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(54) PD/V2O5 DEVICE FOR COLORIMETRIC H2 DETECTION

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(57) **ABSTRACT**

A sensor structure for chemochromic optical detection of hydrogen gas over a wide response range, that exhibits stability during repeated coloring/bleaching cycles upon exposure and removal of hydrogen gas, comprising; a glass substrate (**20**): a vanadium oxide layer (**21**) coated on the glass substrate; and a palladium layer (**22**) coated on the vanadium oxide layer.

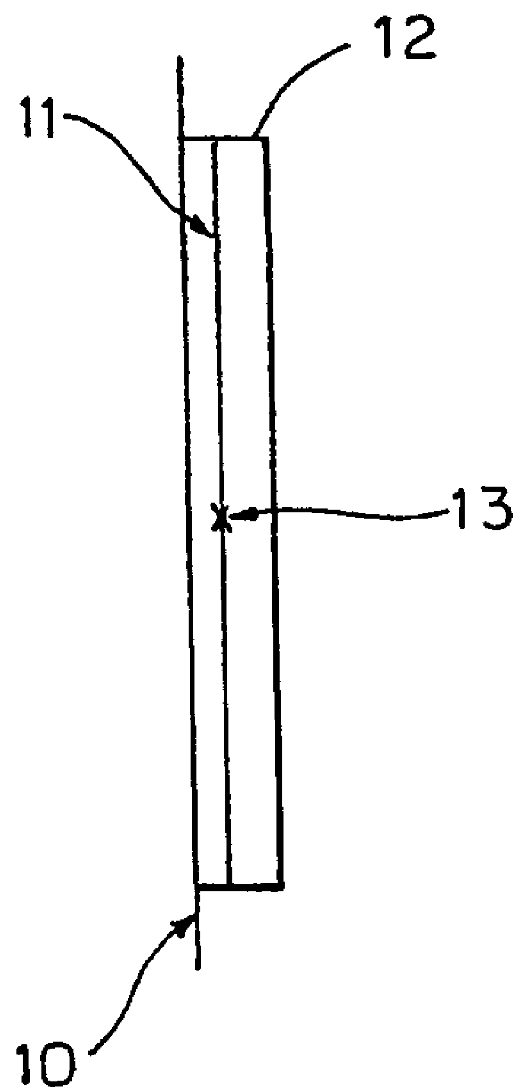


FIG. 1A

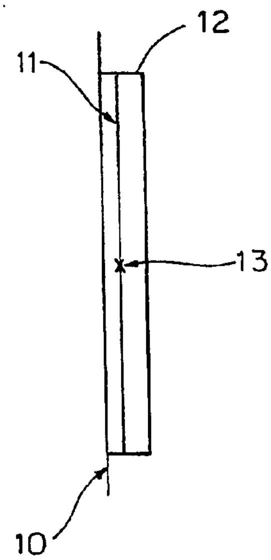


FIG. 1B

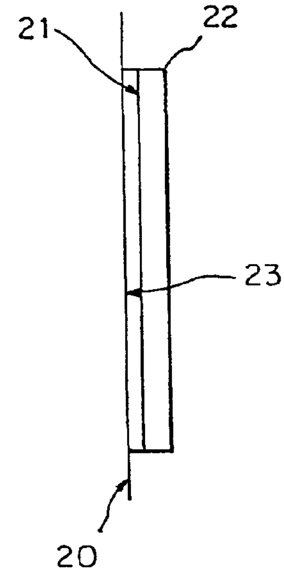


FIG. 3

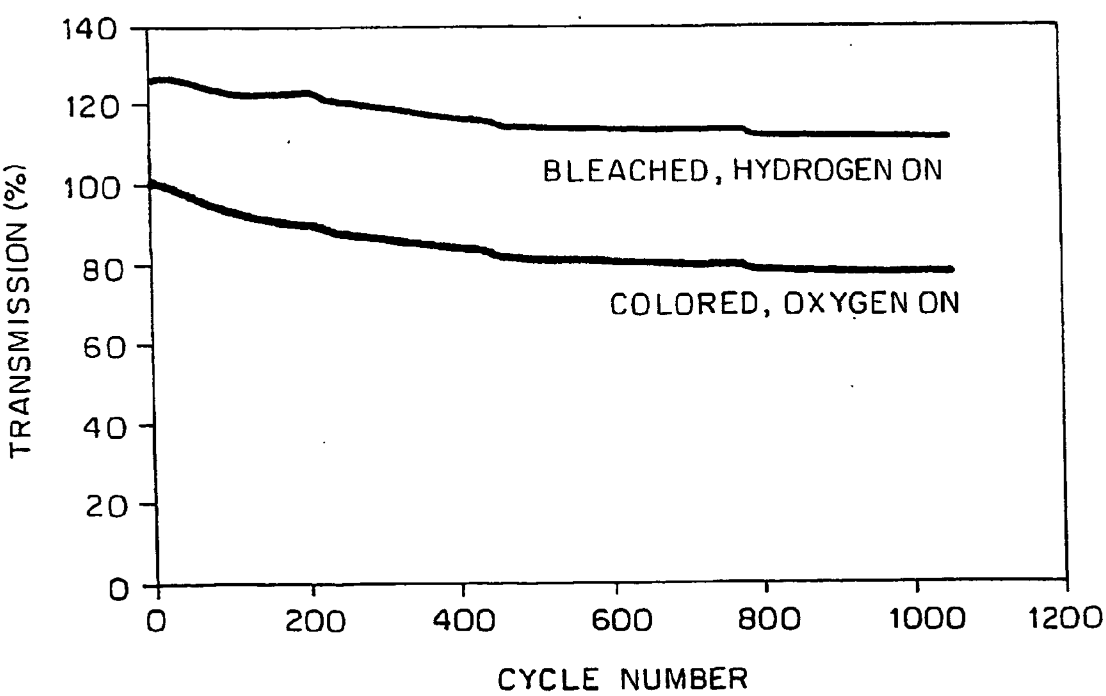
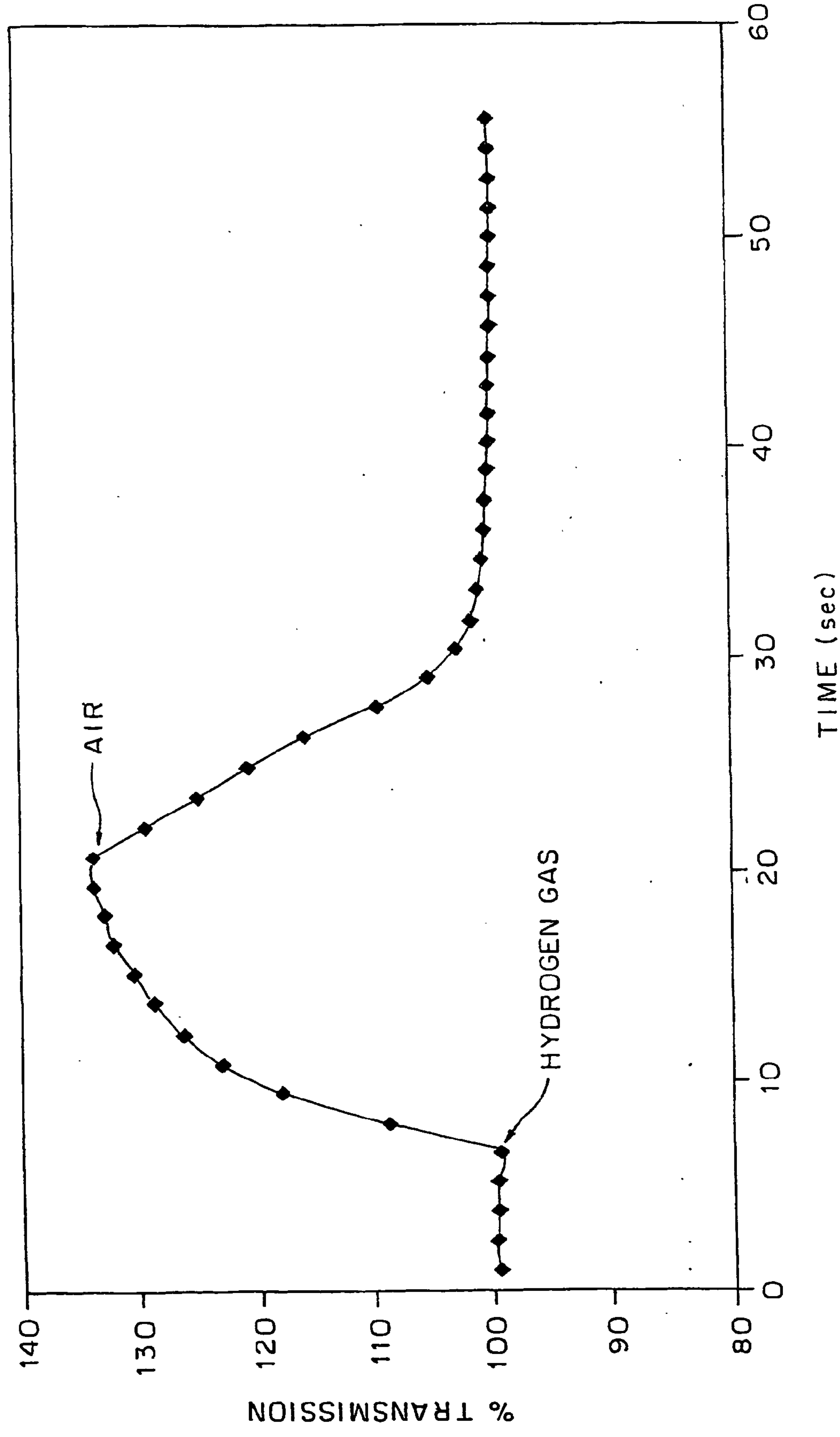


FIG. 2



AIR
HYDROGEN GAS
% TRANSMISSION
TIME (sec)
140
130
120
110
100
90
80
0
10
20
30
40
50
60

PD/V2O5 DEVICE FOR COLORIMETRIC H2 DETECTION

[0001] This application claims priority from U.S. Provisional Application Serial No. 60/202,153, filed May 5, 2000.

CONTRACTUAL ORIGIN OF INVENTION

[0002] The United States Government has rights in this invention under Contract No. DE-AC3699GO10337 between the United States Department of Energy and the National Renewable Energy Laboratory, a division of the Midwest Research Institute.

BACKGROUND ART

[0003] The invention relates to an ultra-stable vanadium oxide thin film structure for the detection of hydrogen gas. The hydrogen gas is dissociated on the Pd catalyst into H atoms, and the V_2O_5 layer on which the Pd is coated functions as a H^+ insertion host. The Pd layer is thus stabilized, which upon combination with hydrogen is chemochromically changed.

[0004] Hydrogen is a plentiful, clean, non-polluting fuel. Hydrogen is currently used in many industries, and the US demand for hydrogen is approximately 140 billion cubic feet per year and growing. However, hydrogen is explosive at 4% in air. Therefore, it is critical to measure, monitor and control hydrogen wherever it is used.

[0005] In the gas detection art where sensors and measurement instrumentation for hydrogen gases detect and/or measure hydrogen, typically there is required a portable sensing device, a kit (where hydrogen gas detection and/or measurement is required in existing equipment), and sensor heads installed at points where hydrogen leaks are possible, or where monitoring is necessary (i.e., in internal combustion engines which operate using hydrogen as a fuel).

[0006] The problems associated with current H_2 detection devices is that these devices do not exhibit stable cycling during repeated coloring/bleaching processes and are encumbered by a narrow response range for detecting H_2.

DESCRIPTION OF THE RELATED ART

[0007] At present, H_2 detection may be accomplished through the use of various and sundry devices, including thin film Pd oxide devices. However, several problems or drawbacks are associated with the use of these hydrogen detecting devices. These problems are: they do not exhibit stable cycling during repeated coloring/bleaching processes; and they are encumbered by a narrow response range for detecting hydrogen.

[0008] Inadequate cycling stability during repeated coloring/bleaching processes and the narrow response range for detection of hydrogen gas, in the case of the Pd thin film is due to the fact that, in the presence of high concentrations of H_2, palladium hydride is formed and the sensor is destroyed.

DISCLOSURE OF THE INVENTION

[0009] One object of the present invention is to provide an ultra-stable palladium vanadium oxide film structure for chemochromic detection of hydrogen.

[0010] Another object of the present invention is to provide an ultra-stable palladium vanadium oxide structure for chemochromic detection of hydrogen that exhibits stable cycling during repeated coloring/bleaching processes.

[0011] A further object of the present invention is to provide an ultra-stable vanadium oxide film structure for chemochromic detection of hydrogen in which the proton insertion material contributes to stabilize the palladium layer, and exhibits a wider response range for detecting H_2.

[0012] In general, the invention is accomplished by providing a palladium/vanadium oxide layer sensor device in which, a V_2O_5 thin film is coated on a transparent or glass substrate. Thereafter, a palladium layer is evaporated onto the V_2O_5 thin film. The palladium layer serves as a catalyst material that facilitates reaction with hydrogen gas. That is, the hydrogen gas is dissociated on the Pd catalyst into H atoms, which diffuse into the V_2O_5 film

[0013] The vanadium oxide layer acts as a hydrogen insertion host while the palladium layer is responsible for optical modulation. The presence of an ion storage host is vital to the stability of the palladium layer, and the sensor formed therefrom exhibits a wide response range for detecting hydrogen and shows very stable cycling during repeated coloring/bleaching processes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **FIG. 1A** shows a hydrogen sensor comprising SiO_2 deposited on a glass substrate, with Pd in turn deposited on the SiO_2 layer in which the interface between the SiO_2/Pd layer blocks the H_2.

[0015] **FIG. 1B** shows a hydrogen sensor in which $V_2\ O_5$ is deposited on a glass substrate, with Pd in turn coated on the V_2O_5 layer in which the Pd/$V_2\ O_5$ interface does not block H_2.

[0016] **FIG. 2** is a graph showing percent relative transmission versus time for a 20 nm VO_x/30 nmPd sensor in the presence of 4% hydrogen.

[0017] **FIG. 3** is a graph showing percent relative transmission versus cycle number as a measure of cycling stability for a 20 nm VO_x/30 nmPd sensor in an environment of 4% H_2.

DESCRIPTION OF THE INVENTION

[0018] Due to the fact that Pd/WO_3 sensors are saturated in the presence of just 2% H_2, and the fact that Pd sensors in the presence of H_2 form palladium hydride that results in destruction of the sensor, there is a need in the interest of safety to provide a H_2 sensor that still signals a chemochromic response to H_2 over a wide response range and in excess of 2%.

[0019] A further need exists in the art of chemochromic detection of hydrogen for a sensor that exhibits stable chemochromic cycling during repeated coloring/bleaching processes upon exposure and removal of H_2.

[0020] The Pd/V_2O_5 chemochromic hydrogen sensor is capable of providing a response above the narrow range of 2% hydrogen because, unlike WO_3, the Pd/V_2O_5 is not saturated at 2% H_2 or higher.

[0021] While not wishing to be bound by any theory as to why the Pd/$V_2\ O_5$ sensor is capable of functioning beyond the H_2 saturation point compared to a Pd/WO_3 sensor, it is nevertheless believed that, the $Pd/V_2\ O_5$ sensor structure does not change the thermodynamics of the system, i.e., if fully equilibrated, the Pd still forms a hydride; however, when a kinetically steady state is achieved, the sensor still has the capacity to detect high concentrations of hydrogen even in a higher than normal atmospheric pressurized hydrogen atmosphere.

[**0022**] Reference is now made to **FIG. 1A** in which there is shown a sensor comprising a glass substrate **10** on which is coated SiO_2, **11**. A Pd layer **12** is coated onto the SiO_2. In this sensor device, as is depicted by arrow **13** directed onto the interface designated by x between the SiO_2 and Pd layers, H_2 **13** is blocked at the interface, because SiO_2 cannot react with hydrogen. Pd hydride is formed that undergoes phase transition at hydrogen concentration higher than 4%, resulting in substantial volume change and failure of the sensor.

[**0023**] On the other hand and by contrast, in **FIG. 1B** in which a glass substrate **20** is coated with a V_2O_5 layer **21**, which in turn is coated by a Pd layer **22**, H_2 **23** is not blocked at the interface between V_2O_5 and Pd. Accordingly, the vanadium oxide layer acts as a hydrogen insertion host in the $Pd/V_2\ O_5$ hydrogen sensor, while the palladium layer is responsible for the optical modulation.

[**0024**] The presence of an ion storage host is vital to the stability of the palladium layer, and, unlike the case, when SiO_2 is used in conjunction with a Pd layer, the Pd layer does not peel off and is not degraded in the presence of 2% H_2 (but actually starts forming hydride at room temperature in the presence of about 4% H_2).

[**0025**] The insertion of hydrogen in V_2O_5 is governed by the following equation:

$$\underset{\text{yellow}}{V_2H_5} + xH^+ \;\underset{\not\leftarrow}{\rightarrow}\; \underset{\text{light blue}}{H_x V_2O_5}$$

$$\underset{\text{Light blue}}{H_x V_2O_5} + yH^+ \;\rightarrow\; \underset{\text{light blue}}{H_{x+y} V_2O_5}$$

[**0026**] A control experiment was performed to show that the optical response was from the palladium layer.

[**0027**] The optical modulation is governed by the following equation:

[**0028**]

$Pd + XH_2) = PdH_{2X}$	
(less transmissive)	(more transmissive)

[**0029**] A hydrogen sensor of $Pd/V_2\ O_5$ was then prepared in which the V_2O_5=2014 Å and the Pd =31 Å.

[**0030**] A cathodic optical response of 2% transmittance change is observed, and this compels the conclusion that the Pd layer is contributing to the optical response of the sensor, but that the V_2O_5 layer acts as a non-coloring ion storage layer and operates to stabilize the entire chemochromic hydrogen detector structure.

[**0031**] **FIG. 2** is a graph depicting percent relative transmission versus time for a 20 nm VO_x/30 mn Pd hydrogen sensor when exposed to a 4% hydrogen environment, and subsequently exposed to air.

[**0032**] The cycling stability of a 20 nm VO_x/30 nm Pd hydrogen sensor at 4% hydrogen is shown in the graph of transmission relative percent versus cycle number in **FIG. 3**, where excellent cycling stability is exhibited during repeated coloring/bleaching cycles. The difference of transmittance between bleached and colored curves does not decrease with cycling.

[**0033**] From the foregoing, it is apparent that ion insertion host capability of the vanadium oxide layer is necessary to obtain stable cycling, and that, in the absence of an ion insertion host (as in the case of SiO_2) control experiment stable chemochromic cycling is not obtained due to the fact that palladium hydride is formed and the sensor is destroyed.

[**0034**] The $Pd/V_2\ O_5$ hydrogen sensor results show that: a proton insertion material is vital to stabilizing the palladium layer, although it does not contribute to the optical response; that the $Pd/V_2\ O_5$ hydrogen sensor is easy to make via thermal evaporation processes; and that a wide response range of between 1 to 100% H_2 concentration is available for detecting hydrogen.

1. A sensor structure for detection of hydrogen gas over a wide response range, that exhibits stability during repeated coloring/bleaching cycles upon exposure and removal of hydrogen gas, comprising:

a substrate;

a vanadium oxide layer coated on said substrate; and

a palladium layer coated on said vanadium oxide layer

2. A method of preparing an improved sensor for chemochromic detection of hydrogen gas over a wide response range, that exhibits stability during repeated coloring/bleaching cycles upon exposure and removal of hydrogen gas, comprising:

providing a substrate;

depositing a V_2O_5 layer on said substrate; and

depositing a palladium layer onto said V_2O_5 layer.

3. An improved method of chemochromic detection of hydrogen gas over a wide range that exhibits stability during repeated coloring/bleaching cycles upon exposure and removal of hydrogen gas, comprising:

subjecting a sensor structure comprising a substrate, a layer of V_2O_5 coated on said substrate, and a layer of palladium (Pd) coated on said layer of V_2O_5 to an environment comprising hydrogen to cause a reaction governed by the equation:

$$V_2O_5 + xH^+ \;\underset{\not\leftarrow}{\rightarrow}\; H_x V_2O_5$$

$$H_x V_2O_5 + yH^+ \;\underset{\leftarrow}{\rightarrow}\; H_{x+y} V_2O_5$$

and an optical response governed by the equation:

$$Pd+XH_2=PdH_{2x}$$

4. The sensor structure of claim 1 wherein the formed VO_x/Pd sensor is characterized by dimensions of 20 nm VO_x/30 mn Pd.

5. The sensor structure of claim 1 wherein the substrate is transparent.

6. The sensor structure of claim 1 wherein the substrate is glass.

7. The method of detection of claim 3 wherein the Pd/V_2O_5 structure is not saturated a 2% H_2 or higher.

8. The method of claim 3 wherein hydrogen gas over a wide range that exhibits stability during repeated coloring/bleaching cycles is between about 1 to about 100% H_2 concentration .

9. The method of claim 2 wherein said palladium layer is deposited by evaporation.

10. The sensor structure of claim 1 wherein V_2O_5 functions as a hydrogen insertion host and said Pd functions as an optical modulator.

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