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Effect of the Pd–Au thin film thickness uniformity on the performance of an optical fiber hydrogen sensor

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Abstract

Thin alloy film of Pd and Au, formed by simultaneous electron-beam and thermal evaporation techniques, respectively, is used in the design of an optical fiber hydrogen sensor. The sensor consists of a multimode fiber (MMF) in which a short section of single mode fiber (SMF), coated with the Pd–Au thin film, is inserted. Due to core diameter mismatch, the SMF cladding guides light, allowing the interaction between the sensing layer and the guided light. When the sensor is exposed to hydrogen, the Pd–Au layer refractive index diminishes and causes attenuation changes on the transmitted light. Several samples with different layer thickness uniformity were fabricated and tested in a very simple experimental set-up. We have observed that the sensor signal change is dependant on layer thickness uniformity, since the effective interaction length between the evanescent field and the sensing layer is increased. By contrast, such uniformity practically has no influence on the time response of the sensor. The resulting Pd–Au film can detect 4% hydrogen with a response time of 15 s.

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Keywords: Optical fiber sensors; Hydrogen sensors; Evanescent wave absorption; Core diameter mismatch; Thin film coating

1. Introduction

The unique properties of hydrogen (as an extremely clean and renewable source of energy) make it suitable as a fuel for internal combustion engines [1]. However, hydrogen is very volatile, extremely flammable and highly explosive; so, special safety procedures are necessary to store, manipulate, and transport it. Hence, the widespread use of this energy source will require reliable, cheap, fast, robust and durable monitoring systems to detect any eventual hydrogen leakage. Such sensors must be able to detect hydrogen at concentrations below the lower explosive limit (LEL) of 4% in air at normal conditions [2].

Most hydrogen sensors employ palladium as the transducer element due to its high sensitivity and selectivity towards hydrogen [3]. When palladium is exposed to hydrogen, the physical dimensions [4–9], and the electrical [10–13] and optical [14–26] properties of the metal are affected. The vast majority of hydrogen sensors rely on the monitoring of these parameters changes when palladium is exposed to hydrogen. Some authors have proved that Pd alloys can reduce the response time, and increase the stability and durability of a hydrogen sensor [14,16,21].

The inherent properties of optical fibers (such as light weight, immunity to electrical and magnetic noise, lack of a spark, remote and multiplexing capabilities) make them ideal for hydrogen sensing. Most of the optical fiber hydrogen sensors reported so far have been based on the interaction of the evanescent wave with a Pd thin film deposited over a section of the fiber [4,5,20–25]. When the Pd film is exposed to hydrogen the real and imaginary part of the film dielectric constant diminishes. As a consequence, the transmitted light suffers attenuation changes. The majority of the techniques used to enhance the evanescent field of an optical fiber consist in the reduction of the physical dimensions of the fiber (by etching, polishing or heating and pulling methods). Although, these techniques can produce strong evanescent fields, they actually weaken the fiber. One alternative to produce evanescent waves without reducing the fiber diameter consist in the insertion of a small piece of single mode fiber (SMF) between two multimode

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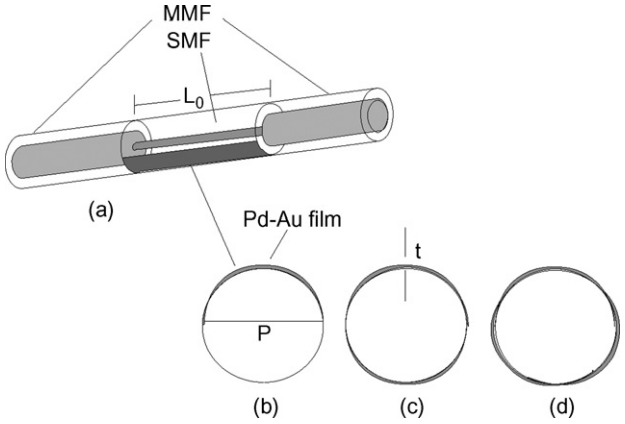

Fig. 1. Representation of the core diameter mismatch structured fiber. (a) This structured fiber consists of a small piece of single mode fiber (SMF) of 8 mm in length (L) between two multimode fiber (MMF) pieces. The sensing element is coated with a sensitive layer on (b) one side, (c) two sides at 180°, and (d) three sides at 120° of the SMF section.

fibers (MMF), as it is shown in Fig. 1(a), this optical fiber is known as core diameter mismatch structured fiber (CDMSF). In such a structure some modes guided by the MMF core are forced to propagate along the cladding of the SMF, and those modes produce an evanescent field in the cladding outer medium interface. In CDMSF, the outer diameter along the fiber is 125 μm. When the SMF section is coated with a Pd or a Pd alloy thin film, the fiber can be used for hydrogen sensing.

In this paper we propose the use of a CDMSF to make an experimental study of the response of a Pd–Au thin film deposited over the SMF section using a novel evaporation technique. The coating procedure consists in the simultaneous evaporation of Pd and some other elements, such as Au and Ag, which have been found to improve the Pd characteristics for hydrogen sensing. The alloying proportions of the composites are determined by the evaporation conditions.

The difficulty to produce a homogeneous thin film around the fiber, when thermal or electron-beam evaporation is used to coat the fiber, has motivated us to study the influence of the layer uniformity on the sensor response. Hu et al. [21] have proposed to rotate the fiber during the evaporation process, but this technique can be difficult to use when the fiber diameter is thinner than 20 μm, when two or more materials are deposited simultaneously at different evaporation rates, or when the thickness of the layer is less than 10 nm. In such cases, there is an alternative in which the fiber to be coated is placed into a mechanical mount in the shape of an equilateral triangle with a small window – of length L – on each side. A single layer is evaporated onto each window of the mount, which is equivalent to depositing a layer onto the structured fiber every 120°. This process ensures a nearly circular layer of thickness t [28–30].

We have fabricated and tested three different Pd–Au coated CDMSF for hydrogen sensing. In the first one, we evaporated the thin film over one side of the fiber (see Fig. 1(b)). In the second, the film was deposited over two opposite sides of the fiber (see Fig. 1(c)), and in the final structure, three film depositions were done by rotating the fiber 120° between two consecutive depositions (see Fig. 1(d)). All the Pd–Au films evaporated have the same thickness.

2. Sensor fabrication and working mechanism

The proposed CDMSF is represented in Fig. 1(a). This fiber has been previously reported for acidity [27] and refractive index [30,31] measurement. The fabrication of our sensors was carried out in two sequential steps. First, the CDMSF was constructed by inserting a small piece of single mode fiber into a graded index multimode fiber. The end of each fiber pieces was cleaved with a high-precision fiber cleaver (S321, Furukawa Ltd.); after that, a thermal fusion splicer (S-147S, JDS FITEL Inc.) was used to incorporate all the elements to the structure. We used an 8-mm length of standard step-index SMF and two pieces of graded-index MMF of 40 m in length each; the core diameter of SMF and MMF was 9 and 62.5 μm, respectively. In a CDMSF, the light guided by the multimode fiber core is partially coupled to the single mode fiber core and the rest is forced to propagate as modes of the cladding. The evanescent wave is extended beyond the SMF cladding and may interact with the surrounding medium. The evanescent field strength can be enhanced by increasing the core diameter differences between the MMF and SMF's. Note that this CDMSF is very easy to fabricate, taking only a few minutes, and it was fabricated with standard SMF and MMF so the cost is low. In contrast with the traditional methods to enhance the evanescent field, where the fiber diameter is reduced, in CDMSF, the outer diameter of the fiber is not modified, so the final structure is strong and easy to handle.

In the next step, samples were cleaned with alcohol and acetone; after that they were mounted on individual rigid metallic pieces and put inside a vacuum evaporator chamber. These metallic pieces prevent the fiber bending that can seriously affect the sensor performance. Before the evaporation, an argon ion discharge was applied to the samples in order to clean them. Palladium and gold were deposited simultaneously at different evaporation rates to coat the SMF. The alloying of the Pd can decrease the time response of a sensor and increase the durability of an optical fiber hydrogen sensor, as was demonstrated by Carpenter and coworkers [16]. Palladium was evaporated by an electron gun with a current of 26 mA at a rate of 2 Å/s. Gold was deposited by thermal evaporation with a current of 12 A at a rate of 1 Å/s and 1.4×10^{-4} mbar vacuum. The evaporation rate and layer thickness of Pd and Au were measured with two crystal quartz monitors. Palladium and gold pellets of high purity (99.99%) were used. The total Pd–Au thickness of 10 nm was measured. After the first film deposition, the chamber was opened and some samples were taken out. Some of the samples that were left in the chamber were rotated 180°, while the rest were rotated 120°. The second evaporation was carried out following the same procedure described above; after that, we took out the fibers that had been rotated 180°. Finally, we rotated the fibers another 120°, and deposited over them the last Pd–Au thin film. It is important to notice that this evaporation technique, in contrast with that reported in [21], allows us to fabricate several