Sensors and Actuators B 245 (2017) 516–523

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Hydrogen sensor based on polymer-filled hollow core fiber with Pt-loaded WO_3/SiO_2 coating

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ARTICLE INFO

Article history:
Received 6 October 2016
Received in revised form 30 January 2017
Accepted 31 January 2017
Available online 2 February 2017

Keywords:
Optical fiber sensor
Pt-loaded WO_3/SiO_2 coating
Hydrogen sensor
Fabry–Pérot interferometer
Temperature

ABSTRACT

A simple, compact and highly sensitive hydrogen sensing device based on a polymer-filled hollow core fiber coated with Pt-loaded $WO_3/SiO_2$is demonstrated. The device is composed of a tiny segment of hollow core fiber (HCF) spliced to a standard single mode fiber (SMF) incorporated with a fiber Bragg grating (FBG). The HCF is filled with polymer and the inner air-gap near the interface between SMF and polymer forms a micro-cavity Fabry–Pérot interferometer (FPI). With Pt-loaded WO_3/SiO_2 coating acting as the catalytic layer, hydrogen undergoes an exothermic reaction with oxygen in air and releases heat when the device is exposed to hydrogen, which induces local temperature change of FPI and hence leads to reflection spectrum shift of the proposed device. Here, the FBG is used to compensate the surrounding temperature effect and eliminate the temperature cross-sensitivity of the device. A wavelength shift of over 35 nm is obtained with a 242-μm-long polymer-filled HCF for 4% (vol%) H_2 concentration, and the maximum sensitivity of 17.48 nm/% (vol%) H_2 is achieved within the range of 0–4.0% (vol%) H_2 in air. The sensor device also exhibits fast response time to hydrogen.

1. Introduction

Hydrogen is extensively used in many fields, such as petroleum and chemical industries, physics and engineering, electrical industry, automotive, aerospace, etc., as a reactant, shielding gas, rotor coolant or clean and sustainable energy [1]. However, hydrogen is also dangerous because of its very low minimum ignition energy and explosive limit (4%) [2]. Thus, the fast detection of hydrogen leaking at storage and accurate hydrogen concentration measurement (especially below 4% or even lower) is extremely important for safely use of hydrogen.

Many types of hydrogen sensors have been proposed and practically used. Traditional hydrogen sensors are based on electrochemical mechanism, such as calorimetric thermoelectric [3] and conductometric sensors [4], and have high precision and low detection threshold. However, optical sensors, especially fully fiber-optic hydrogen sensors have advantages of intrinsic safety, remote access to potentially explosive areas and immunity to electromagnetic interference, and hence specially required in some environment [5–16]. Usually, two major types of hydrogen sensitive materials are adopted in these fiber hydrogen sensors, Palladium (Pd) and Tungsten oxide (WO_3).

Pd or its alloy coating has the property of absorbing up to hundreds of times of its volume in hydrogen and consequently changing its RI [8–10]. Some Pd-coated sensors have high hydrogen sensitivities but require precise control of the thickness of the coating, typically in the order of nanometer. Many FBG or fiber interferometers types sensors based on strain induced by Pd coating on their surface have only low sensitivities (in the order of pm/%) [10,11], due to the large value of Young's modulus ($\sim 7.29 \times 10^4$ MPa). Although fiber tapering or etching processing can be effectively used to enhance the hydrogen sensitivity [12–15], it makes the sensors extremely fragile. The fiber Pd film-based sensors suffer from fatal fracture of Pd film caused by its α–β phase transition [16], and Pd can be oxidized by oxygen, which has negative effects on its hydrogen response capability [17]. Furthermore, humidity is another factor to affect the performance of these sensors [16,18].

WO_3 is a transition metal oxide with wide bandgap and perovskite-like atomic configuration based on corner-sharing WO_6 octahedra [19], and it exhibits significantly gasochromic response to hydrogen, which makes it useful for gas sensing [20]. Especially, in the presence of catalyst, such as Pt, WO_3 is easy to react with hydrogen at room temperature and results in refractive index variation [21,22] and heat emission [23–27]. Moreover, WO_3 film

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http://dx.doi.org/10.1016/j.snb.2017.01.206
0925-4005/

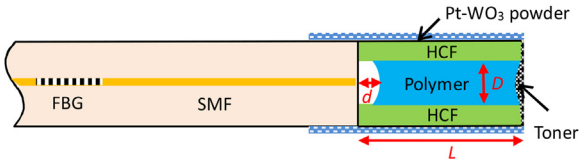

Fig. 1. Schematic of the proposed hydrogen sensor.

in nanostructure (including nano-particle, nano-rod, nano-wire, nano-platelet, etc.) appears to be more sensitive to hydrogen especially for relatively low hydrogen concentration due to its large surface to volume ratio [28,29]. Based on these features, various fiber hydrogen sensors coated with Pt-loaded WO_3 have been investigated. They are featured with ultra-high sensitivities, especially for those based on thermal effect [23–27]. For instance, the hydrogen sensors based on selectively infiltrated photonic crystal fiber or panda fiber with Pt-loaded WO_3 coating have sensitivities of 32.3 and 7.877 nm/% (vol%), respectively [26,27]. However, due to the large size of the sensing component (with length of several centimeters), the response (~100 s) and recovery time (several minutes) of these sensors to hydrogen are rather long.

In this paper, we report a highly sensitive hydrogen sensor prototype with compact size (<1 mm in length) and fast response (<30 s) and recovery time (<10 s). The sensor is based on an air-gap fiber Fabry-Pérot interferometer (AG-FFPI) coated with Pt-loaded WO_3/SiO_2 and incorporated with a FBG. The FPI is fabricated by fusion splicing of a single-mode fiber (SMF) with a short segment of hollow-core fiber (HCF) filled with polymer, which forms an air FP cavity. The heat induced by the chemical reactions between hydrogen and Pt/WO_3 modulates the cavity length of AG-FFPI, and by measuring the interference spectrum of the FPI, hydrogen concentration can be measured. The FBG cascaded with AG-FFPI can effectively compensate the surrounding temperature effect. The experimental results obtained show that the device proposed has a high sensitivity, short response and recovery time, good repeatability, and simple fabrication process.

2. Sensing principle

Fig. 1 shows the schematic of the proposed sensor. It consists of a FBG and a short segment of HCF filled with polymer. An air-gap at the interface between the SMF and the polymer forms a micro FP cavity. The lateral surface of the HCF is coated with Pt-loaded WO_3/SiO_2 powder which is sensitive to hydrogen while toner covered at the HCF end face is used to eliminate the undesired light reflection.

When the sensor is exposed to mix air with hydrogen (H_2), an exothermic reaction in catalytic layers (such as WO_3/SiO_2) that coated on the HCF surface was generated leading to the increase of ambient temperature [23,30]. Under a constant hydrogen concentration, such a process continuously provides heat to establish a thermal equilibrium in the catalytic layer, resulting in a local temperature change of the HCF, which changes the length of micro-cavity due to the thermal expansion of the polymer. As the micro-cavity forms a fiber in-line FPI, the hydrogen sensing can be achieved by monitoring the resonance wavelength shift induced by the temperature change.

For the AG-FFPI, the wavelength space between two adjacent resonance peaks/dips of the reflection spectrum is the free spectral range (FSR) given by [31]

$$\mathrm{FSR} = \frac{\lambda_m \lambda_{m+1}}{2nL}, \tag{1}$$

where m is an integer, λ_m and λ_{m+1} are any two central wavelength of adjacent peaks/dips of the reflection spectrum of the AG-FFPI and n is the refractive index (RI) of the medium in the micro-cavity (for an air cavity, n = 1). Based on this equation, the absolute cavity length L can be retrieved from the measured reflection spectrum. The wavelength shift of certain resonance peak/dip can be expressed as [31]

$$\Delta\lambda_m = \frac{\Delta L}{L} \cdot \lambda_m, \tag{2}$$

where $\Delta\lambda_m$ denotes the wavelength shift of the m^{th} interference dip, it depends on the variation of cavity length ΔL. When hydrogen reacts with WO_3 with Pt as the catalyst, heat releases during the chemical process. The air gap between SMF and polymer then is compressed because of the volume expansion of the polymer. Thus, the cavity length of AG-FFPI decreases and its reflection spectrum experiences a blue shift. Hence, hydrogen concentration can be obtained by measuring the wavelength shift.

It should be noted that surrounding temperature variation can also induce interference spectrum shift even when AG-FFPI is not exposed to hydrogen. In order to compensate such a surrounding temperature effect, a FBG without Pt-loaded WO_3/SiO_2 coating is adopted in our device, as displayed in Fig. 1. Such a FBG is placed far from the AG-FFPI to ensure that the FBG is only affected by the surrounding temperature. The shift of the Bragg wavelength, $\Delta\lambda_B$, due to temperature variation, ΔT_{FBG}, can be expressed as [32]

$$\Delta\lambda_B = \lambda_B \left(\alpha_F + \frac{1}{n_{eff}} \frac{dn_{eff}}{dT}\right) \Delta T_{FBG}, \tag{3}$$

where λ_B is the Bragg wavelength of the FBG, $\alpha_F$is the thermal expansion coefficient of the SMF, n_{eff} is the effective RI of the core material, dn_{eff}/dT is the thermo-optic coefficient, respectively. These parameters are all constants, so the Bragg wavelength shift is proportional to the variation of temperature, which provides a simple and convenient means for temperature compensation.

By combining Eqs. (2) and (3), and measuring the spectrum shift of the AG-FFPI, the hydrogen concentration can be easily and accurately determined.

3. Experiment

3.1. Fabrication of sensor

The proposed sensor is composed of a SMF with FBG splicing with a HCF. The FBG is written by traditional UV laser focused on hydrogen-loaded SMF, and its Bragg wavelength is ~1540.03 nm. The HCF is filled with a section of the monomer and the inner air-gap near the SMF-monomer interface forms a micro-cavity FPI (Fig. 1), and the end face of HCF is covered with toner. The surface of HCF is coated with Pt-loaded WO_3/SiO_2.

To fabricate the structure described above, the first step is to splice a segment of HCF to the SMF with a FBG. Then, to insert the HCF tip into liquid monomer, Norland Optical Adhesive 65 (NOA65), which is a photo-polymerizable liquid that can be cured by ultraviolet (UV) light with a maximum absorption in the range of 350–380 nm. Owing to the capillary action, the monomer gradually infiltrates into the HCF and forms an air-gap at the SMF-monomer interface. Fig. 2(a) shows the filling length versus time. According to Eq. (3) and the measured interference spectra, the total length of the original empty HCF is calculated as ~242 μm. The insets of Fig. 2(a) show the typical micrograph of the AG-FFPI and its reflection spectra for different cavity lengths. As one end of the HCF is closed, the filling speed is very slow. The micro-cavity length can be controlled by monitoring the reflection spectrum and adjusting the filling time duration. The second step is to take the HCF tip out from monomer when the air-gap reaches the desirable size, and then expose it to UV light. In order to diminish the disturbing light reflection occurred at the end face of the HCF tip, the end