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Abstract

In this study, we developed a hydrogen sensor based on a palladium microfiber network on a paper substrate. A 60-nm pure palladium film was deposited on photocopy paper using a vacuum evaporation technique. The photocopy paper was employed as the sensor substrate because of its low cost and the simple and rapid fabrication process. The texture of the microfiber network on the paper greatly increased the surface area to volume ratio for the palladium thin film, which is crucial for rapid response sensors. The experimental results showed that the hydrogen sensor exhibited a rapid response and linear gas response characteristics at room temperature and pressure. The gas response of the paper-substrate sensor was much higher compared with the glass substrate.

Keywords: high surface area to volume ratio, hydrogen sensor, palladium microfiber network, paper substrate

1. Introduction

Hydrogen (H₂) is a clean combustible gas with a low minimum ignition energy, high combustion heat, wide flammable range, and high ignition temperature [1]. In addition, hydrogen gas cannot be detected by the senses of a human because it is odorless, colorless, and tasteless. Therefore, the rapid, economical, and reliable detection of hydrogen gas is critical for improving the safety of hydrogen-based applications, such as propulsion systems, fuel cells, and H₂-fuelled cars [2].

Conventionally, metal oxide hydrogen sensing materials [1] have been used widely for manufacturing hydrogen sensors. However, these sensing materials can also detect various other common combustible gasses during the hydrogen detection process, which reduces the selectivity and sensitivity of hydrogen gas sensing. Due to its high selectivity for hydrogen, palladium (Pd) has been commonly utilized as a promising sensing material for hydrogen leakage detection and concentration measurement [1-4]. Pd-H hydride is formed during the hydrogen absorption process, where the interstitial sites of the Pd lattice are occupied by hydrogen atoms. The physical properties of Pd are changed because of lattice expansion, such as its volume, electrical resistivity, and optical reflectivity [5-8]. Hydrogen is desorbed when Pd is under non-equilibrium conditions, i.e., the concentration of hydrogen in Pd is higher than that on the surface. The necessary driving force can be provided because of the hydrogen concentration gradient in Pd. Thus, hydrogen atoms can break the chemical bonds with Pd to move to the surface and finally be released into the air [9].

The miniaturization of hydrogen sensing materials [10] is a major research field for the new generation of hydrogen gas sensors [1-10]. Low-dimensional nanostructures can relax the compressive stress in the sensing material during gas testing to reduce the likelihood of fractures [6]. Furthermore, the nanostructure provides a large surface area to volume ratio for Pd to improve the performance of Pd-based hydrogen sensors. The conventional method introduced by Offermans et al. [11] employs a technique called deposition and etching under angles to produce a single Pd

nanowire hydrogen sensor with a rapid response speed. Lim et al. [12] developed a high sensitivity and rapid response hydrogen sensor by suspending a single Pd-functionalized carbon nanowire approximately 10 μm above a substrate while monolithically bridging two carbon posts. They fabricated the Pd nanowire using the carbon microelectromechanical system process. This hydrogen sensor achieved high sensitivity and a rapid response because of the large surface area to volume ratio of the single Pd nanowire. Lim et al. [2] developed another Pd nanowire hydrogen sensor, where a Pd grating was transferred to a flexible polycarbonate for rapid response and low leakage detection. Wang et al. [5] investigated a high sensitivity and rapid response hydrogen sensor based on a palladium-silver (Pd-Ag) thin film. The surface roughness and the surface area to volume ratio of the Pd thin film were increased because of the texture of the porous alumina substrate and the thickness of the film. However, all of the low-dimensional Pd-based hydrogen sensors mentioned above are highly complex to fabricate and they require expensive nano-fabrication facilities for mass production.

In our previous study [6], we investigated a low-cost two-dimensional resistive palladium-yttrium (Pd-Y) alloy based hydrogen sensor for hydrogen detection. Due to the different atomic sizes of Pd and Y, the lattice structure of Pd can be significantly expanded after doping Y atoms into Pd, which enhances the hydrogen permeability and diffusion rate in the Pd-Y alloy. We demonstrated that this Pd-Y nanosheet hydrogen sensor exhibited high sensitivity to hydrogen and the fabrication process was simple and inexpensive. However, the surface area to volume ratio needs to be enhanced significantly by increasing the surface roughness of the nanosheet to further improve the response and recovery times.

In the present study, we fabricated a novel hydrogen gas sensor with Pd microfibers. Normal photocopy paper was utilized as the substrate for the sensor to increase the surface roughness. The microfibers on the surface of the paper had diameters of up to approximately 30 μm. The fabrication process was fairly simple for the 60 nm Pd microfiber-based hydrogen sensor, where the steps involved vacuum evaporation and silver epoxy electrode adhesion. Therefore, the proposed fabrication process is inexpensive with a short manufacture process and it is suitable for mass production. The experimental testing results showed that the hydrogen sensor

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could detect hydrogen at a concentration of 10,000 ppm with a gas response of 2.13%, which was 1.69 times higher than that of Pd deposited on glass using the same process at the same thickness of 60 nm.

2. Design and Experiment

A schematic diagram illustrating the hydrogen sensor based on Pd microfiber networks is shown in Figure 1. The starting substrate material was normal photocopy paper (A4/80 gsm, Paper Australian Pty Ltd), which is inexpensive, flexible, and biodegradable. The Pd thin film was deposited on the paper substrate as the sensing material using a vacuum evaporation technique. As shown in Figure 1, electrodes were attached to two edges of the Pd thin film. Silver epoxy conductive adhesive was utilized as the conductivity material for both electrodes.

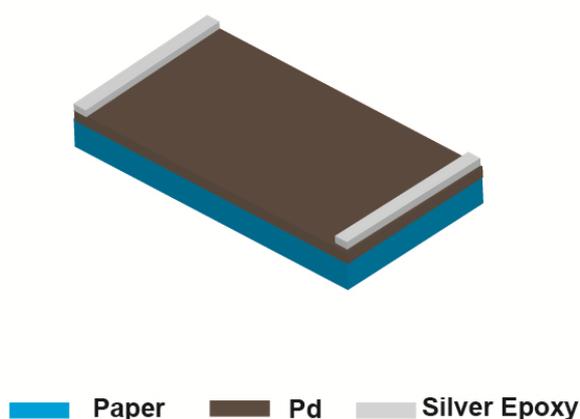


Figure 1. Schematic illustration of the hydrogen sensor.

Figure 2 shows the fabrication process flow for the hydrogen sensor based on pure Pd microfiber networks. Normal photocopy paper was selected as the substrate for the hydrogen sensor because of its low cost and flexibility, but especially the microfiber network texture of the paper. First, a high pressure nitrogen gun was utilized to remove dust from the surface of the substrate (Figure 2(a)). Next, Pd was deposited on the paper substrate using a vacuum evaporation system (VPC-260, ULVAC Technologies, Inc.) to obtain a Pd film with high density and purity. The high film density enhanced the mechanical properties and the abrasion resistance of the Pd thin film. A Pd target with a purity of 99.95% was used as the evaporation material. During the Pd deposition process, the operating pressure was kept at 2.0×10^{-5} Torr, and the distance between the sample and target was 35 cm. To enhance the density and smoothness of the Pd film, the operating current was kept stable at 90 A for 3 min to deposit a 60 nm layer of Pd. A glass substrate was placed beside the paper sample in the same process for comparative purposes and thickness measurements. The paper substrate was then removed from the vacuum evaporation system and cut into pieces that measured 20 mm by 5 mm (Figure 2(b)). Finally, silver epoxy was attached to two edges of the Pd thin film as electrodes (Figure 2(c)).

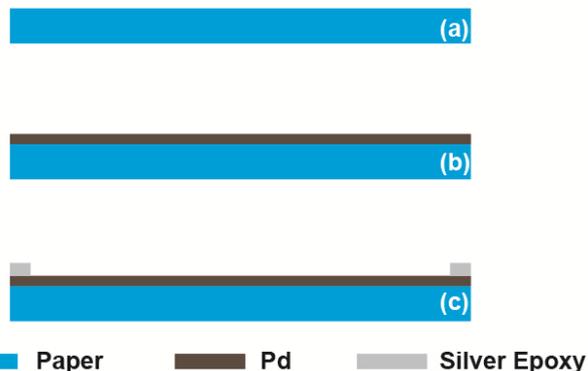


Figure 2. Process flow employed for fabricating the Pd hydrogen sensor.

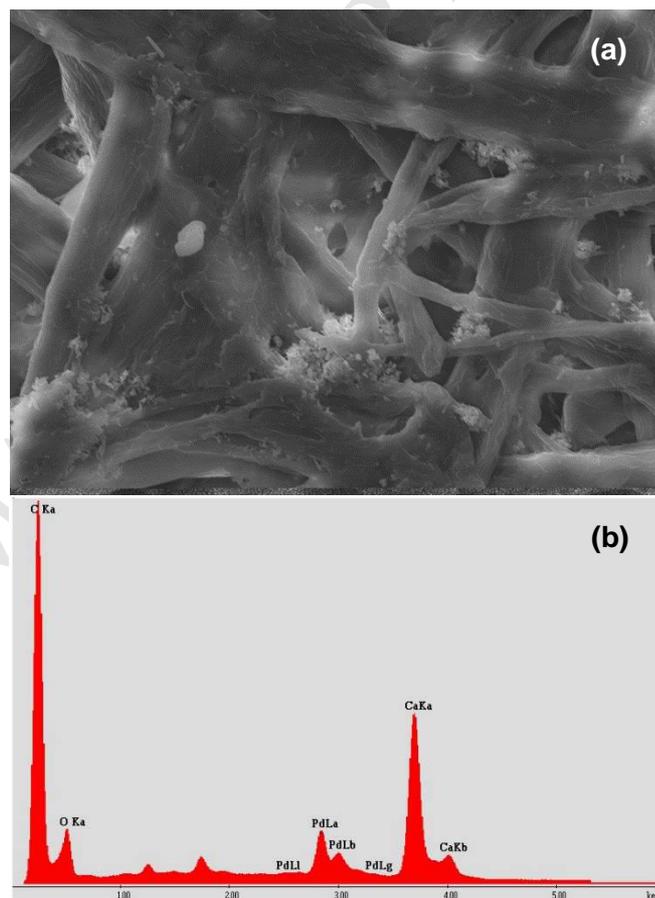


Figure 3. Characterization of the paper-based hydrogen sensor. (a) Scanning electron microscope image of the surface morphology. (b) Surface elemental analysis of the sensing area.

An image was acquired by scanning electron microscopy of the paper substrate coated with Pd at a thickness of 60 nm to investigate the surface morphology of the hydrogen sensor. The network of Pd microfibers with clean surfaces is shown in Figure 3(a), which indicates that the multilayer Pd microfibers had diameters of up to 30 μm . The random and continuous textures greatly increased the surface roughness of the paper, thereby increasing the surface area to volume ratio for the Pd microfibers. The elements on the paper-based sensor surface were analyzed by energy dispersive X-ray analysis after depositing Pd on the paper, as shown in Figure 3(b), which indicates that carbon was the main element detected. In addition, Pd was identified as an element on the surface of the paper-based hydrogen sensor.

The hydrogen gas sensor was tested in a custom-made gas chamber. The test probes were sealed and positioned inside the chamber to acquire electronic measurements from the outside while the sensor was exposed to hydrogen gas inside the chamber. Figure 4 depicts

a schematic diagram illustrating the hydrogen gas testing system. The mass flow controller could produce various concentrations of hydrogen gas. During the gas test process, hydrogen concentrations of 100 ppm, 2,000 ppm, 4,000 ppm, 6,000 ppm, 8,000 ppm, and 10,000 ppm with nitrogen were produced via the mass flow controller at a gas flow rate of 100 standard cm³ per min. The hydrogen gas was fed into the gas chamber sequentially at specific concentrations. The hydrogen gas was switched off after each measurement and the residual hydrogen gas was replaced with pure nitrogen through the outlet. A personal computer (PC) and voltmeter were included in the gas testing system for data collection and elemental analysis, respectively. The measured data were logged by a digital multimeter once per second. The gas response (G_r) for each hydrogen concentration was calculated as:

$$G_r = \frac{R_b - R_a}{R_a} \times 100\%, \quad (1)$$

where R_b is the resistance of the sensing element after exposure to a specific hydrogen concentration and R_a is the initial resistance before measuring the concentration.

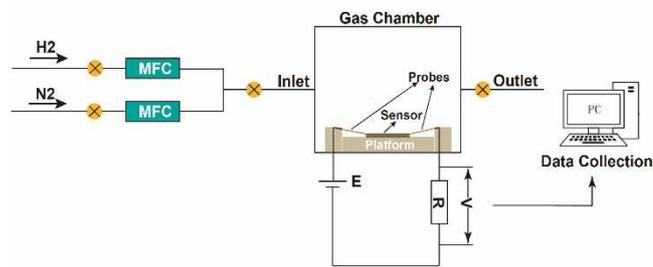


Figure 4. Hydrogen gas testing system.

3. Results and Discussion

Figure 5 illustrates the output from the hydrogen sensor under specific hydrogen concentrations. The resistance of the hydrogen sensor was measured at room temperature when exposed to hydrogen concentrations of 100 ppm, 2,000 ppm, 4,000 ppm, 6,000 ppm, 8,000 ppm, and 10,000 ppm. Each hydrogen gas concentration was injected during the gas testing process and the data collected are plotted in Figure 5. In this study, the hydrogen concentration was controlled up to 10,000 ppm due to safety considerations. According to the Langmuir adsorption isotherm model [12], the adsorption rate of hydrogen increased at the high hydrogen concentration, thereby increasing the resistance of the sensor and yielding a more rapid response. Thus, the resistance of

the sensing element increased rapidly when exposed to a hydrogen concentration of 10,000 ppm and it decreased after the hydrogen gas was stopped. However, the hydrogen adsorption rate decreased when 100 ppm hydrogen was injected into the chamber, which led to a smaller change in the resistance and a slower response compared with that to 10,000 ppm hydrogen. Figure 5 shows that the resistance of the hydrogen sensor clearly changed with the hydrogen concentration. Furthermore, the sensor exhibited stable and repeatable changes in resistance during continuous gas testing over a period 5 h, as shown in Figure 5.

The sensor responses of 60 nm Pd layers on glass and paper substrates were also compared in the same concentration range (from 2,000 ppm to 10,000 ppm in nitrogen) at room temperature and pressure, as shown in Figure 6. In order to ensure a consistent comparison, all of the conditions were exactly the same apart from the substrate materials (normal photocopy paper and glass). Thus, the experimental results were obtained with the same deposition thickness and hydrogen concentrations, but the surface morphologies of the paper and the glass substrates were different. The surface morphology of the paper substrate shown in Figure 3(a) demonstrates that it had a rough surface and the microfibers had diameters of up to 30 μm . The multilayer Pd microfiber network significantly increased the surface roughness and the surface area to volume ratio of the Pd sensing element. Therefore, the gas response of the hydrogen sensor was improved by increasing the likelihood of the surface palladium atoms reacting with hydrogen. In addition, a large amount of hydrogen atoms diffused in the sensor to obtain a faster phase transition (from α to β), thereby increasing the response speed and gas response [2, 6].

As shown in Figure 6, the hydrogen sensor on the paper substrate could detect a hydrogen concentration of 10,000 ppm with a gas response of 2.13%, which was 1.69 times higher than that of the Pd deposited on glass. The glass substrate had a smooth and flat sensing surface, and thus the reaction area between the Pd and hydrogen molecules was limited to the top of the Pd film. The gas responses of the paper-based hydrogen sensor were 1.28%, 1.62%, 1.84%, 2.00%, and 2.13% with hydrogen concentrations of 2,000 ppm, 4,000 ppm, 6,000 ppm, 8,000 ppm, and 10,000 ppm, respectively. The linear relationship between the gas response and hydrogen concentration is indicated in Figure 6. The linear fitting lines had coefficients of determination values (R^2) of 0.9647 and 0.85 for the paper-based and glass-based sensors, respectively. Furthermore, the standard deviations ($N = 5$) of the gas responses for the paper-based and glass-based sensors were less than $\pm 0.05\%$, thereby indicating their high repeatability and stability.

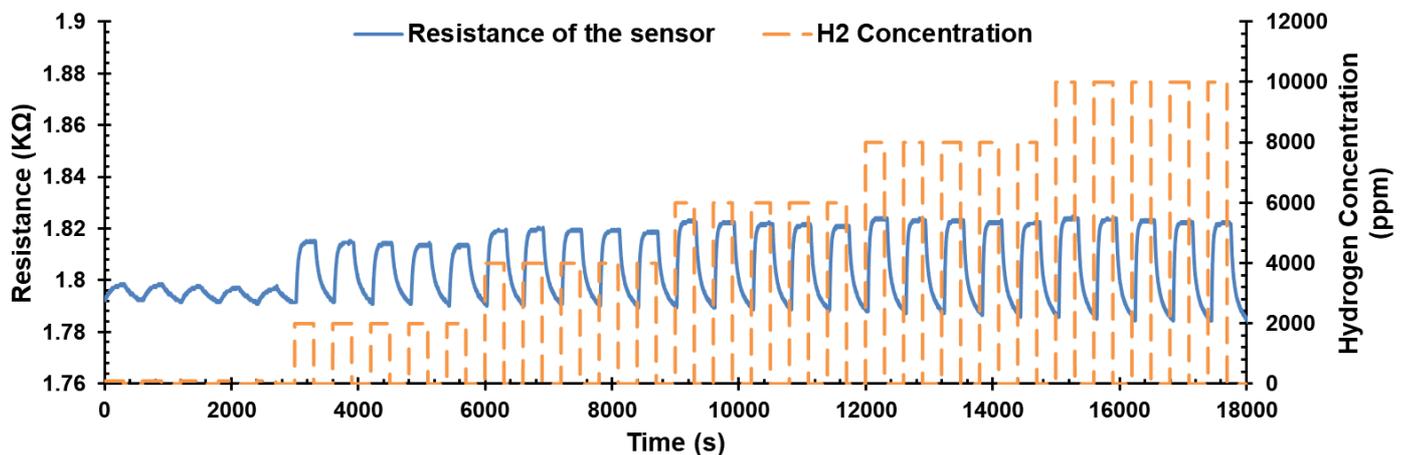


Figure 5. Changes in the resistance of the hydrogen sensor with specific hydrogen concentrations.

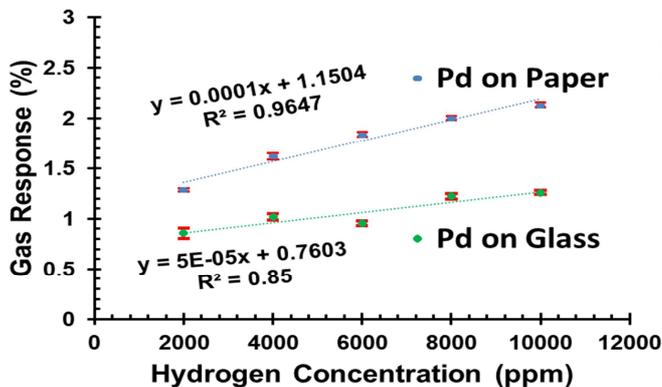


Figure 6. Gas responses (with standard deviation, N = 5) versus hydrogen concentration for the sensors on glass and photocopy paper substrates.

The response time is defined as the time required from the initial resistance value to 90% of the stable resistance value, and the recovery time is defined as the time required from the stable resistance value to 10% of that value. The response and recovery times for the hydrogen sensor at specific hydrogen concentrations are plotted in Figure 7. The concentration of hydrogen was an important parameter that directly influenced the response time and recovery time. For the paper-based hydrogen sensor, a response time of 140 s and recovery time of 230 s were obtained at a hydrogen concentration of 100 ppm. The response and recovery times were decreased significantly when the hydrogen concentration was increased to 10,000 ppm, where the response time was 42 s and the recovery time was 165 s. By contrast, the glass-based sensor had a slightly slower response time of 47 s and a recovery time of 186 s when the hydrogen concentration was 10,000 ppm. In principle, the paper-based sensor provided a faster response and recovery time because of its high surface area to volume ratio. However, as shown in Figure 7, there were no obvious differences in the response and recovery times between the paper-based and glass-based sensors, possibly because the gas penetrated into the paper fibers, which required a longer time to reach a saturation/stable state.

Table 1 compares the results obtained using our sensor and those reported in other studies. Table 1 shows that compared with the sensors developed by Wang [5], Jeon [13], and Walia [14], our paper-based Pd hydrogen sensor fabrication process is simple, inexpensive, and lithography-free. Due to the high surface roughness of the paper substrate, our hydrogen sensor obtained similar or even better gas sensing performance in terms of the gas response, response time, recovery time, and minimum detection

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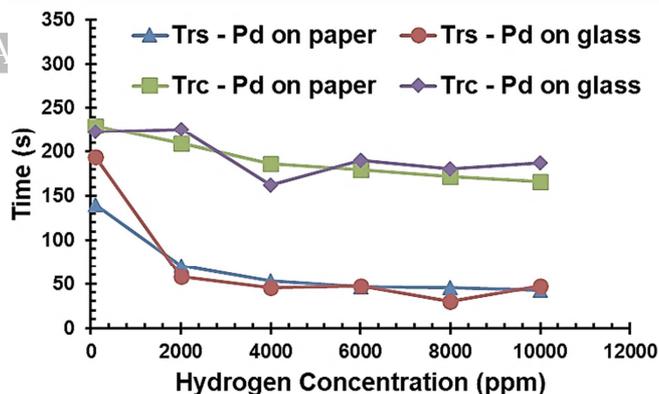


Figure 7. Response time (Trs) and recovery time (Trc) for the hydrogen sensors (on glass and photocopy paper substrates) at various hydrogen concentrations.

limit compared to the previously reported sensors.

4. Conclusions

In this study, a Pd micro-network was fabricated on normal photocopy paper to fabricate a hydrogen sensor. A vacuum evaporation technique was employed to deposit a 60 nm layer of Pd on the surface of the paper and the sensing element area was $20\text{ mm} \times 5\text{ mm}$. We compared the gas response and recovery times for the different surface morphologies produced on normal photocopy paper and glass substrates. Our results indicated that the Pd on the paper substrate had a larger surface area to volume ratio than the Pd on the glass substrate, which significantly influenced the gas response of the hydrogen sensor. The Pd microfiber network with nano-scale thickness on the paper substrate provided a rapid and linear gas response. The hydrogen sensor based on a pure Pd microfiber network exhibited a reversible and reproducible response to hydrogen concentrations as low as 100 ppm. The response time of the hydrogen sensor was reduced from 140 s to 42 s by increasing the hydrogen concentration from 100 ppm to 10,000 ppm. The simple, inexpensive, and rapid fabrication process employed in this study may facilitate the mass production of sensors. The manufacture of a hydrogen sensor on normal photocopy paper has potential applications in biodegradable and flexible products, such as in Internet of Things wearable sensors and biomedical sensors [15, 16]. In future research, we will investigate the production of multilayer nanofiber substrates using electrospinning technique [17-19] to further increase the surface area to volume ratio in order to obtain a greater and more rapid gas response.

Table 1. Comparison with other previously reported sensors

	Wang et al.[5]	Lee et al.[9]	Jeon et al.[13]	Walia et al. [14]	Our previous work [6]	This work - 1	This work - 2
Fabrication	Complex	Simple	Complex	Complex	Simple	Simple	Simple
Material	Pd-Ag	Pd	Pd	Pd	Pd-Y	Pd	Pd
Substrate	Porous alumina substrate	SiO ₂ /Si	SiO ₂ /Si	SiO ₂	Glass	Glass	Paper
Thickness	200 nm	100 nm	20 nm	~50 nm	19.3 nm	60 nm	60 nm
Response time (Concentration)	10–20 s (2%)	130 s (1%)	~7 s (1%)	~44 s (1%)	83 s (4%)	47 s (1%)	42 s (1%)
Recovery time (Concentration)	60 s (2%)	-	-	~101 s (1%)	210 s (4%)	186 s (1%)	165 s (1%)
Gas Response (Concentration)	1.5% (2%)	~5% (1%)	3.83% (1%)	~3% (1%)	18.67% (0.5%)	1.26% (1%)	2.13% (1%)
Minimum detection limit	2%	0.6%	0.05%	0.02%	0.05%	0.01%	0.01%

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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- *Simple and low cost hydrogen sensor fabrication process for mass production.*
- *Large surface to volume ratio for palladium achieved using normal photocopy paper.*
- *Gas response of paper-substrate sensor higher than glass substrate counterpart.*

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