

Eye readable metal hydride based hydrogen tape sensor for health applications

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ABSTRACT

Using the change in the intrinsic optical properties of YMg-based thin films upon exposure to hydrogen, we observe the presence of hydrogen at concentrations as low as 20 ppm just by a change in color. The eye-visible color change circumvents the use of any electronics in this device, thereby making it an inexpensive H₂ detector. The detector shows high selectivity towards H₂ in H₂-O₂ - mixtures, and responds within 20 s to 0.25% H₂ in the presence of 18% O₂.

Keywords: tape sensor, Eye readable sensor, hydrogen sensor, breath analysis, lactose intolerance, yttriumhydride, thin film

1. INTRODUCTION

The use of hydrogen in the society ranges from chemical manufacturing to energy storage for mobile and stationary devices. Hydrogen detection is also finding applications in medical diagnostics such as in a hydrogen breathe test for the diagnosis of lactose intolerance and malabsorption. Recently we demonstrated an elegant way to realize an inexpensive eye-readable H₂ detector by exploiting the reversible change in the optical properties of Y combined with the interference due to a Pd cap-layer¹. In the rare earth (RE) hydrides optical switching results due to the absorption of hydrogen². While increasing the hydrogen pressure, the absorbed hydrogen induces the formation of the fcc YH₂ and hcp YH₃ hydride phase at well-defined pressure thresholds. The presence of hydrogen is revealed by changing from a highly reflective appearance to three different colors at hydrogen concentrations between 0-0.1 mbar H₂ partial pressure. Here, we make use of the fact that the hydrogenation reaction occurs through three different phases: Y → (YH_{1.9} ↔ YH_{2.1}) ↔ YH_{2.7}. Within the single dihydride YH₂ phase, we can clearly distinguish between the high and the low hydrogen content state.

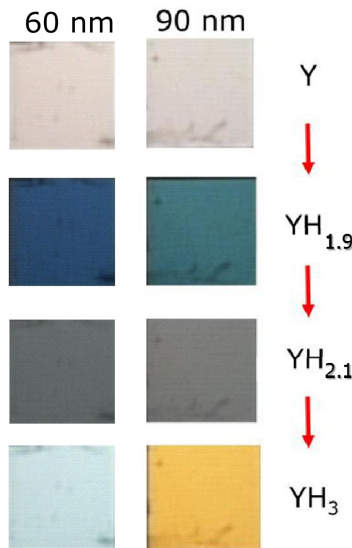


Fig.1: Various colors of a thin film of 50nmPd/Y on hydrogenation showing the consecutive hydrogen pressure threshold levels. The films is deposited on quartz. The colors are those seen by the naked eye and depend on the Yttrium film thickness (60 and 90nm) .

While the three stages of hydrogen detection might be convenient sometimes, there is also a need to have a single detection level with an adjustable threshold level. For that purpose we would like to alter the hydrogenation thermodynamics of the Y sensing layer, while preserving its optical properties. Here, we investigate the effect of alloying Yttrium with Magnesium³⁻⁵. In 400nm thin films, it was shown that on hydrogenation, the Mg-RE alloy disproportionate into RE-H₃ and MgH₂ via an intermediate state where metallic Mg coexists with RE-H₂³. Due to the highly reflective nature of the Mg, a single optical transition was observed. It was inferred that the plateau pressures of hydrogenation was modified, due to the internal stresses induced by the different phases. Hence, here we report on the sensing properties of Y_x-Mg_{1-x} alloys showing how the concentration of Mg in the alloy influences the sensing properties.

2. EXPERIMENTAL

2.1.1 Film preparation

50 nm Y or Y_xMg_{1-x} thin films are deposited at room temperature on 1 cm x 1 cm quartz substrates in an ultrahigh-vacuum (UHV) DC/RF magnetron sputtering system. The system base pressure is 10⁻⁹ mbar, while during deposition 0.003 mbar Ar is added. To improve the adhesion of the sensing layer to the substrate a 3 nm intermediate Ti layer is deposited on the quartz substrate before starting the deposition. A 25 nm Pd cap layer is sputtered on top of the YMg film to protect the film from oxidation and to catalyze the dissociation of the hydrogen. Finally, the films are protected by a 30 nm sputtered polytetrafluoroethylene (PTFE) coating to minimize the effect of H₂O based interactions on the surface. The Y_xMg_{1-x} alloy is prepared by co-sputtering of Y and Mg at certain predetermined sputtering rates. The chemical composition and thickness of the gradient film is determined by measuring the thickness of single component layers.

2.1.2 Structural characterization and optical H₂ sensing measurements

The optical response of the samples upon hydrogenation and dehydrogenation was characterized using hydrogenography⁶. With this technique it is possible to investigate the hydrogenation behavior (thermodynamics and kinetics) of uniform and gradient samples. The logarithm of the change in transmittance $\ln(T/T_0)$ is related to the H₂ concentration in the thin film and enables us to obtain the pressure transmission isotherms. By using a gradient sample, many alloy compositions can be analyzed simultaneously under the same conditions. Thereby an easy selection of the most optimal alloy composition can be obtained. The phase composition and microstructure of the films are characterized by standard X-ray diffraction analysis with a Bruker D8 Advance XRD equipped with Co source (0.178897 nm).

3. RESULTS AND DISCUSSION

3.1.1 Configuration and microstructure

Figure 2A and B shows the configuration of the eye-readable hydrogen detectors with a 50 nm thin film of Y and Y-Mg alloy respectively as the sensing layer. The Pd thin film catalyzes hydrogen dissociation and association (hydrogenation and dehydrogenation). It also acts as optical mirror enabling the interference of light. This enhances the visualization of the optical effects that occurs in the sensing layer due to the presence of hydrogen. For pure Yttrium films, this leads to a set of four different bright colors, depending on the hydrogen pressure applied (figure 1).

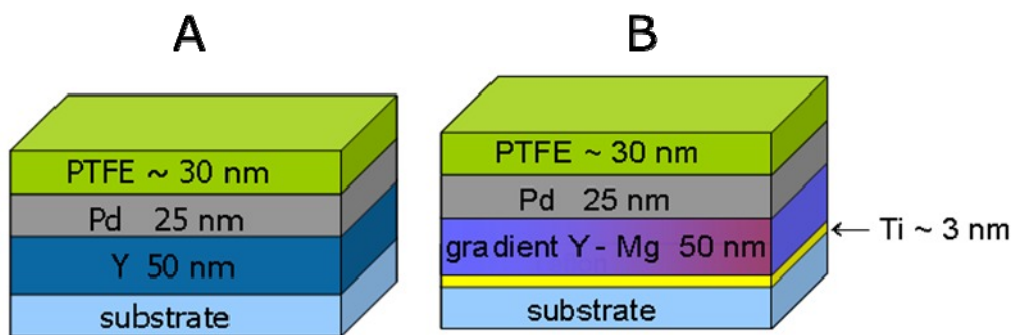


Fig. 2. Configuration of the eye-readable H_2 detector with Y (A) and Y_xMg_{1-x} (B) as a sensing layer

Comparing the as-prepared Y/Pd and $Y_{50}Mg_{50}$ /Pd we find that the addition of about 50 at.% Mg to the Y results in a clear change in the XRD pattern as compared to the pure Y. The Y(002) peak disappears while a new peak due to Mg-Y alloy is seen at 2θ equals 37° . After hydrogenation and dehydrogenation the XRD spectra become featureless suggesting the formation of an amorphous state.

The sensing mechanism of a pure Y sensing layer is based on the different transparency windows in the visible range of the three different YH_x states ($YH_{1.9}$, $YH_{2.1}$ and $YH_{2.7}$), this gives rise to three colors that corresponds to $YH_{1.9}$, $YH_{2.1}$ and $YH_{2.7}$. Together with the highly reflective pure Yttrium four optical states can be discerned (A, B, C and D in the pressure transmission isotherm (PTI) in Fig. 3). Note, that the plateau pressure for the transition $Y \rightarrow YH_{1.9}$ is $\sim 10^{-27}$ mbar⁷. Therefore, the sloping plateau we observe in Fig. 3 starting from 5×10^{-4} mbar is due to the slow kinetics of this initial hydrogenation process and does not represent a thermodynamic threshold. It is not possible to revert back to Yttrium without applying extreme conditions. We obtain the Yttrium dihydride phase $YH_{1.9}$ when we remove the hydrogen and apply 20% oxygen. This makes the sensor reversible in air.

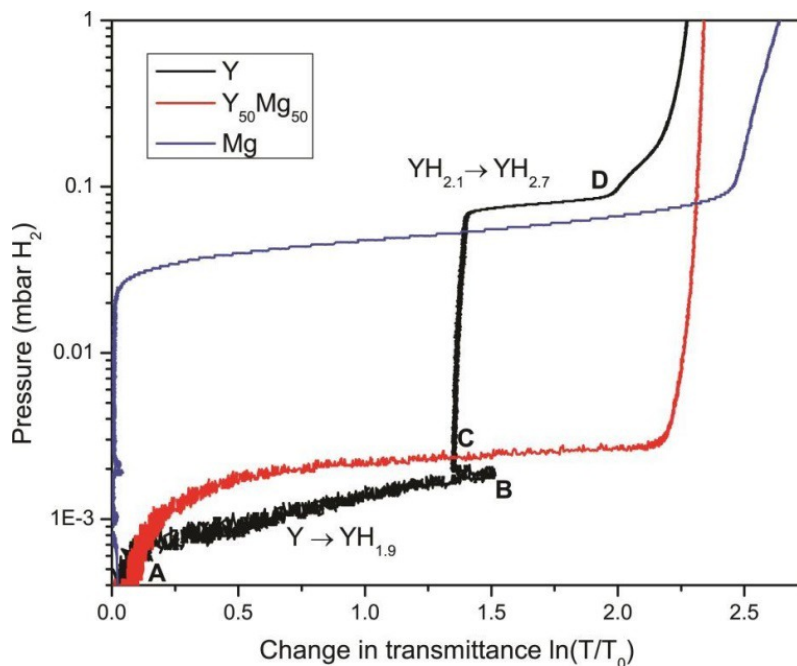


Fig. 3. Comparing the pressure transmission isotherm (PTI) of the Y/Pd/PTFE, Mg/Pd and $Y_{50}Mg_{50}$ /Pd/PTFE films on first loading. The pressure of a 0.1% H_2 mixture is logarithmically increased in 492 steps from 1 mbar to 1000 mbar. A stabilization time of 300 s is used at each hydrogen absorption step to ensure equilibrium. Measurement time at room temperature is 48 hours.

In the present work we concentrate on detectors with 50 nm Y-Mg sensing layer. Unlike the absorption isotherm of Y with 3 optical transitions (corresponding to $Y \rightarrow YH_{1.9} \rightarrow YH_{2.1} \rightarrow YH_{2.7}$), only one transition is observed for $Y_{50}Mg_{50}$. The plateau pressure for the optical transition in the alloyed sample ($Y_{50}Mg_{50} \rightarrow Y_{50}Mg_{50}H_x$) is at a slightly higher pressure than for $Y \rightarrow YH_{2.1}$, but significantly lower than $YH_{2.1} \rightarrow YH_{2.7}$ or $Mg \rightarrow MgH_2$. Hence, we now observe only one color change in $Y_{50}Mg_{50}H_x$. From the large size of the plateau, we deduce this change to be due to the hydrogenation of Mg, which has a much larger optical contrast than Yttrium. Hence, as previously suggested, the Mg hydrogenation fully dominates the optical behavior of the YMg films³.

3.1.2 Effect of Mg concentration on the color change and the hydrogenation pressure

To investigate the effect of the Mg concentration, we co-deposited Y and Mg on a 5 mm x 70 mm quartz strip in such a way that the concentration of Y and Mg varies along the entire length of the strip. In the hydrogenated state (after applying 0.1% H_2 /Ar) the bluish color of the detector varies slightly with the concentration of Mg in the sample (see figure 4). We propose that this color is due to a mixture of YH_2 and MgH_2 . However in the unloaded (dehydrogenated) state the color is almost of the same metallic nature, irrespective of the Mg concentration. In the Yttrium rich concentrations the color of the unloaded states deviates slightly from the as-deposited state, suggestive of the formation of the $YH_{1.9}$ state observed in pure Yttrium films on dehydrogenation. The largest contrast we find is at intermediate (around 50/50) concentrations.

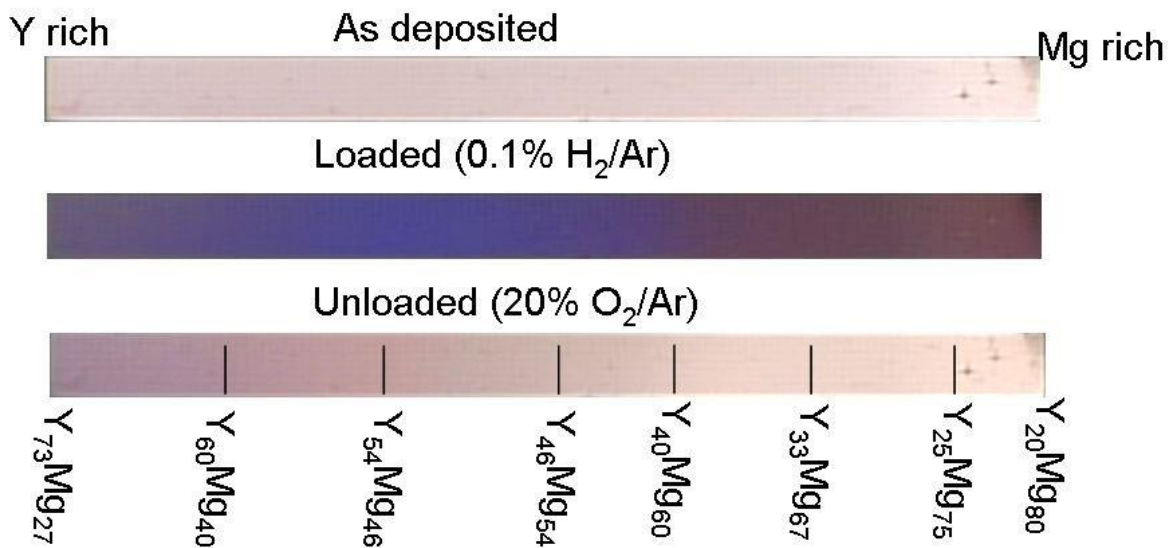


Fig. 4. 3CCD camera images of a 70 mm x 5mm H_2 detector strip with varying concentrations of Y and Mg along the strip. It shows the effect of Mg concentration on the color of the detector in the as-prepared state, upon exposure to 0.1% H_2 /Ar, and after unloading (dehydrogenation) in 20% O_2 /Ar. On top of the Y_xMg_{1-x} film is deposited 25 nm Pd thin film as catalyst and 30 nm PTFE thin film

Comparing the hydrogenation behavior between the various compositions, we find again a single plateau for almost all of them (Figure 5). Note, that when comparing the first and the second cycle, the main plateau pressures have hardly changed. The width of the plateau scales with the Mg content, which is another indication that this plateau is related to the hydrogenation of Mg. The fact that this pressure is so much lower than that of pure Mg, suggests that the Mg lattice is expanded. It is well-known that an expanded lattice allows for hydrogenation at a much lower pressure. However, qualitatively, this is in contrast to what was reported earlier³. In that paper indications were found for a compression of

the Mg lattice. These films were much thicker (400nm) and only dynamic hydrogenation experiments were performed at a fixed overpressure. Our films are one order of magnitude thinner and have been measured under equilibrium circumstances. Assuming that the Mg lattice expansion is due to the segregation and hydrogenation of Yttrium, the thickness of the film might be quite relevant. Due to clamping, the expansion will only take place in the direction normal to the film surface. If the segregated entities are of the same size as the film thickness, one may envisage that the hydrogenation stretches the Mg entities lying next to the Yttrium. We observe that the decrease in equilibrium pressure is only weakly depending on the Mg content. Only at 70% Mg, a second plateau is observed at a higher pressure. This might indicate, that the amount of Yttrium at a certain critical concentration is not high enough to fully expand the all the Mg particles. The remaining Mg will then hydrogenation at a pressure close to the equilibrium Mg pressure. A further optical study will be needed to fully understand the details of the hydrogenation process.

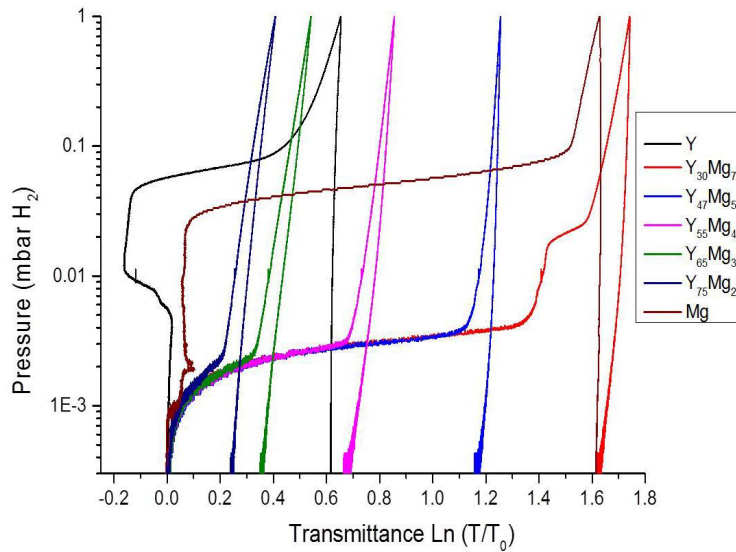


Fig. 5. Comparing the pressure transmission isotherm (PTI) of the Y/Pd/PTFE, Mg/Pd and Y_xMg_{1-x} /Pd/PTFE films in their second loading cycle. The pressure of a 0.1% H_2 mixture is logarithmically increased in 492 steps from 1 mbar to 1000 mbar and a stabilization time of 300 s is used during each hydrogen absorption step to ensure equilibrium. Measurement time at room temperature is 48 hours. Note, that the pure Yttrium film now starts from the dihydride $YH_{1.9}$ state ('B' in figure 3).

We tested the stability of our device by doing several loading and unloading cycles on the $Mg_{50}Y_{50}$ sample in a flow set-up. During at least 40 cycles no change in color of the detector are observed. In terms of selectivity, the sample can be loaded and unloaded several times in a mixture of 0.25 % H_2 +18% O_2 without noticeable effects on kinetics. The response time (25 s) of the detector in oxygen is much lower than the 800 s required in the detector based on pure Y in the presence of a similar hydrogen/oxygen mixture¹.

4. CONCLUSION

We present an eye-readable hydrogen detector based on a Mg-Y alloy. Instead of the three detection levels observed in Yttrium, this alloy only shows a single pressure detection level. Unfortunately, the pressure plateau is only weakly depending on the Mg/Y ratio. The optical change is deduced to be mainly due to the hydrogenation of Magnesium. The fact that this hydrogenation occurs at a much lower pressure than usual, is attributed to tensile strain on the phase segregated Mg. The tape sensor is highly reproducible and relatively fast in detecting 0.25% hydrogen in 18% oxygen, reversibly. This pressure level is particularly suitable to detect lactose intolerance in the patient's breath.

REFERENCES

- [1] P. Ngene, T. Radeva, M. Slaman, R. J. Westerwaal, H. Schreuders, B. Dam, "Seeing Hydrogen in Colors: Low-Cost and Highly Sensitive Eye-Readable Hydrogen Detectors", *Adv. Funct. Mater.* 24 2374–2382 (2014).
- [2] J. N. Huijberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, "Yttrium and lanthanum hydride films with switchable optical properties", *Nature*, 380 231-234 (1996).
- [3] D. D. Nagengast, A.T.M. van Gogh, E.S. Kooij, B. Dam, R. Griessen, "Contrast enhancement of rare-earth switchable mirrors through microscopic shutter effect", *Appl. Phys. Lett.* 75 2050-2052 (1999).
- [4] S.J.van der Molen, D.G. Nagengast, A.T.M. van Gogh, J. Kalkman, E.S. Kooij, J.H. Rector, R. Griessen, "Insulating fcc-YH_{3-δ} stabilized by MgH₂", *Phys. Rev. B* 63 235116-235123 (2001).
- [5] I. Giebels, J. Isidorsson, R. Griessen, "Highly absorbing black Mg and rare-earth-Mg switchable mirrors", *Phys. Rev. B* 69 205111 (2004).
- [6] Gremaud, R., Ch.P. Broedersz, D.M. Borsa, A. Borgschulte, P. Mauron, H. Schreuders, J.H. Rector, B. Dam and R. Griessen, "Hydrogenography: an optical combinatorial method to find new light-weight hydrogen storage materials", *Advanced Materials* 19 2813-2817(2007)
- [7] E. S. Kooij, A. T. M. van Gogh, R. Griessen, "In-situ resistivity measurements and optical transmission and reflection spectroscopy of electrochemically loaded switchable YH_x films", *J. Electrochem. Soc.* 146 2990-2994 (1999).