Quasi-distributed fiber Bragg gratings sensor for hydrogen leak detection in air

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We present a multipoint in-fiber sensor capable of hydrogen leak detection in air as low as 1% concentration with a response time smaller than a few seconds. Our solution makes use of fiber Bragg gratings covered by a catalytic sensitive layer made of a ceramic doped with a noble metal. This sensitive layer induces a temperature elevation around the fiber Bragg gratings in the presence of hydrogen in air. The sensor interrogation is based on the monitoring of the resonant wavelength shift.

Introduction

Hydrogen participates to a wide range of chemical processes and also appears during energy production and transport. It is becoming an attractive fuel source for use in clean-burning engines and power-plants. Hydrogen is an extremely reactive gas. In air, it can burn at concentrations from about 4 % with a flame velocity almost ten times higher than that of natural gas. Therefore, in order to mitigate the risk of explosion, efficient H_2 leak sensors are required. Optical fiber sensors are particularly interesting, especially because of their explosion proof nature and ability to provide numerous sensing points.

A great deal of the researches has been devoted to fiber Bragg gratings (FBGs). FBGs covered with Palladium have been widely investigated for H_2 sensing [1-4]. The sensing mechanism, based on the swelling of the Pd-coating, results in a stress on the grating. In practice, the Pd-coated sensors suffer from a long response time leading to a hysteresis effect between the responses obtained for increasing and decreasing H_2 concentrations. A solution has been proposed in [5] to overcome this drawback but it still remains the problem of the environment. Such sensors have been tested in nitrogen environments and are not able to properly operate in air. This is an issue since many applications such as the monitoring of storage places and pipes require the use of H_2 sensors in air.

We provide here a solution to the H_2 detection problem in air using a cost-effective and fast fiber sensor. It consists of FBGs covered by a catalytic sensitive layer. In the presence of H_2 in air, the sensitive layer undergoes an exothermic reaction and an increase of temperature around the FBG is measured through a wavelength shift.

Conception of the hydrogen sensor

FBGs were inscribed into hydrogen-loaded standard single mode fiber by means of a frequency-doubled Argon-ion laser using the phase mask technique. Several lengths were tested from 5 mm to 4 cm. The gratings were inscribed with the same velocity of the UV beam sweep along the phase mask, i.e. the longer gratings received more fluence than the shorter ones. The gratings were characterized by a strong refractive index modulation, yielding a nearly 100% reflectivity at the Bragg wavelength [6].

Nano-sized tungsten oxide powder was prepared using the sol-gel method [7]. To start, aqueous sol and gel of tungstic acid (H_2WO_4) were prepared from Na_2WO_4 with protonated cation-exchange resin. The nano-tungsten oxide of lamellae in microporous and high specific surface area was obtained by repeatedly washing with distilled water and centrifuging of the gel. Appropriate amounts of H_2PtCl_6 solution were added to WO_3 to obtain the sensitive layer used for H_2 detection.
Every grating was written in the middle of a 5 cm stripped region of the optical fiber. The sensitive layer of several microns was deposited uniformly along the stripped region using the dip-coating technique, ensuring in any case the same experimental conditions.
In the presence of H_2 in air, the following reactions occur in the sensitive layer:

$$\begin{gathered} WO_3 + H_2 \leftrightarrow WO_2 + H_2O \\ WO_2 + \tfrac{1}{2}O_2 \leftrightarrow WO_3 \end{gathered} \tag{1}$$

The oxidation of H_2 molecules by O_2 molecules is an exothermic reaction that elevates the temperature around the FBG. H_2 sensing is therefore based on the monitoring of the Bragg wavelength shift induced by a temperature change. The activation energy of this reaction is equal to 0.15 eV [8].

Experimental results and discussion

Due to the need of activation energy (0.15 eV) to initiate the exothermic reaction, there exists a threshold value in terms of H_2 concentration below which the sensor does not react. In practice, this threshold value can be decreased thanks to an external energy contribution. This could be done for instance by a local heating of the sensitive layer. One efficient way to do this is to take profit from the light energy transported by the optical fiber. Indeed, at 1500 nm, the photon energy is about 0.7 eV and consequently, light that would be coupled from the core of the optical fiber towards the sensitive layer could favor the reaction for lower H_2 concentrations. This is possible since the refractive index of the sensitive layer is slightly higher than that of pure silica.
To achieve this, we have designed the FBGs to obtain a light coupling to the cladding and consequently to the sensitive layer. We have tested different strongly reflective uniform gratings. The longest gratings (the strongest in terms of coupling coefficient) were characterized by the presence of important cladding modes resonances below the Bragg wavelength in the transmitted spectrum, which demonstrates their strong coupling characteristics [6]. Table 1 summarizes the results obtained in terms of detection threshold of H_2 concentrations for 7 FBGs. The data were recorded for H_2 concentrations ranging from 0% to 3% and increasing by step of 0.2%.

Grating length (cm)	**Threshold (% H_2)**
0.5	No response up to 3%
1.0	~ 3.0
2.0	~ 2.5
2.5	~ 1.6
3.0	~ 1.4
3.5	~ 1.2
4.0	~ 1.0

Table 1. Thresholds for the detection of H_2 in dry air as a function of the grating length.

These results reveal that longer FBGs allow an important decrease of the threshold value. This comes from the strong coupling characteristics of long gratings that deliver some energy to the cladding [6]. This energy is finally collected by the sensitive layer.
Fig. 1 presents the results obtained on the transmitted spectrum of the 4 cm long FBG subject to different H_2 concentrations in dry air at ambient temperature. A shift of the Bragg wavelength to the right appears due to the exothermic reaction that occurs inside the sensitive layer. For a 1% concentration of H_2 in dry air, the measured wavelength shift is equal to 2 nm, which is easy to detect with a low cost interrogation system. This is equivalent to a local temperature increase of nearly 200°C.
Fig. 2 presents the wavelength shifts measured for two tested gratings as a function of H_2 concentration. The plain curves were obtained for increasing H_2 concentrations starting from 0% and thus revealed the threshold value. The dotted curves were obtained for decreasing H_2 concentrations starting from 3%. They show that the sensors are able to detect concentrations below the threshold value after it has been reached. This characteristic lasts only 2 to 3 hours and is thus a *short term memory effect*. Hence, only the plain curves represent the sensors characteristics in real-life applications.
The results obtained from these experiments demonstrate that the grating length does not influence the temperature delivered by the chemical reaction. The sensitivity of the sensor is thus not dependent on the grating physical properties.
Another important feature of our sensor is the linear behavior obtained in response to varying H_2 concentrations. Moreover, the data obtained for increasing H_2 concentrations match those obtained for decreasing H_2 concentrations. The lack of hysteresis is surely provided by the extremely small response time of the sensor to varying H_2 concentrations. It was computed of the order of 1 second for all the gratings when H_2 concentrations were above the threshold.
The H_2 FBG sensors were also tested in wet air environments. The obtained results revealed that the detection threshold of H_2 concentration increases when the relative humidity level increases. For the 4 cm long FBG, it increased from 1.0% to 1.5% when the relative humidity level was changed from 0% to 90%. We attribute this increase to the presence of H_2O molecules that tend to inhibit the reaction given in (1). The sensitivity to H_2 concentrations remained the same in wet air as in dry air.
Low temperature environments also led to an increase of the threshold value. At -30°C, the detection threshold reached 1.8% for the 4 cm long FBG. This value is still well below the 4% explosion limit and it can be accepted in our applications.

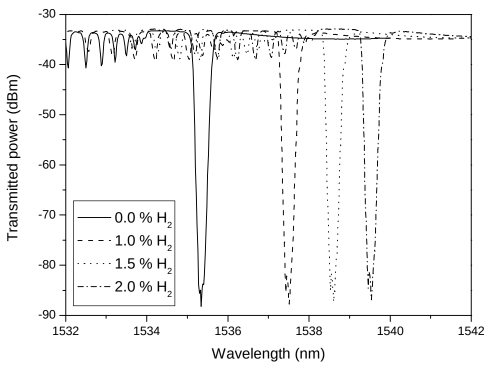

Fig. 1. Transmitted spectrum of a 4 cm long FBG in response to different H_2 concentrations in dry air at ambient temperature.

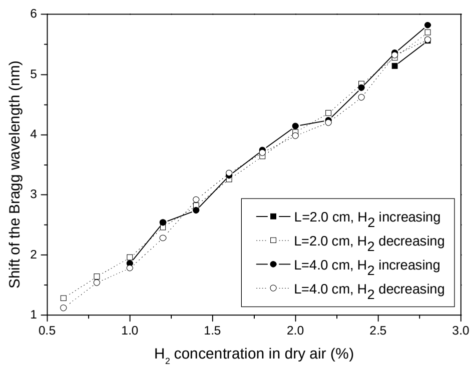

Fig. 2. Shift of the Bragg wavelength as a function of the H_2 concentration in dry air at ambient temperature for two grating lengths.

We demonstrated that the coupling of light from the core of an optical fiber to the cladding allows an important reduction of the threshold value. There are other ways to reach that goal. As we wanted to keep the sensor as cheap as possible, we investigated the use of radiating long period gratings (LPFGs) that lead to a strong coupling to the cladding modes [9]. With a 3 cm long 500 µm period LPFG characterized by a rejection band of about 5 dB in the spectral range of the optical source, we obtained a decrease of the threshold value to 0.8 % of H_2 concentration in dry air at ambient temperature. The decrease of the threshold value was also confirmed in wet air and for temperatures below 0°C. However, LPFGs are characterized by a broader transmitted spectrum (several tens of nanometers) in comparison to uniform FBGs (several hundreds of picometers). Consequently, they are less compatible with quasi-distributed sensing systems unless broadband optical sources are used but it leads to an important increase of the cost. They are moreover sensitive to macro bending, rendering difficult their use in practical applications. It is the reason why, as the application fields of our H_2 sensor are essentially the detection of leaks in air for the monitoring of storage places and pipes, we believe that uniform FBGs remain the most appropriate candidates to obtain a simple and low cost sensing system. The inscription of different FBGs cascaded along the same optical fiber has given birth to a quasi-distributed H_2 sensor.

Conclusion

We presented a novel sensor prototype in order to detect H_2 leaks in air by means of FBGs covered by a sensitive layer made of WO_3 doped with Pt. In our sensor configuration, the sensitive layer generates an exothermic reaction while FBGs act as probes to measure the wavelength shifts induced by temperature changes. Our H_2 sensor offers a very good sensitivity and a very fast response.

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References

[1] B. Sutapun, M. Tabib-Azar, A. Kazemi, "Pd-coated elastooptic fiber optic Bragg grating sensors for multiplexed hydrogen sensing", *Sensors and Actuators B*, vol. 60, pp. 27-34, 1999.

[2] Y. Tang, T. Peng, J.S. Sirkis *et al*, "Characterization of a fiber Bragg grating (FBG)-based palladium tube hydrogen sensor, Proc. of the SPIE Smart Structures and Materials Conference, vol. 3670, pp. 532-540, 1999.

[3] Y.T. Peng, Y. Tang, J.S. Sirkis, "Hydrogen sensors based on palladium electroplated fiber Bragg gratings", Proc. of the SPIE 13th International Conference on Optical Fiber Sensors and Workshop on Device and System Technology toward Future Optical Fiber Communication and Sensing, vol. 3746, pp. 171-179, 1999.

[4] R.R.J. Maier, J.S. Barton, J.D.C. Jones *et al*, "Palladium-based hydrogen sensing for monitoring of ageing materials", *Meas. Science and Technol.,* vol. 17, pp. 1118-1123, 2006.

[5] M. Buric, K.P. Chen, M. Bhattarai *et al*, "Active fiber Bragg grating hydrogen sensors for all-temperature operation", *IEEE Photon. Technol. Letters*, vol. 19, pp. 255-257, 2007.

[6] T. Erdogan, "Fiber grating spectra", *Journal Lightwave Technol.*, vol. 15, pp. 1277-1294, 1997.

[7] S. Okazaki, H. Nakagawa, S. Asakura *et al*, "Sensing characteristics of an optical fiber sensor for hydrogen leak", *Sensors and Actuators B*, vol. 93, pp. 142-147, 2003.

[8] C. Appel, J. Mantzaras, R. Schaere *et al*, "Catalytic combustion of hydrogen-air mixtures over platine: validation of hetero/homogeneous chemical reaction schemes", Clean Air, vol. 5, pp. 21-44, 2004.

[9] T. Erdogan, "Cladding-mode resonances in short- and long-period fiber grating filters", *J. Opt. Soc. Am. A*, vol. 14, pp. 1760-1773, 1997.