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Micro-sized pH sensors based on patterned Pd structures using an electrolysis method

Young Tack Lee [a], Eunsongyi Lee [b], Jun Min Lee [b], Wooyoung Lee [a,b,*]

[a] Nanomedical National Core Research Center, Yonsei University, 262 Seongsanno, Seodaemoon-ku, Seoul 120-749, Republic of Korea
[b] Department of Materials Science and Engineering, Yonsei University, 262 Seongsanno, Seodaemoon-ku, Seoul 120-749, Republic of Korea

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ABSTRACT

We report a novel low-cost and simple technique to fabricate micron-scaled pH sensors using Pd patterned structures. We utilized a combination of photolithography and a lift-off technique to fabricate a V-shaped 4-probe device from a continuous Pd film. The device could detect the pH of a buffer solution by electrolysis. The hydrogen gas (H_2) in the solution generated during electrolysis was sensed by the Pd structure. Our results demonstrate that micron-scaled pH sensors based on V-shaped Pd structures can be used to quantitatively detect the pH of a wide pH range of buffer solutions.

1. Introduction

A number of fabrication methods for pH sensors [1–5] have been proposed due to the high utility of these sensors in environmental, biomedical, and biological applications, as many chemical and biological processes are pH-dependent. Several conventional pH sensors have been developed such as IS-FET (ion-sensitive field-effect transistor) sensors [5–9], electromotive force sensors, and optical sensors [10]. However, conventional pH sensors are recognized to have some drawbacks, namely slow response times, complex structures, and expansiveness. To overcome these limitations, nanotechnology has been applied to the fabrication of nanostructures for pH sensors e.g., carbon nanotubes (CNT) [4] and Si nanowires [11]. In particular, Si nanowires as pH sensors [11] have recently attracted considerable interest due to their wide detection range and high sensitivity.

In this work, we present a simple method to fabricate pH sensors using Pd micro-patterned structures. Pd has been investigated intensively for more than 40 years, and Pd is used in devices for hydrogen storage, hydrogenation catalysis, and hydrogen gas sensing [12–14]. The absorption of molecular hydrogen by Pd to form Pd–H hydride can cause changes in physical properties such as mass, volume, and electric resistance, all of which can be used to signal H_2 partial pressure changes [15–18]. Recently, we found that Pd patterned structures could successfully detect hydrogen gas over a wide concentration range at room temperature by measuring changes in the electrical resistance of these Pd patterned structures [19]. In this paper, we discuss the working principle of a micron-scaled pH sensor with Pd patterned structures based on an electrolysis method. We demonstrate that Pd micro-patterned structures can be used for pH sensors and that these sensors offer many advantages over conventional electrochemical approaches, including high sensitivity, rapid response time, and easy fabrication.

2. Experiment

The Pd thin films were deposited on a thermally oxidized Si(1 0 0) substrate in a dc magnetron sputtering system with a base pressure of 4×10^{-8} Torr. A combination of photolithography and a lift-off process was used to fabricate Pd structures ($w = 5$ µm, $l = 30$ µm) with $t = 40$ nm from continuous Pd films. Outer Ti/Au

* Corresponding author. Address: Nanomedical National Core Research Center, Yonsei University, 262 Seongsanno, Seodaemoon-ku, Seoul 120-749, Republic of Korea. Fax: +82 2 312 5375.
E-mail address: wooyoung@yonsei.ac.kr (W. Lee).

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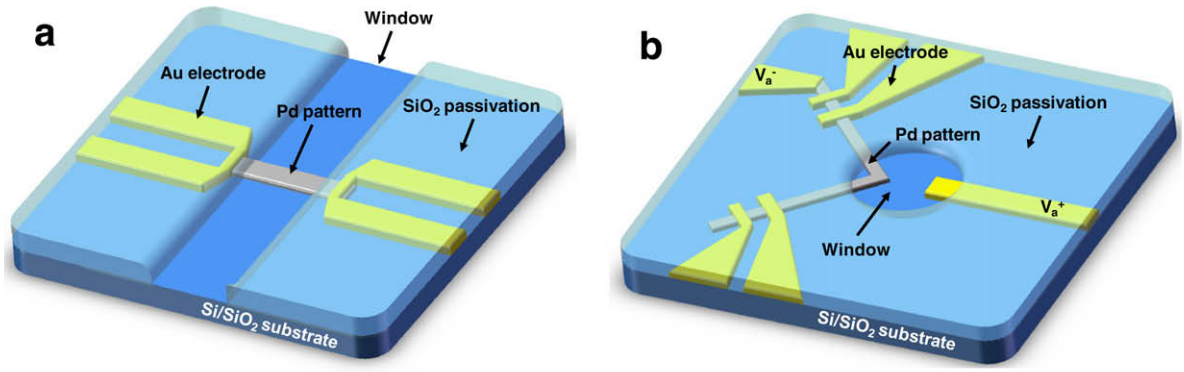

Fig. 1. Schematic diagrams of (a) a standard quasi-4-probe device and (b) a special 4-probe device with a V-shaped Pd patterned structure that uses an electrolysis method to sense pH.

electrodes and inner micron-scaled Ti/Au electrodes connecting a Pd structure with the outer electrodes were fabricated by photolithography and a lift-off process. After the electrode deposition, the devices were capped with a 200 nm-thick SiO_2 film for passivation and a window for the sensing areas. Fig. 1 shows schematic diagrams of (a) a standard quasi-4-probe pH-sensing device and (b) a V-shaped 4-probe device that uses an electrolysis method to sense pH. The comparison of the devices as pH sensors will be described later. The buffer solutions were purchased from Thermo Electron Corporation (Beverly, MA). A Keithley 236 current source (I) and Keithley 2400 source meter (V) with a current resolution of 100 μA was used to detect small changes in pH-dependent resistance. All data acquisitions were carried out using the LabView software program through a GPIB interface card.

3. Results and discussion

Fig. 2 presents the real-time electrical resistance responses of a standard quasi-4-probe device consisting of a lithographically-patterned Pd structure to a buffer solution of pH 4 (Fig. 1a). The pink arrows in Fig. 2 indicate dropping of the pH 4 buffer solution in the window of the device, whereas the black arrows indicate removal of the pH solution from the window of the device. When the device was exposed to the buffer solution, the resistance of the device was found to increase rapidly. In contrast, the resistance of the device decreased as the solution was removed. The signals, however, were found to be unstable and noisy.

The hydrogen gas (H_2)-sensing mechanism of Pd is based on the change of electrical resistivity when H_2 is absorbed at the octahedral interstitial site in the Pd fcc lattice [18]. The resistivity of PdH_x is higher than pure Pd, because hydrogen atoms play a key role as additional scattering centers thereby increasing Pd resistivity. Recently, we demonstrated that lithographically-patterned Pd nanowires can be used as hydrogen gas sensors to quantitatively detect H_2 over a wide concentration range [18]. However, the reason for the resistance variation of the device in the presence and absence of the buffer solution with the pH 4 remains unclear.

Here, we describe a novel method to fabricate a pH sensor using a V-shaped Pd patterned structure, based on a specially designed 4-probe device (see Fig. 1b). The operating principle of the device is to sense pH using an electrolysis method. To detect hydrogen gas (H_2) from a pH buffer solution, a potential difference was applied between a counter electrode (V_a^+) and a V-shaped Pd electrode (V_a^-). Electrolysis reactions involving H^+ ions are fairly common in acidic solutions. In the V-shaped Pd electrode (V_a^-), which acts as a cathode, hydrogen ions (H^+) combine with electrons to generate H_2 as follows

$$2H^+ + 2e^- \rightarrow H_2, \qquad (1)$$

Fig. 3 shows the variation in resistance with an applied voltage (V_a) in the device with the V-shaped Pd patterned structure. The initial applied voltage was 1.0 V. The applied voltage was gradually increased by 0.1 V when the device was exposed to a buffer solution with pH 4, but the resistance was found to decrease very slightly with increasing applied voltage until it reached 2.0 V, as seen in the inset of Fig. 3. Subsequently, the resistance was found to increase dramatically when the applied voltage became 2.0 V, implying that electrolysis occurred at 2.0 V.

In Fig. 4, we present the real-time signal output characteristics for three different buffer solutions of pH 4, pH 7, and pH 10 at an applied voltage of 2 V using source current of 100 μA. When the

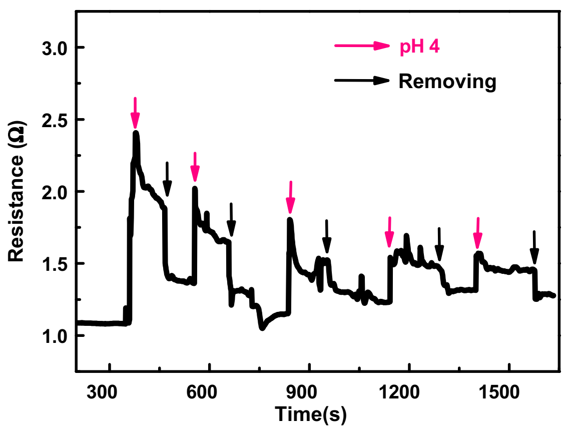

Fig. 2. The real-time electrical resistance response to a buffer solution with pH 4 in a standard quasi-4-probe device consisting of a patterned Pd structure.

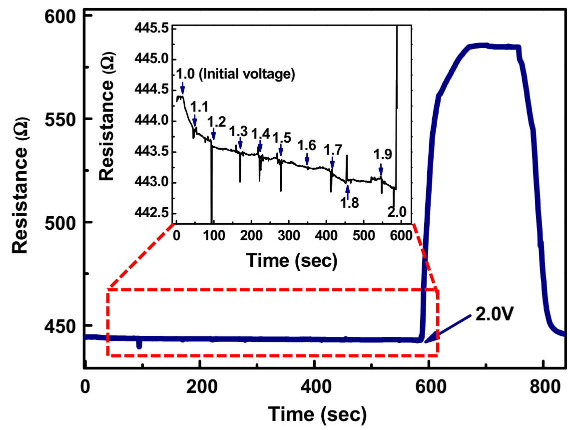

Fig. 3. The variation of the resistance with an applied voltage (V_a) in a device with a V-shaped Pd patterned structure.

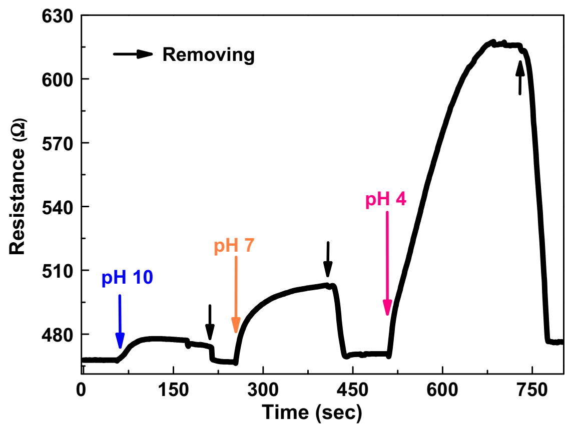

Fig. 4. The real-time signal output characteristics of the V-shaped Pd patterned structure for three different buffer solutions of pH 4, 7, and 10 at an applied voltage of 2 V using a source current of 100 μA.

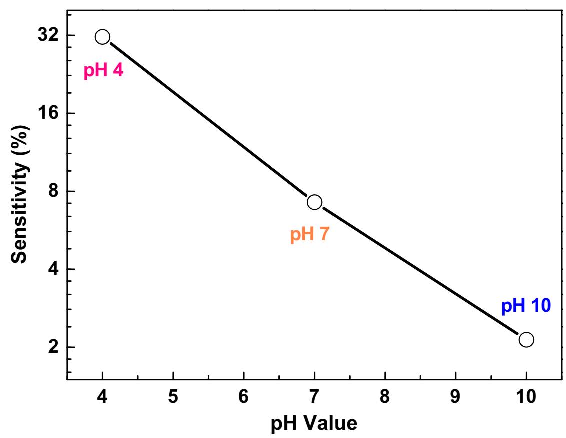

Fig. 5. A log plot of the sensitivity of the V-shaped Pd structure device as a function of pH.

device with the V-shaped Pd patterned structure was exposed to the pH 4 buffer solution, the resistance of the device increased from an initial resistance of 464 Ω to a saturated resistance of 477 Ω. The resistance was recovered as soon as the buffer solution was removed, as indicated by the black arrow in Fig. 4. Electrolysis took place at 2.0 V, generating H_2. H_2 is detected by the 4-probe device with a V-shaped Pd structure as follows: H_2 is adsorbed on the surface of the Pd structure, followed by dissociation of the adsorbed hydrogen atoms and their diffusion into the interstitial sites along grain boundaries. The diffused hydrogens then react with Pd atoms to form Pd hydride (PdH_x), the concentration of which is dependent upon the H_2 concentration in the solution [18].

The lowest pH solution resulted in the highest resistance change in the V-shaped Pd structure device. This indicates that the high hydrogen ion concentration of the buffer solution (low pH value) created more H_2, causing more change in the resistance of the device. The pH sensitivity (S) of a device in a buffer solution is defined as

$$S = \frac{(R_f - R_i)}{R_i} \times 100\%, \tag{2}$$

where R_f and R_i are the resistances in the presence and the absence of the pH solution, respectively.

Fig. 5 displays the log plot of the sensitivity in the V-shaped Pd structure device as a function of pH value. The log-scaled sensitivity tends to increase linearly when the pH value decreases, i.e. as the hydrogen ion concentration increases. This is because the pH value is defined as in [5,20]

$$\mathrm{pH} = -\log[\mathrm{H}^+], \tag{3}$$

According to Eq. (3), the sensitivity of the device to the pH in the buffer solution should be linear according to the hydrogen ion concentration. Our results suggest that a pH sensor based on a V-shaped Pd structure that uses an electrolysis method can be used to quantitatively detect a wide range of pH values in buffer solutions.

4. Conclusions

We have investigated Pd patterned structures for use as pH sensors. A 4-probe device with a V-shaped Pd patterned structure senses pH using an electrolysis method. The resistance of the device in the presence of a pH solution was found to increase drastically when a voltage of 2.0 V was applied, implying that electrolysis occurred at 2.0 V. The increase in the resistance originates from the generation of hydrogen gas (H_2) during electrolysis. When hydrogen molecules in the solution were adsorbed on the surface of the V-shaped Pd structure, the absorbed hydrogen molecules dissociated into hydrogen atoms that diffused into the interstitial sites along grain boundaries of the Pd structure. The hydrogen atoms then reacted with the Pd atoms to form Pd hydride (PdH_x), the concentration of which was dependent on the H_2 concentration in the solution. We demonstrated that a pH sensor based on a V-shaped Pd structure can be used to quantitatively detect a wide range of pH values in solutions. This is a low-cost and simple technique to fabricate pH sensors using Pd patterned structures that have high sensitivity and can detect pH in real-time.

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