Optical fiber hydrogen sensor based on photothermal reflectance detection technique

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Abstract. This article proposes an optical fiber hydrogen (H₂) sensor based on photothermal reflectance [hereinafter modulated optical reflectance (MOR)] technique. Our H₂ sensor is based on a technique that detects the changes of MOR signals in palladium film, which is widely known to absorb H₂ gas. The sensor element is a palladium film deposited on a 2.5-mm-diameter FC-ferrule made from zirconium to realize the optical fiber sensor. Our recently developed “laptop” MOR instrument assembled with optical fiber components is applied to this technique. Thus, an extremely compact photothermal H₂ gas sensor system can be constructed. We certified that our technique has hypersensitive less than 1% with a concentration of H₂ gas and also demonstrated that the response time is approximately 5 seconds when the sensor head is filled with H₂ gas.

1. Introduction

The current intense interest in hydrogen (H₂) sensors reflects applications concerned with the potential use of metal-H₂ systems in energy storage and for monitoring pipeline corrosion [1],[2]. This is because the dangers associated with the use and storage of H₂ have always been tremendous. For example, a leak of gaseous H₂ leads to an easily ignited explosive atmosphere for H₂ concentrations by volume of more than 4% in air at room temperature and atmospheric pressure [3]. For this reason, highly sensitive H₂ sensors are required to prevent accidents caused by leaks. Several H₂ sensors have been proposed, developed, and commercialized; however, all have technical shortcomings. Most H₂ sensors, which are based on the detection of electrical resistance with semiconductors, have high sensitivity and rapid response, but they consume large amounts of electric power during operation because of maintaining the sensing element of device to high temperature [3],[4].

Recently, a photothermal electrostatics pyroelectric H₂ gas sensor system was proposed by A. Mandelis et al. to obtain high sensitivity and to improve the previous shortcomings [3],[5],[6]. It is widely recognized that a fiber optics technique provides a means to deal with the electromagnetic noise that interferes with the H₂ sensor’s electrical output signal. Accordingly, the adoption of a fiber optics technique is significant, not only for reducing the weight of the sensing element but also to avoid malfunctioning due to the external electromagnetic noise, despite non-shielding [2]. In this article, we propose a new optical fiber hydrogen sensor based on a photothermal reflectance [hereinafter modulated optical reflectance (MOR)] detection technique. Our photothermal H₂ sensor is based on a technique that detects the changing of MOR signals in palladium (Pd) film, which is widely known to absorb H₂ gas. Our recently developed laptop MOR instrument, assembled with optical fiber components, is applied to this technique, suggesting the advantage of a photothermal technique based on fiber optics [7].
2. Measurement system

Figure 1 shows the H₂ sensing head composed of a FC-ferrule prepared for a MOR detector with the following sensing principle. The thermoproperties of the evaporated palladium (Pd) film, which absorbs H₂, are believed to transit generously, changing the detected MOR signal, when the H₂ gas fills the sensing head. In other words, this result was tentatively attributed to the adsorption of H₂ molecules on the Pd surface that caused a shift of the thermal diffusivity. To confirm this phenomenon, we prepared (Fig. 1) a 250-nm-thick Pd film and deposited it on a cross section of a 2.5-mm-diameter FC-ferrule made from zirconium, whose single mode fiber and its core diameters were 125 and 6 μm, respectively. Consequently, the actual net size of the sensing element is just 6 μm in diameter. Furthermore, 250 nm in film thickness was tentatively chosen for a trial study with our proposed technique.

Figure 2 shows our recently developed laptop MOR instrument whose primary feature is that all of the optical routes for pumping and probing the MOR and the two light sources using a laser diode are composed of optical fiber and fiber components such as a fiber coupler [7]. A laser diode module with a wavelength of 1.47 μm and a fiber output power of 110 mW was used as the pumping beam’s light source, and a super luminescence diode (SLD) module with a wavelength of 0.83 μm and a fiber output power of 1 mW was used as the probe beam. The laptop-sized and weighted instrument case contains optical components, such electro-optics devices as a laser diode, and electronics for driving these devices. Consequently, due to the actualization of this instrument, we believe that a H₂ gas sensor can be achieved using a photothermal sensing element less than a few hundred μm in diameter without deleterious effects from electromagnetic noise.

To instantly confirm the above phenomena, we adopted the following techniques. Maximum length (M)-sequence random numbers were used as the pseudo modulation signal [8], and a vector signal analyzer (Agilent 89410A) was used to display and confirm the frequency characteristics of the MOR signal in real-time. Due to this technique, the MOR signal, which is associated with the optical reflectance, became a cross spectrum signal between the modulation signal by the M-sequence random numbers and the output signal from our MOR instrument.

Figure 1. H₂ sensing head.

Figure 2. Measurement system based on laptop MOR instrument.
3. Measurement results

First, the most widely used digital pseudorandom techniques in photothermal applications were derived from pseudorandom binary sequences (PRBS), generated as two level signals using shift registers [8]. The PRBS in our technique was based on an M-sequence in which \( N=2^n-1 \), where \( N \) is a binary bit in the sequence and \( n \) is an arbitrary integer. Here, \( n \) corresponds to the degree of the shift register, and we used handmade electronic circuits for generating the M-sequence signal with \( n=42 \). The power spectrum of this signal was DC to approximately 500 KHz. The pumping beam from the laser diode module with a wavelength of 1.47 \( \mu m \) was electrically modulated with this signal. Thus, the distribution probability density of this signal can be assumed to be in the frequency range between a few Hz and a few hundred KHz, which is as flat as possible, even though the M-sequence PBRS remains mathematically quite different from pure white noise.

The gas chamber contains the sensing head shown in Fig. 1 and \( \text{H}_2 \) gas of high purity (99.9 %) was filled in the chamber after the air was purged using a turbo molecule pump with the pressure reaching at least \( 5 \times 10^{-4} \text{ Pa} \). Here, it is generally known that Pd metal absorbs \( \text{H}_2 \) gas selectively, resulting in a cubical expansion, so that other gases included in atmosphere, such as nitrogen and oxygen does not assume reactivity in our sensor until \( \text{H}_2 \) gas exposing.

Figure 3 shows the cross spectrum between the MOR signal and the pseudo modulation signal dependence on the frequency as a function of the volume concentration of the \( \text{H}_2 \) gas. The frequency-domain signal (Fig. 3) was calculated by a vector signal analyzer. Correlation and spectral processing, which averaged over 100 frequency sweeps with 1024 data points per sweep, required just a few seconds. Such signal processing time is dramatically high-speed due to using a vector signal analyzer compared with the conventional PRBS photothermal technique [8], thereby realizing real-time frequency-domain measurement. As seen in Fig. 3, the MOR signal is affected by the absorption of \( \text{H}_2 \). The remarkable point is that our technique has hypersensitive less than 1% with a concentration of \( \text{H}_2 \) gas, suggesting the sensing of a slight \( \text{H}_2 \) gas leak before ignition. Referring to the experimental results shown in Fig. 3, the concentration of the \( \text{H}_2 \) gas dependence of the MOR signal (Fig. 4) was scrutinized when the modulation frequency was fixed at 50 KHz. The concentration of the limit of detection in our \( \text{H}_2 \) sensor is estimated to be approximately 0.05%, and the MOR signal was saturated after the consistency exceeds 3% and when the thickness of Pd film is 250 nm. These results confirmed that our sensor is applicable for high-sensitive sensing during slight \( \text{H}_2 \) gas leaks in industrial plants.

![Figure 3](image1.png)  
**Figure 3.** Cross spectrum between MOR signal and pseudo modulation signal.  
**Figure 4.** Volume concentration of \( \text{H}_2 \) gas dependence of MOR signal.  
Pd film thickness: 250 nm.
Figure 5 shows the specific time response characteristics of our H₂ sensor. A conventional lock-in technique for signal recovering was used in this measurement, and the modulation frequency was set to 50 KHz, which was determined based on the results shown in Fig. 3. As seen in Fig. 5, the response and retrieval start times of our technique are approximately 5 and 30 seconds in case of being filled with and purging the H₂ gas, respectively. Consequently, we confirmed that our sensor technique has sufficient performance from a standpoint of the response time for trapping the H₂ gas. Fig. 5 also shows that the estimated perfect retrieval time is approximately two minutes. This is due to a sufficient time requirement for releasing the H₂ gas absorbed in the Pd. Additionally, the measurement results in Fig. 5 suggest that the detected signals do not completely return to their original values (i.e., 1.0), even though over ten minutes elapsed after the H₂ gas was purged.

The reason for this is probably because the internal mechanical stress in a film, caused by the repetition between H₂ gas adsorption and separation, influenced the thermo properties of the Pd film, resulting in MOR signal transition. Furthermore, we believe that recovery specificities such as a recovery time after the purge of H₂ gas are different, depending on the consistency of oxygen because of a catalytic action of Pd, when H₂ gas is released from Pd film.

4. Summary
This article proposed an optical fiber hydrogen sensor based on an MOR technique. The sensor element is a Pd film deposited on a 2.5-mm-diameter FC-ferrule made from zirconium, and its actual net size is just 6 μm in diameter. This ferrule functions like a sensing probe, and it is fed to our recently developed laptop MOR instrument that is suited for constructing a sensing system for H₂ gas. Basically, our technique’s principle is MOR signal transition, which is attributed to the thermoproperties of Pd film, and is associated with the consistency of the absorbed H₂ gas. We confirmed that our sensor has high sensitivity for actual use, and gas concentration less than 1% can be detected. We assumed that the response and perfect retrieval times are approximately 5 and 150 seconds for being filled with and purging H₂ gas, respectively. We also certified that our sensor technique provides sufficient performance from a response time standpoint for trapping the H₂ gas. Improving the sensing element to prevent performance deterioration with repeated use will be required in the future.

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