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Pd-coated SnO_2 Nanorod Arrays for Detection of Dissolved H_2 in Transformer Oil

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Abstract:

We report the enhanced sensing properties of the Pd-coated SnO_2 nanorod (NR) arrays in detecting H_2 gas in air and transformer oil. The Pd nanoparticles were coated on the SnO_2 NR arrays, randomly ordered and vertically standing, by glancing angle deposition (GLAD) method which utilizes an electron-beam evaporator and DC magnetron sputtering system. The Pd-coated SnO_2 NR arrays were optimized to have a high response (104 at 1 % H_2) in air. The sensor materials were immersed and measured in the transformer oil that contains various concentration of dissolved H_2. We found that the Pd-coated SnO_2 NR arrays showed a superior performance in regard to the response (~96.3), the detection limit (0.3 ppm), and the response time (300 s). The Pd-coated SnO_2 NR arrays had a temperature coefficient of resistance (TCR) of 3.69×10^{-3} °C^{-1} at various oil temperatures (20–80 °C). The sensing mechanism of the Pd-coated SnO_2 NR arrays was also demonstrated by the decrease in the height of Schottky barrier at the interface of Pd/SnO_2, upon exposure to H_2. The excellent sensing performance in both air and oil are attributed to the synergistic effects originated from the high surface-to-volume ratio of NR arrays and the decreased Schottky barrier height of SnO_2.

Key words: hydrogen sensors, SnO_2, Pd, transformer oil, Schottky barrier

Background and Motivation

One of the most challenging ongoing issues in power transformers is monitoring degradation of the internal components in a transformer which involves analyzing dissolved gases in insulating oil. Among the gases that can be generated in transformer oil, H_2 is the most detrimental substance in a transformer due to its capacity to evolve during discharge and thermal deterioration [1].

Until now, the indirect approach such as gas chromatography (GC) has been implemented to detect the dissolved gases in the transformer oil [1]. However, the indirect approach has a fundamental uncertainty in terms of detected gas concentrations due to off-line sampling [1]. In order to overcome the drawbacks of dissolved gas analysis (DGA), several attempts have been made to measure the dissolved gas, in oil, directly by applying oil-immersed gas sensors.

In this work, we have investigated resistivity type *in-situ* real-time monitoring H_2 sensor using Pd-coated SnO_2 NR arrays fabricated by GLAD method.

Results and Discussion

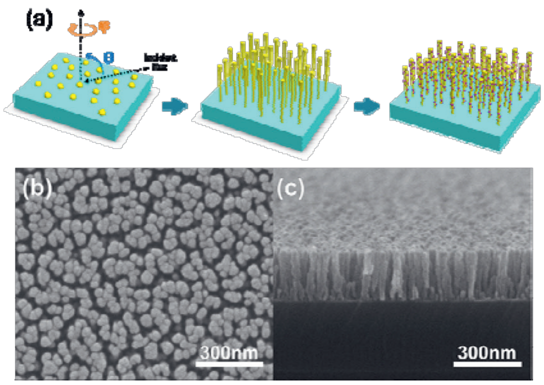

Fig. 1. (a) Glancing angle deposition method; (b) top view and (c) side view SEM images of Pd-coated SnO_2 nanorod arrays.

Figure 1(a) represents a schematic image of the overall fabrication process of Pd-coated SnO_2 NR arrays. The randomly ordered SnO_2 NR arrays were fabricated by a GLAD method using an electron-beam evaporator, and the Pd

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films were sputtered on top of the SnO_2 NR arrays. Figs. 1(b) and 1(c) are the SEM images of top- and side-view of the as-synthesized NR arrays, respectively.

In GLAD, a vertically grown structure can be deposited by inducing a shadowing effect as shown in Fig. 1(c) [2]. Vertically standing NRs are randomly spaced, averaging about diameter 30 nm in diameter, 200 nm in height and 20-40 nm apart from each other.

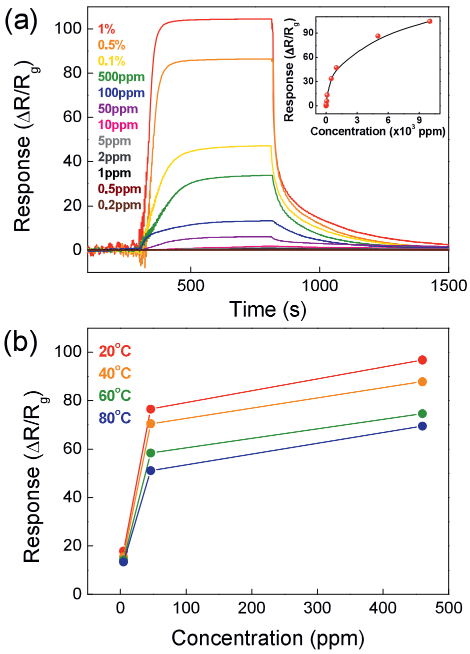

Fig. 2. (a) Real-time response curves of Pd-coated SnO_2 NR arrays for various H_2 concentrations, (b) response curves as a function of H_2 concentrations in oil at various temperatures (20–80 °C).

Fig. 2(a) shows the change in real-time response depending on the H_2 concentration (0.2 ppm-1 %) in air at room temperature. Nitrogen balanced H_2 gas was used in this study, considering the insufficient oxygen in the transformer oil. The resistance decreases from the base of 650 kΩ for the specific H_2 concentrations. The response was defined as $(R_a\text{-}R_g)/R_g$, where R_a and R_g are the electrical resistance of the Pd-coated SnO_2 NR arrays in air and in the H_2 gas, respectively. The responses for 1 %, 0.1 %, 100 ppm, 10 ppm, and 1 ppm concentrations of H_2 were 104, 47.2, 13.3, 1.9, and 0.25, respectively (See the inset of Fig. 2(a)).

The Pd-coated SnO_2 NR arrays were immersed into an oil-filled chamber to detect the dissolved H_2 in the transformer oil, at various temperature. Fig. 2(b) shows the temperature dependence of the Pd-coated SnO_2 NR arrays in oil ranging from 20 °C to 80 °C. As the temperature increases, the H_2 response of the Pd-coated SnO_2 NR arrays decreases by about 28 % (at 460 ppm dissolved H_2). This may be due to the lower solubility of hydrogen in PdH_x at high temperature.

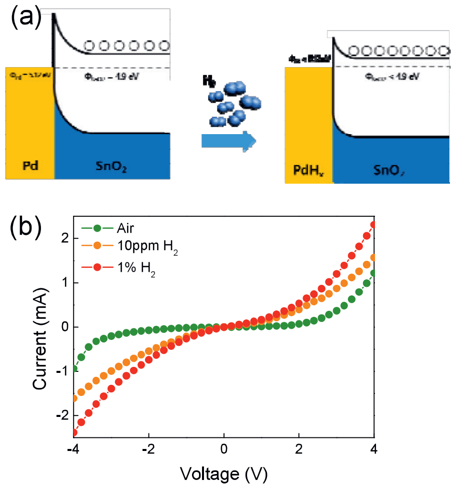

Fig. 3. (a) A schematic illustration of the change in Schottky barrier at the metal (Pd)-semiconductor (SnO_2) junction (b) I-V curves of Pd/SnO_2 junction in various atmospheric conditions.

In a normal state, Schottky barrier ($\phi_M > \phi_{SC}$) is formed because the work function of Pd (ϕ_{Pd}=5.12 eV) is larger than that of SnO_2 (ϕ_{SnO2}=4.9 eV). After H_2 exposure, Pd changes into PdH_x causing the work function of Pd to decrease ($\phi_{Pd} > \phi_{PdHx}$) with the height of Schottky barrier height (Fig. 3(a)) [3]. The change in Schottky barrier can be qualitatively estimated by the tendency of *I-V* curves. The absolute value of the slope in the *I-V* curves increases with increasing H_2 concentration, which indicates a decrease in Schottky barrier at the interface of Pd and SnO_2 (Fig. 3(b)).

Our results demonstrated that Pd-coated SnO2 NR arrays show extremely superior performance in terms of the response (~96), the lowest detection limit (0.2 ppm), and the response time (300 s), having a potential in monitoring of degradation in the internal components of a transformer.

Reference

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