Fiber Optic Hydrogen Detectors

From fundamental research to safety applications

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Switchable mirrors

Rare-earth or transition metal based Mg alloys undergo a transition from metal to semiconductor when hydrogen is absorbed in the lattice. As a result the alloy changes optically from reflective to transparent or in some cases to a light absorbing black state.

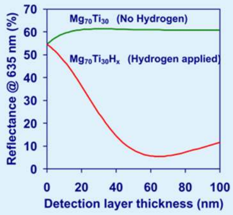
Our goal is to develop a "metal-hydride switchable mirror" which is used as a safety detector in a future hydrogen economy.

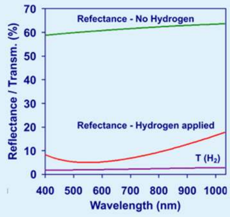
We aim to detect 10% of the lower explosion limit in air, (which is 4%) within seconds and with an optical change of a factor 10. The detector should allow repeated use.

Device architecture

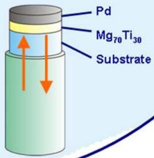
Our best hydrogen detection material is $Mg_{70}Ti_{30}$. This alloy forms a strongly light absorbing metal-hydride when hydrogen exceeds the equilibrium hydrogenation pressure of 0.4 mbar.

The ideal architecture of the sensing layer and its optical response is calculated from the dielectric constants of the used metals [1].





The Mg-Ti alloy layer is covered by a 30 nm thick Pd layer which promotes the hydrogen uptake of the detector and prevents the layer from oxidation.



Patent

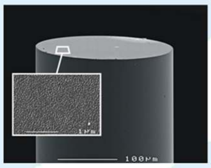
"Optical Switching Device"

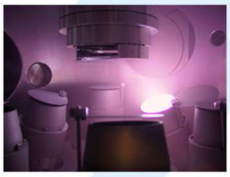
PCT/NL2006/050268

Device preparation

The Mg-Ti detection layer and the Pd cap layer are deposited on freshly cleaved multimode glass fibers.

By using glass fibers no electrical leads are needed near the sensing point in a potentially explosive environment. In a safety application multiple fiber detectors can be read by a single set of light source and detector.

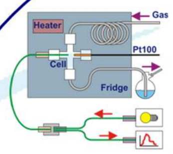


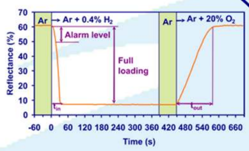


Deposition of the layers is done by magnetron sputtering in argon. The composition and thickness are verified with a stylus profiler and Rutherford Backscattering Spectrometry.

We connect the detector to a standard bifurcating fiber which guides light from a white light source to the detector and guides the reflected light to a CCD spectrometer. A low cost readout can be build from a red LED, a CD-player beam splitter and a PIN diode.

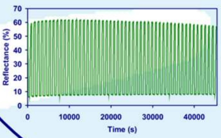
Characterization





The detector regenerates to it's original state when the hydrogen concentration drops below the equilibrium pressure of the hydride. The unloading rate of the detector increases when oxygen is present.

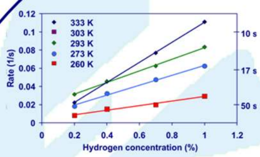
The large optical change upon hydrogen loading allows the use of alarm levels in a hydrogen detector application, which improves the stability and reaction speed of the application.



Over 100 stable cycles are measured, which is more than enough for a safety device.

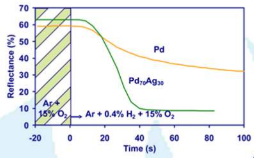
Oxidation of the detection layer due to cycling stress can be reduced by using a thin NbO_x or AlO_x layer between the Pd layer and the $Mg_{70}Ti_{30}$ layer.

Device improvements



Detection of low concentrations hydrogen is within seconds. The detector functions (unlike commercially available detectors) well in oxygen poor environments like argon glove boxes and over a large temperature range.

Oxygen en carbon oxides in the environment of the detector can lower the sensitivity and the kinetics due to surface reactions on the Pd layer. These effects are reduced by alloying the Pd layer with for example Ag [2].



A hydrophobic organic coating on top of the Pd layer prevents the detector from degradation by moist when the detector is stored or used for a long period in air.

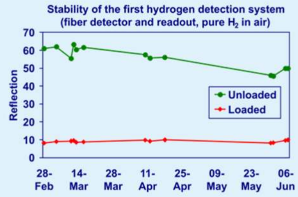
Patent

"Protective coating for M-H based devices"

P6007119NL

Prototypes

A series of fiber optic hydrogen detector prototypes together with a small readout system is currently spread among 10 hydrogen research laboratories in Europe. They will test the behavior of the detector in a variety of conditions like in argon glove boxes or in polluted environments.



So far we observe a reproducible detection of pure hydrogen in air during a test period of several months. Our research will now focus on developing a sensor for quantitative reading of the hydrogen concentration in air.

[1] M. Slaman, B. Dam, M. Pasturel, D.M. Borsa, H. Schreuders, J.H. Rector, R. Griessen, *Fiber optic hydrogen detectors containing Mg-based metal hydrides,* Sens. Actuators B: Chem. 123 (2007) 538-545

[2] M. Slaman, B. Dam, H. Schreuders, R. Griessen, *Optimization of Mg-based fiber optic hydrogen detectors by alloying the catalyst*, Int. J. Hydrogen energy (2007), Available online