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Highly sensitive hydrogen sensors: Pd-coated Si nanowire arrays for detection of dissolved hydrogen in oil

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ABSTRACT

We studied the H_2 sensing properties of Pd nanoparticles on vertical standing Si nanowire (NW) arrays for the detection of dissolved hydrogen (H_2) gas in transformer oil. The Pd-coated Si NW arrays were fabricated by using the aqueous electroless etching method and sputtering. The Pd-coated Si NW arrays were immersed and measured in transformer oil with various dissolved concentrations of H_2. We found that Pd-coated Si NW arrays showed significantly superior performance with regard to the response (~1000%), the lowest detection limit (1 ppm), and the response time (600 s). The Pd-coated Si NW arrays showed a temperature coefficient of resistance (TCR) of 6.53×10^{-3} °C^{-1} at various oil temperatures (20–80 °C). Pd-coated Si NW arrays showed good reliability for the detection of H_2 in oil at room temperature (20 °C), with nearly the same initial resistance for 30 days.

1. Introduction

One of the most challenging ongoing issues in power transformers is the monitoring of degradation in the internal components of a transformer, composed of iron core, coils, and insulators immersed in mineral oil. When the oil-filled-transformer is under abnormal stress, it can lead to the chemical breakdown of the oil or cellulose, disenabling the dielectric insulation [1–3]. The failure to transfer leads to the evolution of a mixture of gases, including hydrogen (H_2), hydrocarbons (methane, ethane, ethylene, acetylene), and carbon oxides (mono- and di-) [1–3]. The generated gases dissolve in oil, with the concentration of each gas in oil increasing with time. Eventually, the failure in the transformer causes catastrophic accidents, with the inability to safely supply electric power [1–3].

The detection of generated gases can be one of the markers to diagnose the failure or predict the lifespan of a transformer [1–3]. IEEE recommends that the status of oil-immersed transformers be classified based on a 4-level criterion, using the concentrations of dissolved gases and the total concentration of all the combustible gases [4]. Among the gases that can be generated in transformer oil, H_2 is the most important one to be monitored in a transformer, due to its capacity to evolve during both, discharge and thermal deterioration [4]. Until now, the indirect approach, which uses the off-line analysis of carrying out sampling from a transformer using gas chromatography (GC), has been implemented to detect the dissolved gases in the transformer oil [3]. However, the indirect approach has a fundamental uncertainty regarding the accuracy of detected gas concentrations, since dissolved gas analysis (DGA) is based on sampling, instead of real-time measurement [5]. Even if a GC-based on-line DGA [3,6–8], which utilizes the extracted gases in oil by using additional equipment (e. g., membrane filter), was designed and applied to large-scale transformers to eliminate the sampling error, it would have limited versatility for transformers at all size scales due to the high cost of maintenance [8].

In order to overcome the drawbacks of DGA, several attempts have been made to measure the dissolved gas in oil directly by using oil-immersed gas sensors, including optical [9,10], electrochemical [11], diode [12,13], and resistivity [9,14,15] types. Among the various sensor types, resistance-based sensors have shown potential as H_2 gas sensors, for the application of DGA in transformer oil due to their low cost, simple structure, and high response [14,15]. Recent progress was made by our group in the development of highly sensitive H_2 sensors, which have Pd nanoparticles deposited on the vertically aligned Si nanowire (NW) arrays [16,17]. The H_2-sensing properties of the Pd-coated Si NW arrays were sufficiently outstanding to be used in the detection of H_2 in oil with regard to the sensitivity (S = 1700% at 1% H_2), the detection range (2–20,000 ppm), and the response time (~3 s) [16]. The sensing mechanism of Pd-coated Si NW arrays was also investigated in the case of *n*- and *p*-type Si NWs [16].

In this work, we developed H_2 sensors, which have coated Pd nanoparticles on the vertically standing Si NW arrays for the detection of dissolved H_2 gas in oil. The Pd-coated Si NW arrays were immersed in a transformer-oil-filled chamber. The real-time electrical current of Pd-

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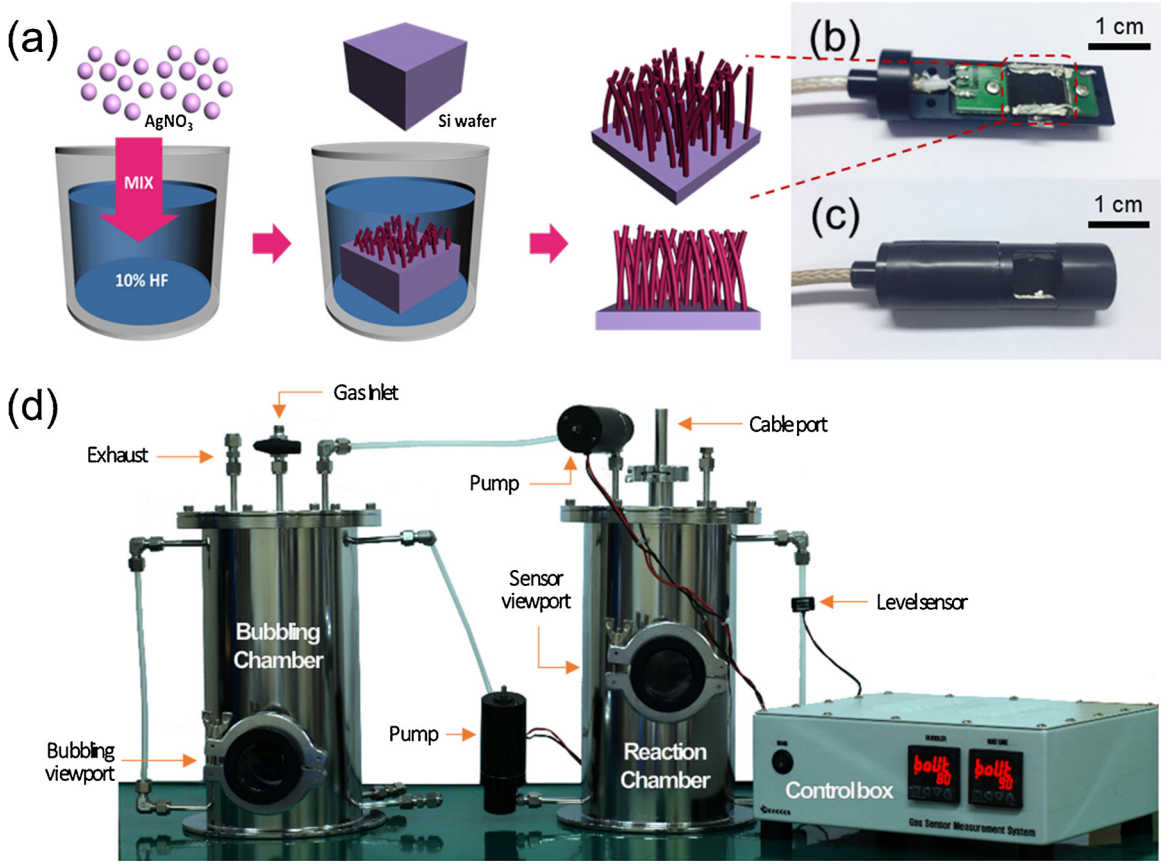

Fig. 1. (a) Schematic illustration of AEE process in Si NW arrays, and (b) image of a Pd-coated Si NW array, loaded on a device composed of a polyimide-based plastic outer-shell (lower part), PCB, and a cable; (c) device image of the upper part of the outer-shell (d) image of the measurement system with home-made H_2 sensing chambers for the transformer oil.

coated Si NW arrays was measured with various introduced concentrations of H_2 in oil. The excellent sensing performance, in terms of a high response of ~1000% upon exposure to 460 ppm H_2, was obtained in the oil. The resistance variation of the Pd-coated Si NW arrays, with its H_2 response, was measured at various oil temperatures (20–80 °C), respectively. Moreover, the long-term stability of the Pd-coated Si NW arrays was also assessed for 30 days.

2. Experiment

2.1. Fabrication of Pd-coated Si NW arrays

Fig. 1(a) schematically illustrates the fabrication process of the vertical standing Si NW arrays using a top-down aqueous electroless etching (AEE) [16,17]. A single-side polished *p*-type (boron-doped; 100) oriented Si wafer, with a resistivity of 1–10 Ω-cm was diced into 1 × 1 cm^2, subsequently being cleaned with acetone, methanol, and distilled water for 15 min at room temperature, respectively. The cleaned wafers were dipped into 50% HF aqueous solution for 1 min to eliminate layers of native oxide. Subsequently, the wafers were etched by immersing them in an aqueous etching solution (0.03 M $AgNO_3$ mixed in 6 M HF) at 75 °C for 50 min. During the etching process, Ag^+ ions dissolved in the etching solution were randomly deposited on the Si surface, oxidizing to become SiO_2. The oxide layer thus formed on the Si surface was etched by HF, providing a new Si site for oxidation. The sequential oxidation/etching process form was vertically aligned to the Si NW arrays [18]. After the etching process, the wafers were rinsed with a 30% HNO_3 aqueous solution and DI water to remove Ag dendrites and particles. The fabricated Si NW arrays were dried in ambient atmosphere.

A 10-nm Pd layer was deposited on the dense Si NW arrays with a power of 20 W using an ultra-high vacuum (UHV) DC magnetron sputtering system (SNTEK Co., Ltd). The working pressure was retained at 2.0 × 10^{-3} Torr under 34 sccm Ar flow rate in a vacuum chamber, with a base pressure of 4.1 × 10^{-7} Torr. The deposition rate of the Pd (3 N purity) at RT was ~4.5 Å/s.

2.2. Characterization and sensing measurements

The morphology of the Pd-coated Si NW arrays was investigated by field-emission scanning electron microscopy (FE-SEM; JSM-7001 F, JEOL Ltd.). The presence of Pd nanoparticles on Si NW arrays was confirmed by an energy dispersive X-ray spectrometer (FE-SEM-EDS; JEOL-7800 F, JEOL Ltd.).

The fabricated Pd-coated Si NW arrays were loaded onto a device, which consisted of a polyimide-based plastic outer shell (lower part), two printed circuit boards (PCB), and a cable connected to the PCB (see Fig. 1(b)). Electrodes were constructed parallelly on each side of the loaded Si NW arrays, being connected to the PCB by using silver paste (P-100, Cans Inc.). After the constructed electrodes were dried at ambient atmosphere for 4 h, the upper part of the plastic outer shell, which had a 0.8 × 0.8 cm^2 square open window, was assembled (see Fig. 1(c)).

The performance of the Pd-coated Si NW arrays was assessed in a handmade gas-testing equipment as shown in Fig. 1(d). The oil tank consisted of two chambers, each with a holding volume of 1.5 L. One was a bubbling chamber, with H_2 injected and dissolved in the transformer oil. The other one was a reaction chamber, in which the Pd-coated Si NW arrays were immersed in oil through a cable port. The transformer oil (KS 1#2, DONGNAM Petroleum Ind. Co. Ltd.) was

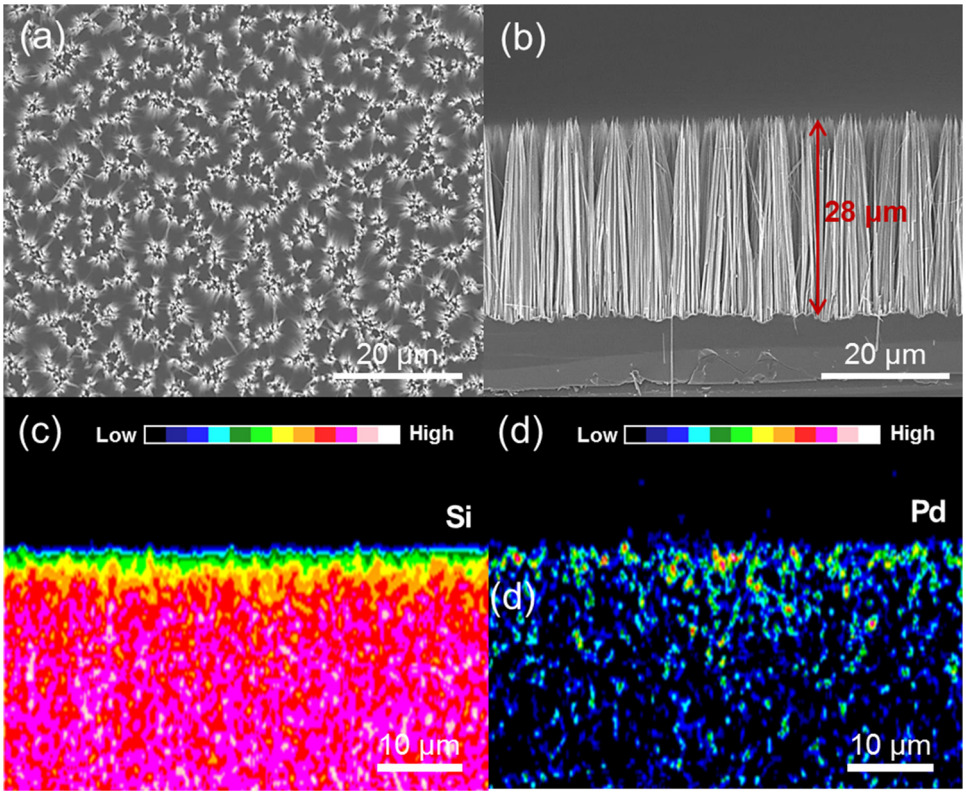

Fig. 2. SEM images of Pd-coated Si NW arrays: (a) top view, (b) cross-sectional view, and (c–d) EDX mapping of the magnified top view.

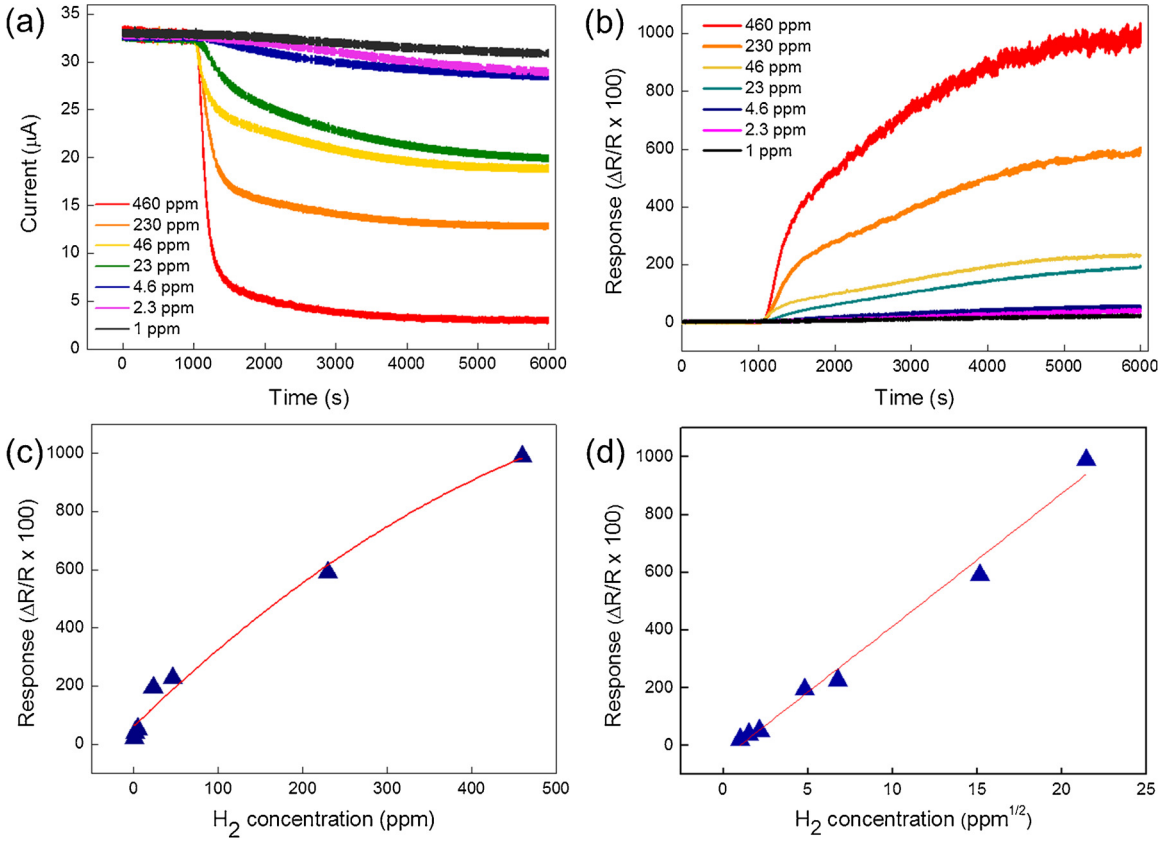

Fig. 3. (a) Real-time current curves of Si NW arrays for various H_2 concentrations in oil, and (b) response curves for specific H_2 concentration. Plots of responses as a function of (c) H_2, and (d) square root of H_2 concentrations.

Table 1
Sensing properties of resistance-based H_2 sensors for the detection of dissolved H_2 in transformer oil.

Materials	Response (%)	Operating temp. (°C)	Low Detection Limit (ppm)	Response time (min)	Ref.
Pd thick film on glass	6	20–120	200	58	[9]
Pd NW arrays	6	21–70	1	23	[14]
Pd decorated ZnO NR arrays	90	40–80	5	48	[15]
Pd-coated Si NW arrays	360	20–80	1	10	This work

circulated through the two chambers using circulating pumps. A series heating cable (100 W) was wrapped around the chamber to increase the temperature of oil in it. Both, the oil temperature and heating power, were controlled by a built-in control system. The H_2 mixed with nitrogen (N_2) balance was supplied to the bubbling chamber through a gas inlet at a constant flow of 1000 sccm. The concentration of H_2 in N_2 was fixed in the range of 50–10,000 ppm by a mass flow controller (MFC). H_2 measurements in oil were carried out at atmospheric pressure. A source-measure unit (Keithley 236, Keithley Instruments Inc.) was used to measure the change in resistance of the Pd-coated Si NW arrays, at a constant voltage (0.1 V) and time interval (1 s).

3. Results and discussion

Fig. 2(a) and (b) show the top- and cross-sectional-view SEM images of the Pd-coated Si NW arrays, respectively. The vertical standing Pd-coated Si NW arrays were bundled at their tips, forming local clusters due to the capillary force of the liquid during the drying process of the etched Si NW arrays [16]. The distance between the adjacent Pd-coated Si NW clusters ranged from 1 to 5 μm, whereas the inter-wire distance in a Pd-coated Si NW cluster was estimated to be in the range of sub-nm to a few nm [16]. As shown in Fig. 2(b), the average height of Si NWs was 28 μm. The thickness of Pd was confirmed to be 10 nm (22 s for deposition Pd) using an α-step of the deposited Pd film on the Si substrate. The EDX mapping images of the magnified cross-sectional-view SEM image are shown in Fig. 2(c) and (d), indicating that Pd nanoparticles exist mainly on the top- and mid-sidewall of the Si NWs. The deposited Pd nanoparticles on the Si NWs were barely found in the bottom region of the Si NWs (the image is not shown) due to shadow effect of the high aspect ratio in Si NWs [16,17].

In order to measure the sensing properties in oil, the Pd-coated Si NW arrays were immersed in an oil-filled reaction chamber, connected to the oil-filled bubbling chamber (see Fig. 1(d)). The solubility of H_2 in the oil was calculated in accordance with Henry's Law ($P_{H_2} = k_H \lfloor H_2 \rfloor_{oil}$), where P_{H_2} is the partial pressure of H_2, k_H as the Henry's Law constant, and $\lfloor H_2 \rfloor_{oil}$ is the dissolved H_2 concentration in oil. We used the values of k_H = 0.001908 M/atm, 21 °C and k_H = 0.00294 M/atm, 70 °C, which correspond to 460.2 ppm/% at 21 °C and 824 ppm/% at 70 °C [14].

The real-time electrical current of Pd-coated Si NW arrays was measured with various H_2 concentrations, ranging from 460 ppm to 2 ppm dissolved H_2 in the oil at 20 °C (see Fig. 3(a)). The current in the Pd-coated Si NW arrays abruptly decreased with increasing H_2 concentrations initially, eventually reaching saturation. The response time of the Pd-coated Si NW arrays was defined as the time required to reach 90% of the total change in current. The fastest response time of the Pd-coated Si NW arrays was 600 s at 460 ppm H_2 in the oil (see red curve). The sensor response is defined according to Eq. (1),

$$\text{Response (\%)} = \frac{R_{H_2} - R_0}{R_0} \times 100 \quad (1)$$

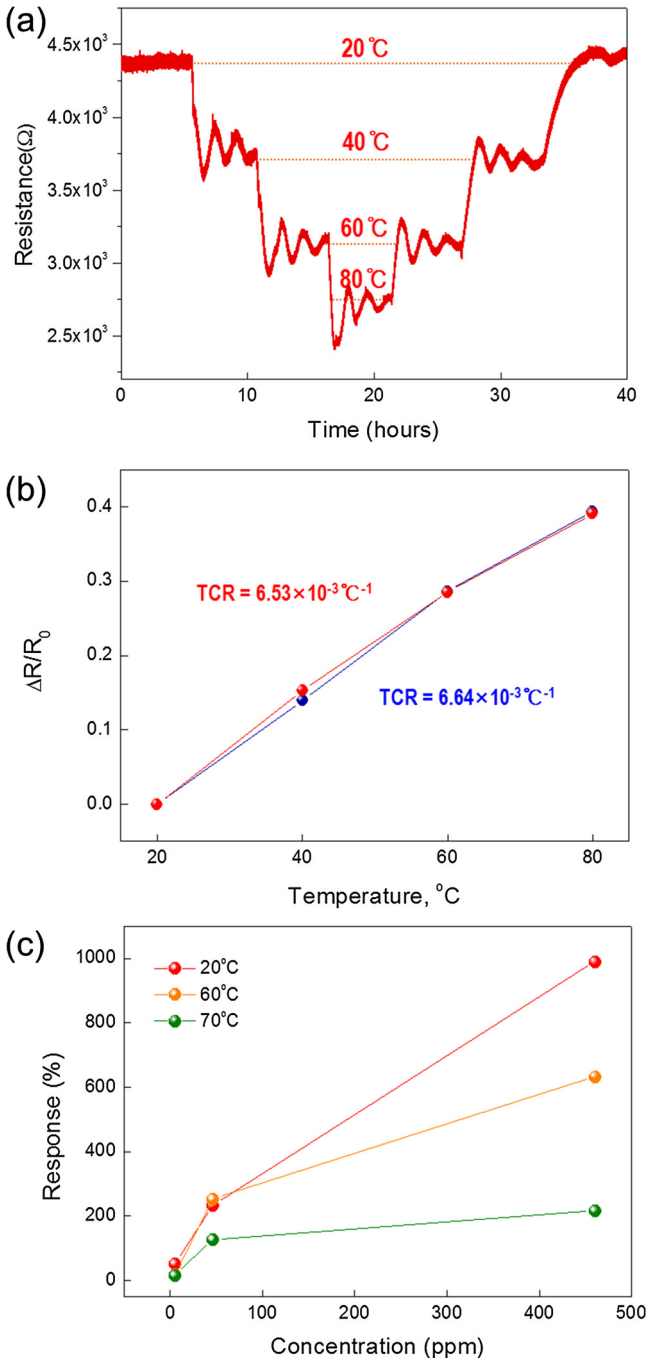

Fig. 4. The temperature dependence of Pd-coated Si NW arrays across a range of 20–80 °C in oil: (a) plot of resistance variation depending on the stepwise temperature modulation, (b) replot of the resistance change ratio vs. temperature, (c) response curves as a function of H_2 concentrations in oil at various temperatures (20–70 °C).

where R_{H_2} and R_0 are the electrical resistances of Pd-coated Si NW arrays in H_2 and N_2, respectively. The changes in current, shown in Fig. 3(a), were rearranged as a plot of the response curves for specific H_2 concentrations by using Eq. (1) (see Fig. 3(b)). The maximum value of the response was 1000% at 460 ppm H_2. The plot of responses showed a parabolic curvature for specific H_2 concentrations (correlation constant, r = 0.98), as shown in Fig. 3(c). The responses for specific H_2 concentrations were plotted as a function of the square root of the H_2 concentrations (see Fig. 3(d)), showing a linear dependency of changes in response to the H_2 concentrations (r = 0.99) in accordance with Sievert's Law [19]. Compared to other oil-immersed type of H_2 gas

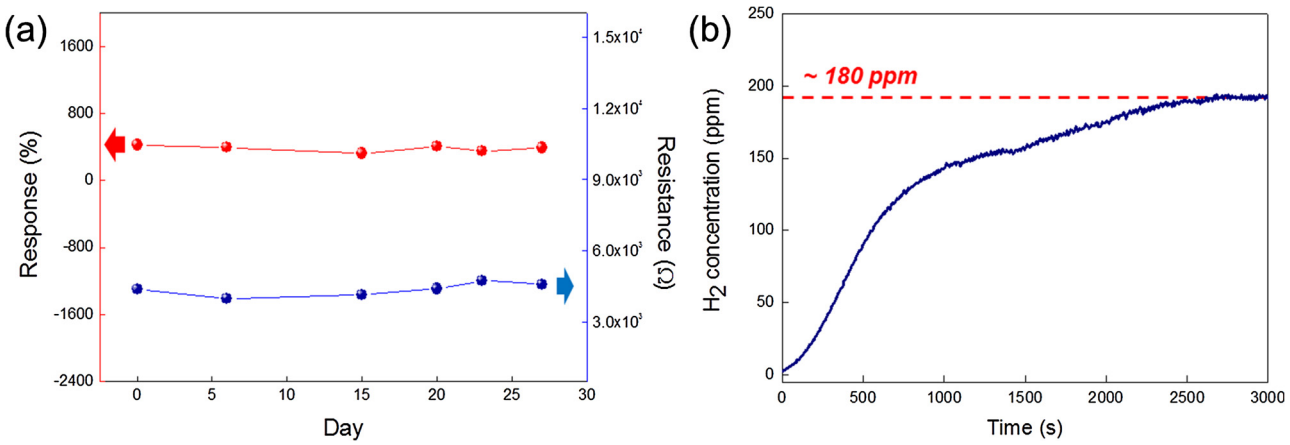

Fig. 5. (a) Long term stability of Pd-coated Si NW arrays in terms of the response and resistance, and (b) the calculated dissolved H_2 concentration curve of Pd-coated Si NW arrays with introduced H_2 concentration in the oil.

sensors, based on resistance change for the purpose of real-time monitoring of dissolved H_2 in oil, Pd-coated Si NW arrays showed extremely superior performance in terms of the response, the lowest detection limit, and the response time (see Table 1). The sensing mechanism of the Pd-coated Si NW arrays is already well-understood, as mentioned in our previous report [16]. In brief, when exposed to H_2, the dissociation of hydrogen molecules into hydrogen atoms converts the coated Pd on Si NWs to PdH_x, lowering the work function of Pd ($\phi_{Pd} > \phi_{PdHx}$), while facilitating the transfer of electrons to the *p*-type Si NWs. The transferred electrons neutralize the hole carriers. Thus, the resistance of the Pd-coated *p*-type Si NW arrays increases [16].

Fig. 4 presents the temperature dependence of Pd-coated Si NW arrays across a range of 20 °C–80 °C in oil: (a) plot of resistance variation depending on the stepwise temperature modulation, (b) replot of the resistance change ratio vs. temperature, and (c) response curves as a function of H_2 concentrations in oil at various temperatures (20–70 °C). The temperature of the oil was increased up to ~80 °C, in steps of 20 °C, by maintaining each temperature for 6 h (see Fig. 4(a)). The resistance of the Pd-coated Si NW arrays immersed in oil showed stepwise decrease with the increase in temperature. Similarly, the resistance of the Pd-coated Si NW arrays ascended stepwise with the decrease in temperature. The gradients of the resistance change at various temperatures are described in terms of the temperature coefficient of resistance (TCR, α) as shown in Fig. 4(b). The TCR is defined according to Eq. (2),

$$TCR(\alpha) = \frac{1}{\Delta T}\frac{R(T)-R(T_0)}{R(T)} \quad (2)$$

where ΔT indicates the difference between T and T_0, with the TCR value of the Pd-coated Si NW arrays being 6.53×10^{-3} °C^{-1}, with the increase in temperature. The TCR value of the decreasing temperature barely changed (6.64×10^{-3} °C^{-1}). The obtained value is comparable to the value for *p*-type bulk single crystal Si ($\alpha \approx 7 \times 10^{-3}$ °C^{-1}) [20]. Fig. 4(c) shows the transient H_2 response of Pd-coated Si NW arrays at various oil temperatures (20–70 °C). We found that the H_2 response of Pd-coated Si NW arrays decreases with the increase in temperature of oil at specific H_2 concentrations. This can be attributed to the reduced solubility of H in PdHx at elevated temperatures [14,21].

Fig. 5 shows the long-term stability of the Pd-coated Si NW arrays in terms of the response and resistance, as well as the calculated dissolved H_2 concentration curve of Pd-coated Si NW arrays with the H_2 concentration introduced in the oil. In order to assess the reliability of Pd-coated Si NW arrays for application in the monitoring of H_2 concentration in a transformer, the Pd-coated Si NW arrays were immersed in oil for 30 days. The long-term stability of the Pd-coated Si NW arrays was tested in terms of the variation in response to an H_2 concentration of 230 ppm, and initial resistance (see Fig. 5(a)). Both, the H_2 response and the initial resistance, barely varied over the 30 days in oil. The exact prediction of the H_2 concentration in oil is one of the important factors in DGA. In order to obtain the value of the dissolved H_2 concentration from the H_2 concentration introduced into the oil, we used the following equation.

$$[H_2]_{prediction} = (\text{Response} - b)/a \quad (3)$$

In the equation, *a* indicates the slope of the trend line in Fig. 3(d), and *b* indicates the constant. Fig. 5(b) shows the real-time dissolved H_2 concentration curve of Pd-coated Si NW arrays, with a certain H_2 concentration introduced into the oil. The curve reached saturation after 2500 s, presenting a dissolved H_2 concentration of 180 ppm. In addition, the concentration of dissolved H_2 was measured by using a gas chromatographer (GC; Calisto 9, Morgan Schaffer), that determined the concentration of dissolved H_2 to be 176 ppm, indicating that the value we calculated was reasonable.

4. Conclusions

In summary, we investigated the H_2 sensing properties of Pd-coated Si NW arrays for the detection of dissolved H_2 gas in transformer oil. The Pd-coated Si NW arrays were fabricated by the aqueous electroless etching method and sputtering process. The Pd-coated Si NW arrays were immersed in transformer oil, being tested with various introduced H_2 concentrations. The excellent sensing properties in oil were obtained with regard to high response of ~1000% and a rapid response time (600 s) upon exposure to dissolved H_2 concentration of 460 ppm. The Pd-coated Si NW arrays showed a temperature coefficient of resistance (TCR) of 6.53×10^{-3} °C^{-1}. Both, the H_2 response and initial resistance, of the Pd-coated Si NW arrays barely varied over the 30 days in oil at room temperature (20 °C). In addition, a simple equation was obtained to predict the dissolved H_2 concentration from the H_2 concentration introduced into the oil. Our results demonstrated that Pd-coated Si NW arrays show extremely superior performance in terms of the response (~1000%), the lowest detection limit (1 ppm), and the response time (600 s), having a potential in monitoring of degradation in the internal components of a transformer.

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