer. On top of this active layer 3 an auxiliary layer 4 according to the invention is arranged.  
15 This is a transition metal layer such as a titanium layer or a palladium layer. The thickness thereof is from 10 nm and more preferably between 50 and 200 nm. On top of the auxiliary layer a catalyst layer 5 is provided being for example a palladium layer having a thickness of about 10 nm.

20 If hydrogen is added to such an optical switching device 1 the  $Mg_2Ni$  layer will convert to  $Mg_2NiH_4$ . The optical properties of this material are completely different from  $Mg_2Ni$ .

According to the invention an artificial double layer comprising the layers 3 and 4 has been synthesized.  $Mg_2NiH_4$  is transparent while hydrogenated titanium which is for example used in layer 4 remains reflective.

25 During tests it revealed that the reflection observed through the layer structure in an energy range 1.25 – 3 eV goes from around 60% before hydrogenation to about 5% at 1.9 – 2 eV in the totally hydrogenated layer 3. This is a ratio of 12 in reflection. At room temperature such hydrogenation, when a 5%  $H_2$  in Ar is used is effected in typical 10 seconds depending on the thickness of layer 4. A sensitivity of 0.3%  $H_2$  has  
30 been observed.

In fig. 2 the use of the optical switching device according to the invention in a hydrogen sensor is shown. The optical switching device according to the invention is indicated with 6 which is connected through fibre optic 7, 9 (with the use of a

bifurcator 8) to a detector 11. 10 is a light source (for example a lamp or a laser) to provide light to the switchable mirror 6. If only small quantities of hydrogen are present in the room in which the optical switching device is present immediately a remarkable change in reflective properties of the optical switching device occurs which is easily  
5 detected by detector 11. Detector 11 can be connected to a number of fibre optics being connected to optical switching devices in the same room or in different areas.

In fig. 3 a further application of the invention is shown. On a schematically shown roof 15 an energy conversion assembly 17 is provided. This comprises a photovoltaic element 13, an optical switch 14 according to the invention and a fluid  
10 heater 18 such as a water heater having heating tubes 19. Depending on the conditions it is desirable that incident light as indicated by arrow 16 will or will not reach heater 18. By controlling optical switching device 14 as indicated above this can be prevented. If the optical switching is in the black condition heat will be absorbed and transferred to  
15 heater 18. If it is in the reflective mode the heat will not be absorbed and reflected back through to the photovoltaic element 13. Even without the photovoltaic device, the invention can be used solely to control the temperature of the water heater.

In the above some applications of the photovoltaic switching device according to the invention have been discussed. However it should be understood that further applications are possible both on Earth and in space. As example the use on the outer  
20 surface of a satellite is mentioned.

## Claims

1. Optical switching device (1) comprising a substrate (2), an active metal layer (3) provided on said substrate having different optical properties at loading/unloading with/of hydrogen and a catalytic layer (5), characterized in that, between said active metal layer and said catalytic layer an auxiliary layer (4) comprising a transition metal layer is provided having a thickness larger than the thickness of said active metal layer and being hydrogen permeable.
2. Optical switching device according to claim 1, wherein said auxiliary metal layer is a transition metal based layer.
3. Optical switching device according to claim 1, wherein said active metal layer is a rare-earth based layer.
4. Optical switching device according to one of the preceding claims, wherein said active metal layer is a Mg based layer.
5. Optical switching device according to one of the preceding claims comprising a black switching condition.
6. Optical switching device according to one of the preceding claims, wherein said active metal layer has a thickness of 100 nm at maximum.
7. Optical switching device according to one of the preceding claims, wherein said substrate comprises glass.
8. Optical switching device according to one of the preceding claims, wherein the metal of said catalytic metal layer comprises titanium and/or palladium and/or silver.
9. Optical switching device according to one of the preceding claims, wherein said transition metal layer has a thickness of 10 nm - 2  $\mu$ m.

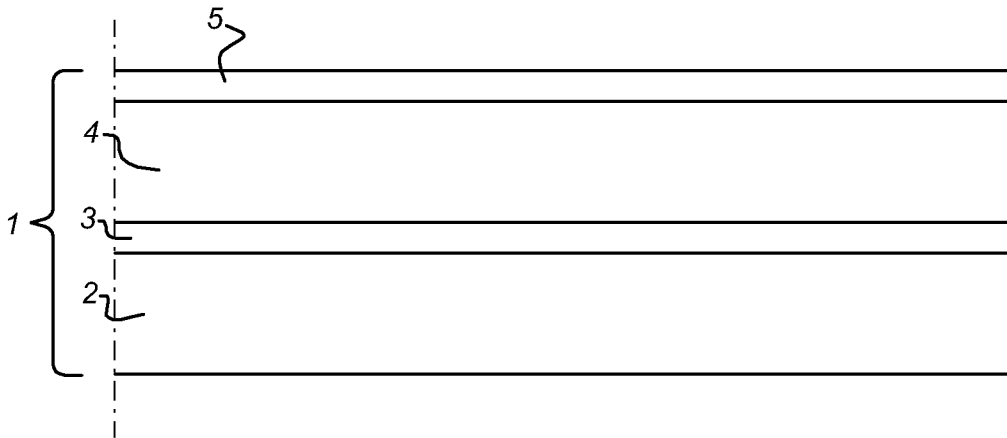


10. Optical switching device according to one of the preceding claims, wherein the transition metal of the active transition metal layer comprises nickel, titanium, palladium.
- 5           11. Method for preparing an optical switching device comprising the provision of a substrate and the subsequent deposition of an active metal layer having a thickness smaller than 100 nm, an auxiliary layer comprising a transition metal layer and having a thickness larger than 10 nm and a catalyst layer.
- 10           12. Method according to claim 11, wherein at least one of said deposition steps comprises (co) sputtering.
- 15           13. Mirror comprising an optical switching device with a substrate (2), an active metal layer (3) provided on said substrate having different optical properties at loading/unloading with/of hydrogen and a catalytic layer (5), characterized in that, between said active metal layer and said catalytic layer an auxiliary layer (4) comprising a transition metal layer is provided having a thickness larger than the thickness of said active metal layer and being hydrogen permeable.
- 20           14. Hydrogen sensor comprising an optical switching device with a substrate (2), an active metal layer (3) provided on said substrate having different optical properties at loading/unloading with/of hydrogen and a catalytic layer (5), characterized in that, between said active metal layer and said catalytic layer an auxiliary layer (4) comprising a transition metal layer is provided having a thickness larger than the  
25 thickness of said active metal layer and being hydrogen permeable.
15. Hydrogen sensor according to claim 13 or 14, comprising an optical sensor (11) to monitor the state of said optical switching device.
- 30           16. Hydrogen sensor according to claim 15, wherein a fibre optic (7, 9) is coupled between said optical switching device (6) and said optical sensor (11).

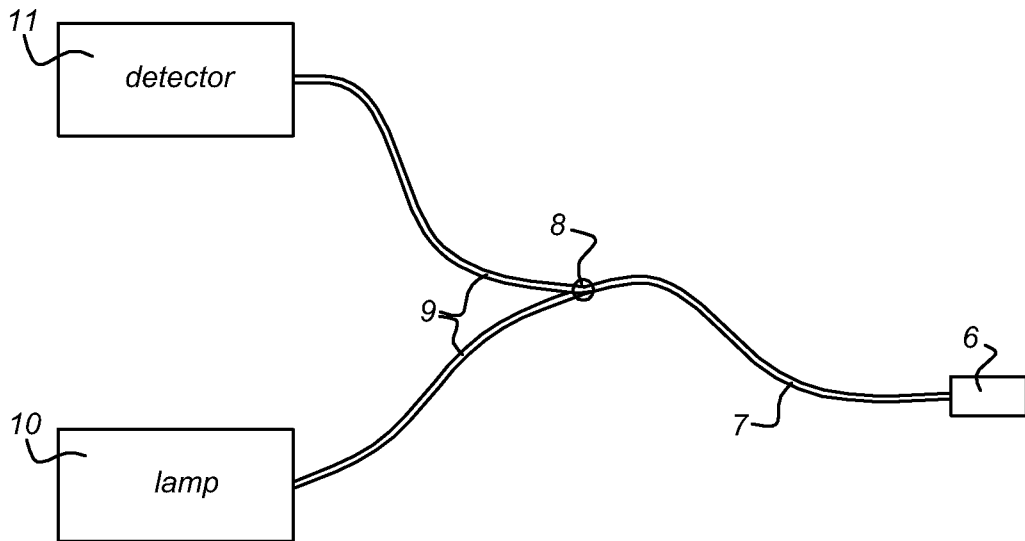
17. Energy conversion assembly comprising a fluid heater (13) and in the direction of incident light (16) in front of said fluid heater an optical switching device (14) with a substrate (2), an active metal layer (3) provided on said substrate having different optical properties at loading/unloading with/of hydrogen and a catalytic layer (5), characterized in that, between said active metal layer and said catalytic layer an auxiliary layer (4) comprising a transition metal layer is provided having a thickness larger than the thickness of said active metal layer and being hydrogen permeable.

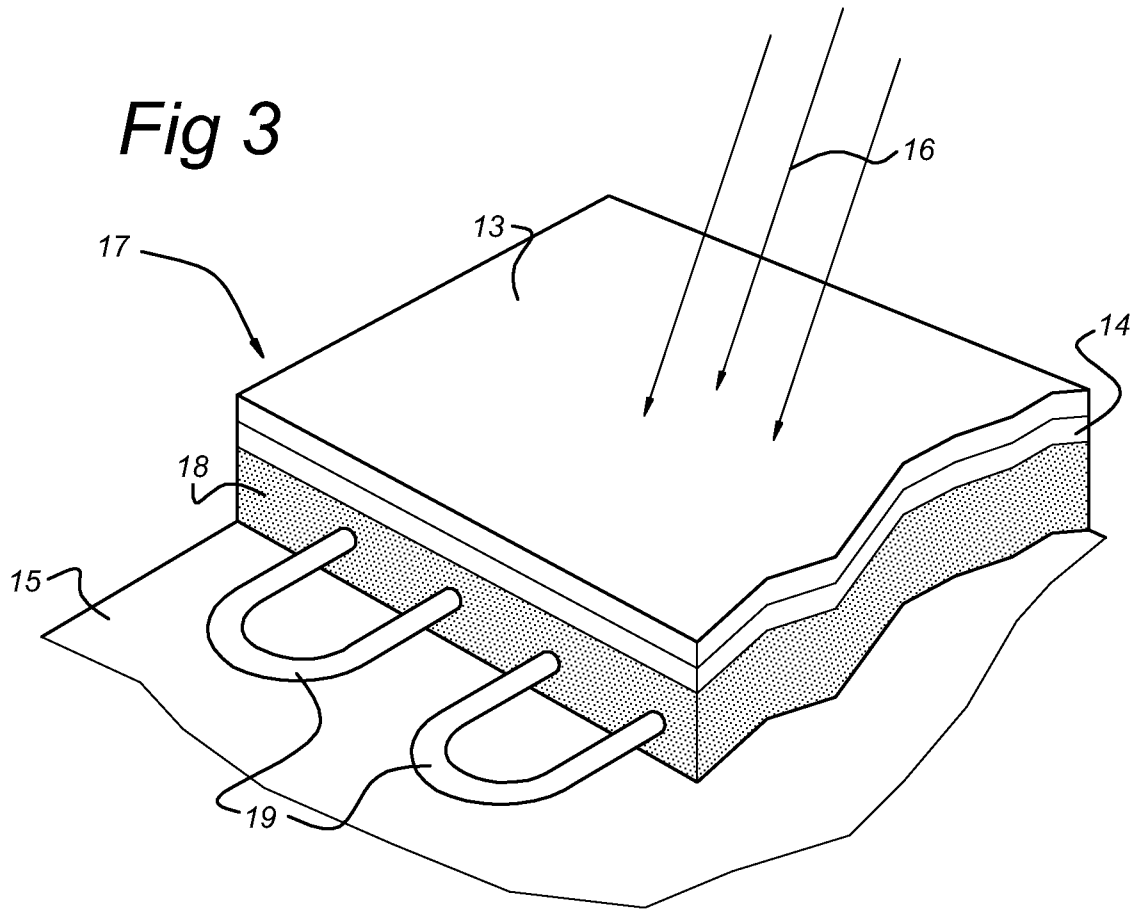
18. Energy conversion assembly according to claim 17 comprising a photovoltaic element (13) wherein in the position of use in the direction of incident light (16) the fluid heater (13) is behind said photovoltaic element, wherein said switching device (14) is arranged between said photovoltaic element and said fluid heater.

*Fig 1*



*Fig 2*





## INTERNATIONAL SEARCH REPORT

International application No  
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INV. G02F1/19 G02F1/15

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/101413 A1 (JOHNSON MARK THOMAS [NL] ET AL) 1 August 2002 (2002-08-01) cited in the application paragraphs [0001], [0002], [0016], [0018]; figure 1B -----	1-18
Y	US 6 006 582 A (BHANDARI GAUTAM [US] ET AL) 28 December 1999 (1999-12-28) column 12, line 22 - line 24; figure 3 -----	1-16
Y	US 2005/173716 A1 (VAN HELDEN WILHELMUS G J [NL] ET AL) 11 August 2005 (2005-08-11) page 2, line 28 - line 31; figure 1 page 3, line 31 - page 4, line 5 ----- -/--	1-14,17,18

 Further documents are listed in the continuation of Box C. See patent family annex.

## \* Special categories of cited documents :

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## INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YOSHIMURA K ET AL: "Optical switching of Mg-rich Mg&ndash" APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US, vol. 81, no. 25, 16 December 2002 (2002-12-16), pages 4709-4711, XP012032792 ISSN: 0003-6951 the whole document -----	1-18

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Information on patent family members

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