

Article

Low-Dimensional Palladium on Graphite-on-Paper Substrate for Hydrogen Sensing

Boyi Wang ¹, Takeshi Hashishin ² , Dzung Viet Dao ³  and Yong Zhu ^{3,*} 

¹ School of Mechanical and Electronic Engineering, Wuhan University of Technology, Wuhan 430070, China; boyi.wang@whut.edu.cn

² Faculty of Advanced Science & Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan; hashishin@msre.kumamoto-u.ac.jp

³ Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia; d.dao@griffith.edu.au

* Correspondence: y.zhu@griffith.edu.au

Abstract: To stabilize the detection signal of palladium-based hydrogen sensors on paper substrates, a graphite intermediate layer was painted on the surface of paper. The graphite-on-paper (GOP) substrate offers advantages such as good thermo-electrical conductivity, low cost, and uncomplicated preparation technology. Quasi-1-dimensional palladium (Pd) thin films with 8 nm and 60 nm thicknesses were deposited on the GOP substrates using the vacuum evaporation technique. Thanks to the unique properties of the GOP substrate, a continuous Pd microfiber network structure appeared after deposition of the ultra-thin Pd film. Additionally, the sensing performance of the palladium-based hydrogen sensor was not affected, whether using GOP or paper substrate at 25 °C. Surprisingly, heating-induced loss of sensitivity was restrained due to the increased electrical conductivity of the GOP substrate at 50 °C.

Keywords: palladium; graphite on paper; hydrogen sensor; low-dimensional; microfibers networks



Citation: Wang, B.; Hashishin, T.; Dao, D.V.; Zhu, Y. Low-Dimensional Palladium on Graphite-on-Paper Substrate for Hydrogen Sensing. *Sensors* **2022**, *22*, 3926. <https://doi.org/10.3390/s22103926>

Academic Editor: Karim Benzarti

Received: 7 May 2022

Accepted: 19 May 2022

Published: 22 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Hydrogen (H₂) gas has a wide range of applications, including in spaceships, commerce, propulsion systems [1], H₂ fuel cells [2], and H₂-fueled cars [3]. Furthermore, it is also widely used in scientific research and industrial manufacturing. As a clean, economical, and environmentally friendly energy carrier, H₂ has the potential to replace fossil fuels [4]. Hence, the problems of air pollution and greenhouse gas emissions can be addressed. Although H₂ is a clean form of energy in our daily life, it explodes when its concentration is over 4% in air. Due to the properties of H₂, leaked H₂ cannot be detected by human senses. To use H₂ with safety, a rapid, economical, reliable, and feasible H₂ detection and measurement device is generally required for all H₂-based applications. Typically, the devices available on the market that have been employed in H₂ detection and measurement are metal-oxide-based H₂ sensors [5]. However, these H₂ sensors do not present the same superior sensing performance as palladium (Pd)-based H₂ sensors [6–10].

Pd and its alloys have been reported as being excellent sensing materials for H₂ detection and measurement, presenting a higher sensitivity to and selectivity for H₂ at room temperature. While Pd alloys show better properties with respect to H₂ sensing and inhibition of α to β phase transition [7], the alloy deposition process is complicated and costly. To achieve higher H₂ sensing performance, pure Pd H₂ sensors with a low-dimensional structure have been investigated for H₂ leakage detection and concentration measurement [4].

Low-dimensional pure Pd H₂ sensors have been a significant subject for research and application in the last few decades. Because they can provide a larger surface area-to-volume ratio and shorter diffusion path, the response time, recovery time, and gas response

of these H₂ sensors can be improved significantly. Recently, various low-dimensional Pd H₂ sensors have been reported by several researchers. Kim et al. [11] demonstrated that a nanoporous Pd film was formed using anodic aluminum oxides (AAOs) template with a microelectromechanical system (MEMS) fabrication technique. The unique template allowed the deposited Pd thin film to have a larger surface area-to-volume ratio than a flat Pd thin film, which led to improved sensing performance for the H₂ sensor. Although it had the advantage of a large surface area-to-volume ratio, the response time was unsatisfactory, and the gas response was lower at increased detection temperatures. As a further development of low-dimensional Pd H₂ sensors, a single Pd nanowire was reported by Offermans et al. [12]. This H₂ sensor showed a faster response and higher gas response when exposed to H₂. While the lower-dimensional Pd nanowire provided a larger surface area-to-volume ratio than the thin film, the fabrication was complex and uncontrollable. The research group of Zeng et al. [1,9] focused on investigating networks of ultrasmall Pd nanowires on filtration membranes. This particular Pd nanowire network structure was easily formed after deposition of Pd on the surface of the expensive filtration membranes. Because the Pd ultra-thin film was directly deposited on the rough surface, the broken Pd nanowires resulted in an unstable sensing performance when exposed to high H₂ concentrations. Therefore, a chromium (Cr) layer was deposited in between the substrate and the Pd thin film to modify the Pd–substrate interaction, which in return reduced the critical thickness of the Pd layer required to form a continuous Pd nanowire network [1]. Although the response speed of the H₂ sensor was improved by decreasing the thickness of the Pd film and increasing the temperature, heating-induced loss of sensitivity still existed, as reported by Li et al. [13]. The solubility of H in Pd was reduced at increased temperatures, resulting in sensitivity disparities between the sensor at room temperature and at high temperature.

In this paper, unstable sensing performance of the ultra-thin Pd film was observed when 8 nm Pd was coated directly onto the paper substrate. To address this issue, we proposed to introduce a graphite layer between the Pd thin film and the paper substrate. Based on the surface texture of the GOP substrate, ultra-thin (≤ 10 nm) and thin (≤ 100 nm) continuous Pd microfiber networks were formed by using a conventional vacuum evaporation technique. The surface morphology of the quasi-1-dimensional (1.5D) Pd sensing layer was clearly observed using a scanning electron microscope (SEM). The effect of the intermediate graphite layer on the H₂ sensing performance of the sensor at different detection temperatures is evaluated and determined in this study. Additionally, heating-induced loss of sensitivity for 60 nm Pd film at 50 °C was restrained.

2. Materials and Methods

2.1. Sensor Fabrication

It is well known that paper (A4/80gsm, Paper Australia Pty Ltd, Victoria, Australia) possesses several advantages, including low cost, light weight, and ubiquity. Hence, as the substrates of the H₂ sensors in this study, these advantages can contribute to the investigation and development of Pd-based H₂ sensors. A thin graphite layer was painted on the surface of the paper to produce a GOP substrate. Subsequently, pure Pd layers with thicknesses of 8 nm and 60 nm were deposited on the surface of the GOP substrates. The physical properties of graphite allow it to be coated onto paper substrates by hand without damaging the surface texture. Therefore, the 1.5D structure of the Pd microfiber network can be formed on the substrate following the deposition process, which in return results in a larger surface area-to-volume ratio. In this context, the H₂ sensor can be improved with respect to its sensing performance.

The simple step-by-step fabrication process of the H₂ sensor is briefly depicted in Figure 1. The most crucial step before the sensor fabrication process is to clean and remove the surface dust on the paper using a high-pressure nitrogen gun (Figure 1 (2)). To acquire a homogeneous graphite layer on the surface of paper, it is necessary to paint the graphite onto a large surface area of the paper under the same conditions. Soft graphite is the

primary material in a 5B pencil, and this was used to coat the graphite layer onto the surface of the paper. However, the GOP substrate was formed with an excessive amount of graphite debris remaining on the surface. Therefore, the debris was removed using a high-pressure nitrogen gun. This treatment makes it possible for the Pd thin film to achieve high-quality adhesion to the surface of GOP during the deposition process (Figure 1 (3)). Prior to Pd deposition, the GOP was cut into pieces with dimensions of 20 mm by 5 mm as the individual substrates for the H₂ sensors. Pd metal wire with a purity of 99.95% was placed on a molybdenum boat in a vacuum evaporation system (VPC-260, ULVAC Technologies, Inc., Methuen, MA, USA). This system was used to achieve a high film density (superficial density), resulting in improvement of the mechanical properties of the Pd thin film. Pd films with two different thicknesses (8 nm and 60 nm) were deposited on the substrates under vacuum of 3.8×10^{-5} Torr and a current of 90 amperes. The deposition times for the films with thicknesses of 8 nm and 60 nm were different, and were controlled in accordance with the deposition rate. Subsequently, Pd microfiber network structures with different film thicknesses were formed on the GOP substrates following the deposition process (Figure 1 (4)). In order to compare their sensing performance, an 8 nm pure Pd thin film was also deposited on the same paper substrate without the graphite under the same evaporation conditions. Finally, silver electrodes were formed on the edges of the sensors using silver epoxy (Figure 1 (5)).

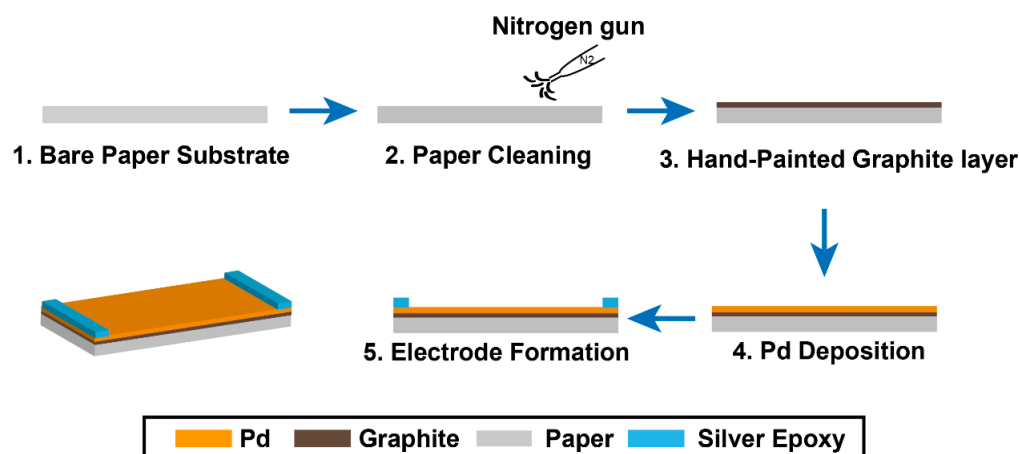


Figure 1. Schematic illustration of the fabrication steps of the palladium (Pd) microfiber network H₂ sensor based on graphite-on-paper (GOP) substrate.

2.2. Sensor Measurements

The fabricated sensors with various thicknesses of Pd film were placed into a sealed quartz tube (gas chamber) for H₂ detection and concentration measurements. Due to the resistive detection mechanism of the Pd-based H₂ sensor, the sensor can be regarded as a variable resistor connected to a simple voltage divider circuit, as illustrated in Figure 2. A mass flow controller (MFC) was employed to control the flow rates of pure nitrogen and 1% H₂ gas, resulting in various concentrations of H₂ as the detection gas. H₂ is well known to be a highly explosive gas; when its concentration reaches or is over 4% in air, a small spark can induce a violent explosion during either application or research. Therefore, for safety reasons, the maximum concentration of H₂ was strictly controlled to be no more than 1% (10,000 ppm).

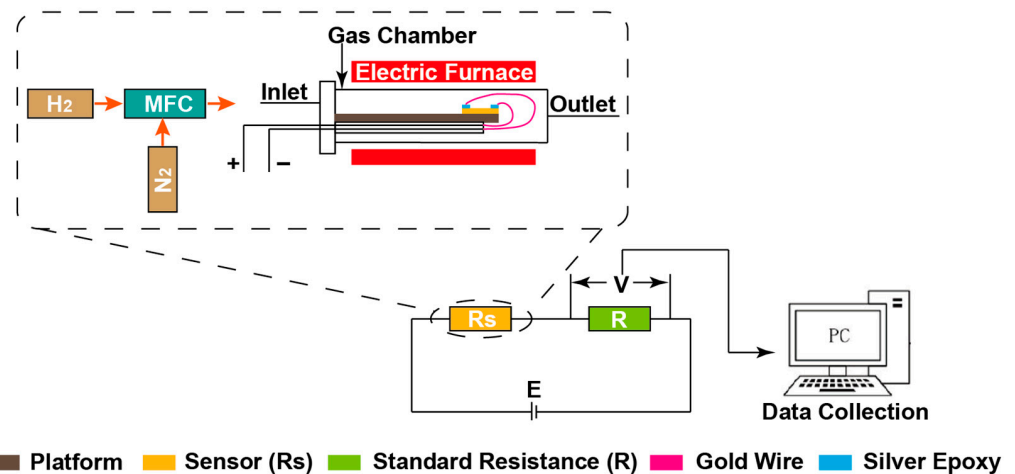


Figure 2. Schematic diagram of a simple H₂ measurement circuit. The inset shows the testing system of the H₂ sensor, including mass flow controller (MFC) and gas chamber.

In this paper, two different thicknesses (8 nm and 60 nm) of Pd film were on GOP substrates, while one reference sample (8 nm Pd) was on a paper substrate. To obtain a reasonable evaluation of the performance for these H₂ sensors, they had to be separately subjected to the same test steps and conditions. When the sensor was placed into the chamber, first, pure nitrogen gas was fed into the chamber for approximately 10 min in order to remove the remaining gases in the chamber. The flow rate of the mixed H₂ gas was kept constant at 100 standard cubic centimeters per minute (SCCM) during the H₂ testing process. To investigate the repeatability during each test, each H₂ concentration was maintained for three cycles, and each cycle was set to a duration of 600 s. Each cycle included 300 s for the interaction of the thin film with mixed H₂ gas, and 300 s for sensor recovery. As shown in Figure 2, based on the simple H₂ measurement circuit, the changes in sensor resistance (R_s) with different H₂ concentrations were converted directly into changes in the measured voltage (V), which comprised the final data that were collected. To minimize the self-heating effect during testing, the applied DC voltage source, E, was chosen to be fixed at a low voltage of 1 V. The standard resistance, R, was adjusted to be similar to the initial resistance of each H₂ sensor, ensuring a linear sensor response. To obtain accurate data, the measured voltage was recorded using a digital multimeter once per second and logged on a computer while the sensor was exposed to each H₂ concentration. Furthermore, the effect of the ambient temperature on the sensing performance is also considered in this paper. Hence, the H₂ sensors were tested separately temperatures of 25 °C and 50 °C. The expression of the gas response (S) was given by

$$S = \frac{R_H - R_0}{R_0} \times 100\% \quad (1)$$

where R_H and R₀ are the sensor resistance upon exposure to H₂ and nitrogen, respectively. All of the measurements were carried out for H₂ concentrations of 100 ppm, 2000 ppm, 4000 ppm, 6000 ppm, 8000 ppm, and 10,000 ppm, respectively.

3. Results and Discussion

3.1. Characterization of Pd Thin Film

The surface morphology of the deposited Pd thin film on the GOP substrate was observed using a scanning electron microscope (SEM). The microscopic surface images of the texture detail are presented in Figure 3.

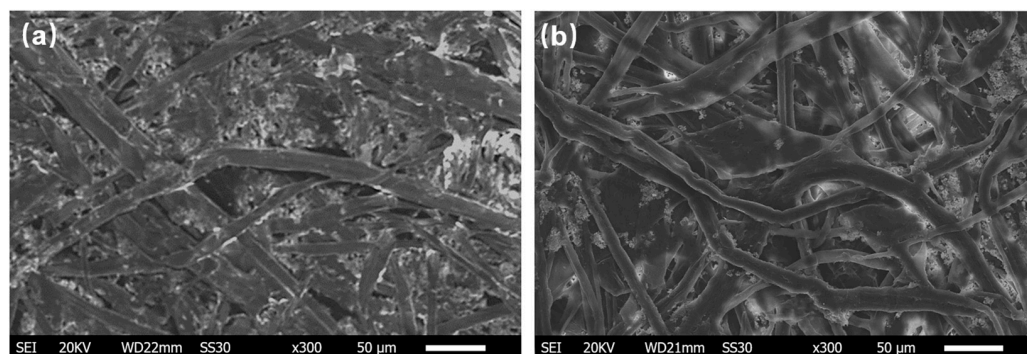


Figure 3. Scanning electron microscope (SEM) images of the surface of (a) the paper coated with graphite (GOP substrate), and (b) 8 nm Pd thin film deposited on the GOP substrate.

The surface texture of paper was not damaged after graphite was coated on the paper substrate, as shown in Figure 3a. The continuous Pd microfiber network structure was formed and is clearly presented in Figure 3b, and the average diameter of the Pd microfibers was approximately 30 μm . The structural characteristics are the key factors for determining the dimensions of the materials. For instance, thin film and nanowire are defined as being two-dimensional (2D) and one-dimensional (1D) structures, respectively [14]. Based on these principles, the nanosized Pd thin film combined with the surface texture of the GOP substrate can be regarded as 1.5D (quasi-1D) structure. This low-dimensional nanostructure contributed to the improvement in H_2 sensing performance, due to the large surface area-to-volume ratio. The detailed performance of the H_2 sensor is further analyzed and discussed later in this section.

3.2. Electrical Properties of the GOP Substrate

To verify that graphite is a suitable intermediate layer for the H_2 sensor, the sensitivity of graphite to H_2 was investigated. Figure 4 demonstrates that the resistance value of the GOP substrate remained steady when it was exposed to 10,000 ppm H_2 over 300 s. Hence, the GOP substrate was confirmed to be insensitive to H_2 , which is due to the electrical properties of the graphite intermediate layer not being influenced by H_2 .

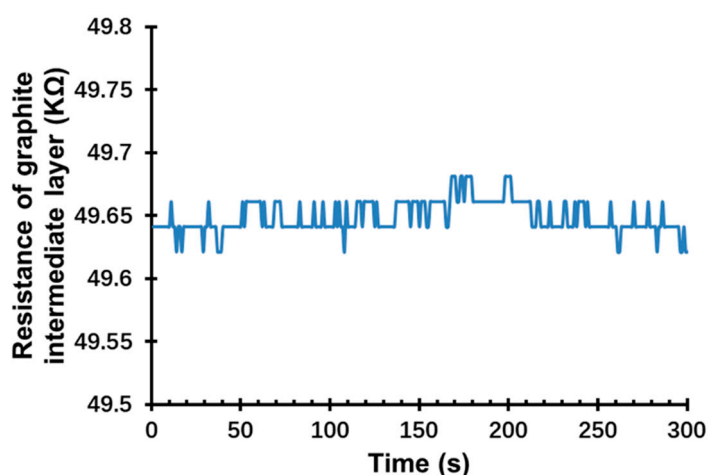


Figure 4. Changes in the resistance of the graphite intermediate layer when exposed to 10,000 ppm H_2 .

3.3. Discontinuity Issue in the 8 nm Pd/Paper and Graphite Intermediate Layer Solution

As observed in Figure 5, the resistance changes in the reference sensor (Pd on paper) resulted in an unstable detection curve, presenting two peaks when H_2 was turned on and off. According to Figure 3, the surface morphology of the paper substrate showed high surface roughness. Therefore, after ultra-thin (8 nm) Pd film was deposited on the surface

of the paper substrate, there were discontinuous microfibers coexisting with the continuous Pd microfibers. When H_2 was turned on, initially, the resistance of the reference sensor increased sharply due to the absorption of H_2 in the continuous Pd microfibers. However, when the Pd lattice had expanded enough to close the gaps between the discontinuous microfibers, the resistance started to decrease, as shown in Figure 5. A similar response behavior was found when H_2 was turned off. When the absorbed H_2 was released from Pd, the affected microfibers shrank to their initial discontinuous state, thereby reopening the gaps between the microfibers [10]. Hence, the resistance of the reference sensor increased significantly at the second peak, as shown in Figure 5. Then, the resistance decreased as a result of the release of H_2 from the continuous Pd microfibers.

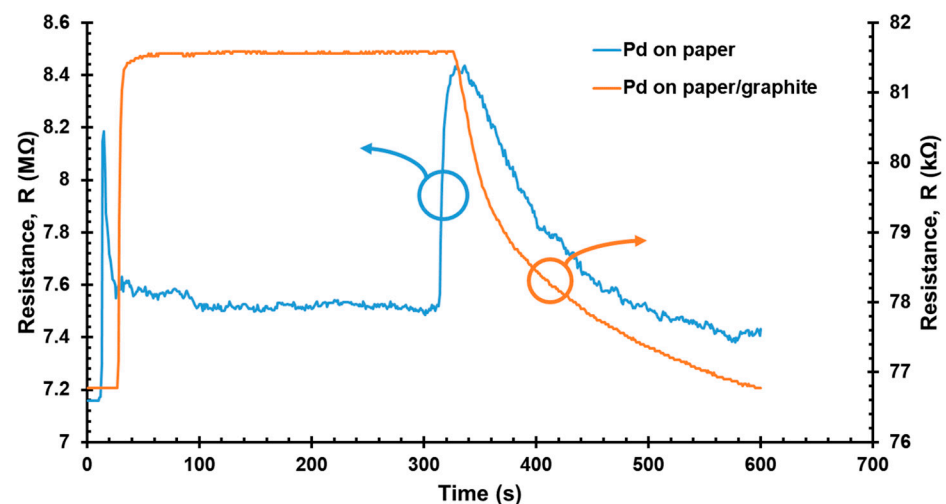


Figure 5. Resistance changes of 8 nm Pd on the normal photocopy paper (NPP) substrate and 8 nm Pd on the GOP substrate when exposed to 10,000 ppm H_2 at 25 °C.

This curious response behavior has previously been reported for pure 7 nm Pd nanowire operating in N_2 [9], it was difficult to determine the response time and gas response of the sensor on the basis of response curves like this. Although the thinner Pd film on roughness surface is able to provide a faster response and higher sensitivity, the unstable detection curve resulting from the discontinuities in the Pd microfiber is a critical issue that needs to be addressed. Therefore, an intermediate layer with high resistance and insensitivity to H_2 was utilized to modify the interaction of Pd with the paper substrate, and to address the issue of discontinuity in the ultra-thin Pd film on the substrate. In this experimental study, graphite is proposed as an intermediate layer for the H_2 sensor based on ultra-thin Pd film. As demonstrated in Figure 5, the sensor with 8 nm Pd on the GOP substrate exhibited smooth resistance changes, and an unsteady detection curve was not observed due to there being no discontinuous microfibers present. Hence, the low-cost and commonly available graphite can be regarded as a potential non-metallic intermediate layer for discontinuous ultra-thin Pd films on paper substrate.

3.4. Sensor Performance of Pd Film on GOP and NPP Substrates at Room Temperature

The response time and gas response are the two primary parameters for the evaluation of H_2 sensors. Response time is defined as the time taken to achieve 90% of the total change in sensor resistance, and the gas response can be determined using Equation (1). To investigate whether the response time and gas response of the sensor are affected by the GOP substrate, the sensing performance of the sensor comprising Pd film with a thickness of 60 nm on a GOP substrate was compared to our prior work [15], as illustrated in Figure 6.

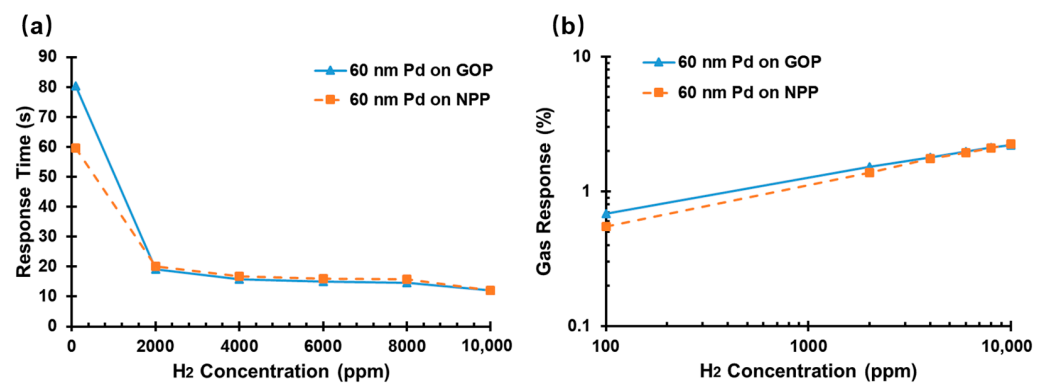


Figure 6. Performance of 60 nm Pd thin film H₂ sensors based on NPP (Reprinted with permission from Ref. [15]. 2022, Springer Nature) and GOP substrate at various H₂ concentrations at 25 °C. (a) Response time; (b) gas response.

A comparison experimental investigation was carried out to illuminate the differences in sensor resistance between the NPP and GOP substrates at 25 °C, as shown in Figure 6. Due to both sensors having the same Pd thickness, the response times showed no obvious differences between when 60 nm Pd on NPP and GOP substrates were exposed to the concentration of 2000 ppm to 10,000 ppm at 25 °C. The response times of 60 nm Pd on both substrates were equal to one another, 12 s (10,000 ppm H₂, at 25 °C). However, the inherent texture of the paper surface was inevitably damaged by using a 5B pencil to hand paint it on paper, resulting in the surface area-to-volume ratio of the same thickness of Pd on GOP substrate being less than that on the NPP substrate. The large surface area-to-volume ratio provided fast response speed at low H₂ concentrations. Thus, 60 nm Pd on NPP substrate appeared to have a faster response speed than on the GOP substrate when they were exposed to 100 ppm H₂ at 25 °C, as shown in Figure 6a. As graphite is insensitive to H₂, the degree of PdH_x reaction is the same for equivalent thicknesses, and the gas responses of 60 nm Pd on NPP substrate and GOP substrate were approximately the same at 25 °C, as presented in Figure 6b. The maximum difference in gas response was smaller than 0.15% between the GOP and NPP substrates (2000 ppm H₂, 1.51% for 60 nm Pd on GOP substrate and 1.37% on NPP substrate).

3.5. Temperature and Thickness Effect for Pd on GOP

Apart from the H₂ concentration, the sensor output is also dependent on the ambient temperature and thickness of the film, as shown in Figure 7.

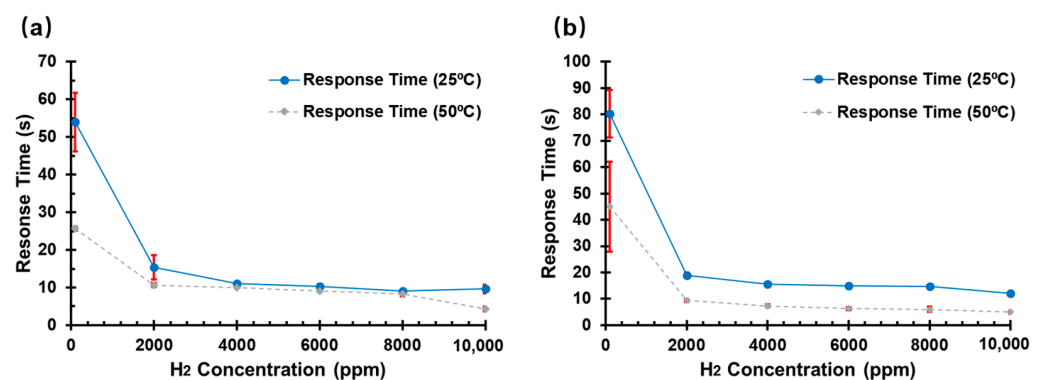


Figure 7. Response time (with standard deviation, sample number (N) = 3) of H₂ sensors based on Pd thin film on GOP substrate at various H₂ concentrations and temperatures (25 °C and 50 °C): (a) 8 nm and (b) 60 nm.

At 25 °C and 10,000 ppm H₂, the response times of the Pd-based H₂ sensors on the GOP substrate with Pd thicknesses of 8 nm and 60 nm were 9.7 and 12 s, respectively. This

phenomenon can be explained by Fick's 1st Law, whereby a shorter H₂ diffusion path will lead to an increase in the H₂ diffusion flux of the Pd film at the same H₂ partial pressure (H₂ concentration). Therefore, the H₂ sensor based on 8 nm Pd on a GOP substrate presented a shorter response time. The effect of temperature on the response times of the H₂ sensors is also illustrated in Figure 7. The response time of 8 nm and 60 nm Pd to 10,000 ppm H₂ decreased from 9.7 s to 4.3 s and from 12 s to 5 s, respectively, when the temperature was increased to 50 °C. The thermal energy increases with increasing temperature, leading to an acceleration in the movement of the gas atoms. Hence, the absorption rate and diffusivity of hydrogen atoms in Pd thin film are strongly promoted. Furthermore, the average standard deviations (N = 3) of the response time for the 8 nm and 60 nm Pd/GOP-based sensors were less than ±1% when the sensors were exposed to concentrations of 2000 ppm to 10,000 ppm, as shown in Figure 7. The Pd/GOP-based H₂ sensors presented good repeatability when H₂ concentration was over 2000 ppm.

3.6. Suppression of Heating-Induced Loss Gas Response

Although the response time was reduced by increasing temperature or decreasing thickness, the gas response of the Pd-based hydrogen sensor can be affected by changes in temperature [15]. As shown in Figure 8a, the gas response of 60 nm Pd on the NPP substrate decreased at elevated temperature, which was due to the reduced solubility of H in Pd with the increased temperature.

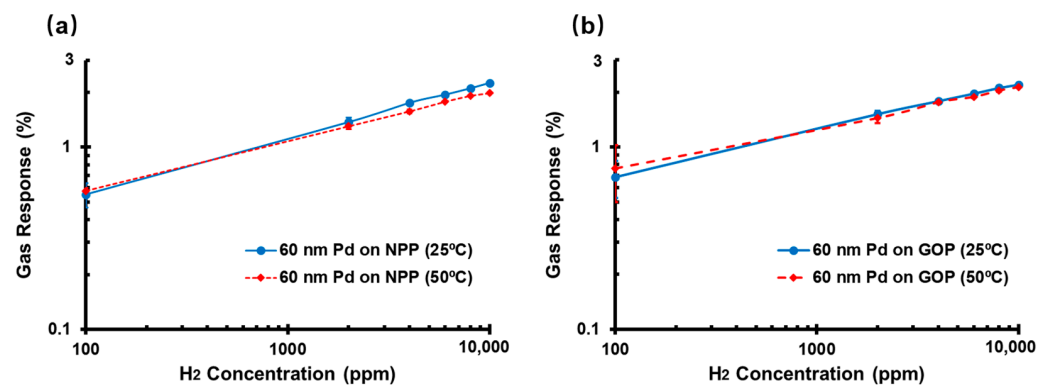


Figure 8. Effect of temperature on gas response for 60 nm Pd on (a) NPP (Reprinted with permission from Ref. [15]. 2022, Springer Nature) and (b) GOP substrates.

By contrast, the temperature has less impact on gas response for 60 nm Pd thin film on the GOP substrate, as presented in Figure 8b. The gas response of the H₂ sensor based on the GOP substrate at two different operating temperatures exhibits the same variation tendency, and is not significantly affected by temperature. The gas response of the Pd thin film on the GOP substrate decreased from 2.2% to 2.1% for 10,000 ppm H₂ at 50 °C, which is 4.5% lower than at 25 °C. Under the same conditions, the prior work indicated that the gas response decreased from 2.25% to 1.98%, which is 12% lower than at 25 °C. The gas response was affected by temperature, whether the 60 nm Pd H₂ sensor as based on the GOP or the NPP substrate. However, due to the inverse relationship between the electrical conductivity of graphite and temperature [16], the heating-induced reduction in gas response was restrained by the reduction in the initial resistance of the sensor at 50 °C. For instance, the initial resistance of 60 nm Pd on GOP substrate decreases from 9.08 KΩ (at 20 °C) to 8.82 KΩ (at 50 °C). According to Equation (1), the initial resistance decreases with increasing temperature, and this change in resistance remains constant at 10,000 ppm H₂, leading to increased gas response. Conversely, the influence on gas response of the solubility of H in Pd is weakened at high temperatures.

4. Conclusions

In this study, a simple, low-cost, and mass-producible fabrication process for 1.5D Pd-based H₂ sensors was presented by using a paper substrate, graphite thin film, and the vacuum evaporation technique. The graphite intermediate layer on the paper substrate formed continuous 8 nm Pd microfiber networks, thereby resulting in better sensor output stability than that obtained for sensors without the intermediate layer. Furthermore, the graphite intermediate layer was confirmed to be insensitive to H₂ and to not influence the sensing performance of the H₂ sensor. The effects of thickness and temperature on the H₂ sensors were investigated through the fabrication of 8 nm and 60 nm Pd-based H₂ sensors on GOP substrates. When exposed to 10,000 ppm H₂ at 25 °C and 50 °C, the response times of the GOP H₂ sensor with 8 nm Pd were 9.7 s and 4.3 s, respectively. These response times are comparable to those of 1D Pd-based H₂ sensors [3,9,12], but the 1.5D sensors proposed in this work have much lower cost, and a simpler and faster fabrication process. Additionally, the Pd thin film H₂ sensor based on GOP substrate demonstrated that the graphite intermediate layer was capable of limiting the influence of temperature on gas response, due to the thermoelectric effect of graphite.

Author Contributions: B.W., D.V.D. and Y.Z. conceived and designed the experiments and analyzed the data; B.W. performed the experiments; B.W. wrote the paper; D.V.D., T.H. and Y.Z. helped supervise the project. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Hiroshi Kubota, faculty of engineering, Kumamoto University, Japan for providing micro-fabrication and characterization facilities. I would like to extend my heartfelt thanks to my research partner, Yasumasa Nara, for supporting and helping perform the experiments, characterization analysis, and data calibration.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zeng, X.Q.; Wang, Y.L.; Deng, H.; Latimer, M.L.; Xiao, Z.L.; Pearson, J.; Xu, T.; Wang, H.H.; Welp, U.; Crabtree, G.W.; et al. Networks of ultrasmall Pd/Cr nanowires as high performance hydrogen sensors. *ACS Nano* **2011**, *5*, 7443–7452. [[CrossRef](#)] [[PubMed](#)]
2. Görgün, H.; Arcaç, M.; Varigonda, S.; Bortoff, S.A. Observer designs for fuel processing reactors in fuel cell power systems. *Int. J. Hydrogen Energy* **2005**, *30*, 447–457. [[CrossRef](#)]
3. Lim, S.H.; Radha, B.; Chan, J.Y.; Saifullah, M.S.M.; Kulkarni, G.U.; Ho, G.W. Flexible palladium-based H₂ sensor with fast response and low leakage detection by nanoimprint lithography. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7274–7281. [[CrossRef](#)] [[PubMed](#)]
4. Buttner, W.J.; Post, M.B.; Burfess, R.; Rivkin, C. An overview of hydrogen safety sensors and requirements. *Int. J. Hydrogen Energy* **2011**, *36*, 2462–2470. [[CrossRef](#)]
5. Wang, B.; Zhu, L.F.; Yang, Y.H.; Xu, N.S.; Yang, G.W. Fabrication of a SnO₂ nanowire gas sensor and sensor performance for hydrogen. *J. Phys. Chem. C* **2008**, *112*, 6643–6647. [[CrossRef](#)]
6. Song, H.; Lou, Z.; Liu, M.; Zhang, G.; Peng, W.; Wang, B.; Zhu, Y. Centrifugal Deposited Au-Pd Core-Shell Nanoparticle Film for Room-Temperature Optical Detection of Hydrogen Gas. *Sensors* **2018**, *18*, 1448. [[CrossRef](#)] [[PubMed](#)]
7. Wang, B.; Zhu, Y.; Chen, Y.P.; Song, H.; Huang, P.C.; Dao, D.V. Hydrogen sensor based on palladium-yttrium alloy nanosheet. *Mater. Chem. Phys.* **2017**, *194*, 231–235. [[CrossRef](#)]
8. Wang, B.; Rahman, M.A.; Nara, Y.; Hashishin, T.; Dao, D.V.; Zhu, Y. Palladium microfiber network as platform for hydrogen sensing applications. *J. Phys. Chem. Solids* **2019**, *131*, 50–54. [[CrossRef](#)]
9. Zeng, X.Q.; Latimer, M.L.; Xiao, Z.L.; Panuganti, S.; Welp, U.; Kwok, W.K.; Xu, T. Hydrogen Gas Sensing with networks of ultrasmall palladium nanowires formed on filtration membranes. *Nano Lett.* **2011**, *11*, 262–268. [[CrossRef](#)]
10. Walter, E.C.; Favier, F.; Penner, R.M. Palladium mesowire arrays for fast hydrogen sensors and hydrogen-Actuated Switches. *Anal. Chem.* **2002**, *74*, 1546–4553. [[CrossRef](#)] [[PubMed](#)]

11. Kim, B.J.; Kim, J.S. Hydrogen sensor using the Pd film supported on anodic aluminium oxide. *Int. J. Hydrogen Energy* **2014**, *39*, 16500–16505. [[CrossRef](#)]
12. Offermans, P.; Tong, H.D.; Rijn, C.J.M.V.; Merken, P.; Brongersma, S.H.; Crego-Calama, M. Ultralow-power hydrogen sensing with single palladium nanowires. *Appl. Phys. Lett.* **2009**, *94*, 223110. [[CrossRef](#)]
13. Li, X.; Liu, Y.; Hemminger, J.C.; Penner, R.M. Catalytically activated palladium@platinum nanowires for accelerated hydrogen gas detection. *ACS Nano* **2015**, *9*, 3215–3225. [[CrossRef](#)] [[PubMed](#)]
14. Lee, J.H. Gas sensors using hierarchical and hollow oxide nanostructures: Overview. *Sens. Actuators B* **2009**, *140*, 319–336. [[CrossRef](#)]
15. Wang, B.; Nara, Y.; Hashishin, T.; Dao, D.V.; Zhu, Y. Palladium on paper as a low-cost and flexible material for fast hydrogen sensing. *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 5298–5304. [[CrossRef](#)]
16. Buerschaper, R.A. Thermal and electrical conductivity of graphite and carbon at low temperatures. *J. Appl. Phys.* **1944**, *15*, 452–454. [[CrossRef](#)]