H₂ Sensing Properties of Diode-type Gas Sensors
Fabricated with Ti- and/or Nb-based Materials

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Abstract

A thermally oxidized TiO$_2$ or Nb$_2$O$_5$ film equipped with a top Pd film electrode and a bottom Ti or Nb plate electrode (Pd/MO(n)/M, MO: oxide film, M: metal plate, n: annealing temperature (°C)) has been investigated as a diode-type H$_2$ sensor under air or N$_2$ atmosphere. Pd/TiO$_2$(n)/Ti sensors showed relatively poor H$_2$ sensing properties in air, in comparison with Pd/anodic-TiO$_2$(n)/Ti sensors constructed with an anodized TiO$_2$ film equipped with a top Pd film electrode and a bottom Ti plate electrode, which were reported in our previous studies. On the other hand, Pd/Nb$_2$O$_5$(n)/Nb sensors showed relatively larger H$_2$ response with fast response and recovery speeds than Pd/TiO$_2$(n)/Ti sensors in air under high forward bias conditions. A Pd/Nb$_2$O$_5$(450)/Ti sensor, which was fabricated by radio-frequency magnetron sputtering of Nb metal on a Ti substrate followed by thermal oxidation at 450°C, showed the largest H$_2$ response and relatively fast response and recovery speeds in air, among the sensors tested. In addition, H$_2$ response of the Pd/Nb$_2$O$_5$(450)/Ti sensor in air was much lower than that in N$_2$, but the logarithm of H$_2$ response was almost proportional to the logarithm of H$_2$ concentration in a wide range of H$_2$ concentration (10~8000 ppm) in air, and the H$_2$ sensitivity in air was much higher than that in N$_2$.

Keywords: Gas sensor, Hydrogen, Titania, Niobium oxide, Palladium
1. Introduction

Recently, numerous efforts have been directed to developing various kinds of H2 sensors [1-6], because H2 gas as a clean energy source is significantly expanding into various fields. We also reported various diode-type H2 sensors with high and reversible H2 response as well as fast response and recovery behavior in both air and N2 atmospheres, compared with other types of gas sensors [7-13]. These diode-type sensors (Pd/anodic-TiO2(n)/Ti, MO: TiO2 or Nb2O5, M: Ti or Nb, n: annealing temperature (°C)) were fabricated by anodic oxidation of a metal plate (Ti or Nb) and then consisted of thin metal oxide films (TiO2 or Nb2O5) having well-developed macropores at their surface and noble metal electrodes (mainly Pd). Their excellent H2 sensing properties seem to arise from much lower Schottky barrier height at the boundary between the Pd electrode and the oxide film in H2 than that in air, due to dissociative adsorption of H2 molecules and subsequent dissolution of H atoms into the Pd electrode. On the other hand, Lee et al. reported that a TiO2 film which was fabricated by thermal oxidation of a Ti plate can also become an attractive H2 sensing material by controlling the fabrication conditions strictly [14].

In this study, therefore, thin metal oxide films (TiO2 or Nb2O5) on Ti or Nb plates were fabricated under different conditions by utilizing thermal oxidation and/or radio-frequency (rf) magnetron sputtering, and H2 sensing properties of these films coupled with a Pd electrode were investigated under both air and N2 atmospheres.

2. Experimental

A Ti or Nb metal plate (5.0 × 5.0 mm²) with a thickness of 0.5 mm was oxidized thermally in air at 600~900°C for 6 h or 400~550°C for 1 h, respectively. In some cases, a Nb thin film was physically deposited on the surface of the Ti plate by rf magnetron sputtering (Shimadzu Emit Co., Ltd., HSR-552S) at 300 W for 5 min, and it was also heat-treated at 450°C for 6 h in air. Back sides of these samples were polished by an emery paper to eliminate any oxide layers to ensure the following electrical contacts. The samples obtained were referred to as MO(n)/M (M: Ti or Nb, MO: TiO2 or Nb2O5, n: annealing temperature (°C)). The microstructure of the oxide films prepared was observed by a scanning electron microscope (SEM; Hitachi, Ltd., S-2250N).

A palladium thin film was sputtered at 300 W for 10 min on the surface of the oxidized films, and then Au wires were attached with a Pd paste (Tanaka Kikinzoku Kogyo K.K., T60) on both sides of the samples. Thereafter, they were fired at 400°C for 1 h in air. The MO(n)/M coupled with a Pd electrode was represented as Pd/MO(n)/M.
A dc voltage of +0.04~1.0 V was applied to the Pd/MO(n)/M under the forward bias conditions, i.e. Pd(+)/MO/M(-), and transient changes in current flowing through the sensors upon exposure to 10~8000 ppm H₂ balanced with dry air or nitrogen were monitored at 200~300°C, by employing a potentiostat (Solartron Analytical, 1287A). The response measurement was conducted in a flow apparatus at a gas flow rate of 100 cm³ min⁻¹. The volume from the switch valve for changing the gas flowing to the installation position of a sensor was about 90 ml in the present flow apparatus. Therefore, the time necessary for complete substitution for gaseous environment over the sensor is estimated to be more than 1 min under the present experimental conditions. Current(I)-voltage(V) characteristics of the sensors were also measured in a range of -2.0~2.0 V at a sweep rate of 10 mV s⁻¹ by employing the potentiostat. The magnitude of sensor response was defined as Ig-Ib, where Ig and Ib represented a sensor current in 10~8000 ppm H₂ balanced with air or N₂ and in a base gas (air or N₂), respectively.

3. Results and Discussions

3.1 Characterizations of TiO₂(n)/Ti and H₂ sensing properties of Pd/TiO₂(n)/Ti sensors

Figure 1 shows XRD patterns of Ti plates thermally oxidized in air at 600~900°C for 6 h (TiO₂(n)/Ti). Small peaks of rutile and anatase phases were observed for TiO₂(600)/Ti, together with those expected of a Ti phase. The fraction of the rutile phase increased obviously when the Ti plate was heated at 700°C, and the anatase phase could not be confirmed at heating temperatures higher than 800°C. SEM photographs of the surface of TiO₂ films thermally oxidized at temperatures higher than 700°C are shown in Fig. 2. The TiO₂ film in the TiO₂(600)/Ti was too thin, and therefore its image was not clearly observed by SEM. A typically dense TiO₂ film with large agglomerates (1.5~2.0 μm wide, ≤ 6.0 μm long) was formed at the surface of a Ti plate after the heating at 700°C (TiO₂(700)/Ti), and a certain number of small particles with a diameter of less than 0.2 μm also existed on the large agglomerates. In addition, grain-boundaries were very obscure. On the other hand, the sizes of both agglomerates and small particles increased with an increase in the annealing temperature (agglomerates: 2.5~6.0 μm wide and ≤ 8.0 μm long for TiO₂(800)/Ti, ≤ 9.0 μm wide and ≤ 20 μm long for TiO₂(900)/Ti; small particles: ≤ 0.5 μm for TiO₂(800)/Ti, ≤ 1.0 μm for TiO₂(900)/Ti in diameter). No submicron-size open pores were observed on the TiO₂ surface of all TiO₂(n)/Ti plates, although many disordered and well-developed macropores (50~130 nm in diameter) were formed at the surface of the anodized TiO₂ films [7-12].

Figure 3 shows I-V characteristics in air and in 8000 ppm H₂ balanced with air of
Pd/TiO$_2$(n)/Ti sensors at 300°C. Response transients of these sensors to 8000 ppm H$_2$ in air at a forward bias voltage of 0.1 V at 300°C are shown in Fig. 4. Pd/TiO$_2$(600)/Ti showed almost metallic conductivity and then was not suitable for a sensor material, probably due to a very thin TiO$_2$ film on the Ti plate (the data is not shown here). The I-V curve of the Pd/TiO$_2$(700)/Ti sensor in air showed ohmic behavior with relatively large current, and its non-linearity was observed in 8000 ppm H$_2$ balanced with air under a forward bias. Accordingly, the base current in air was also too high even at +0.1 V, as shown in Fig. 4(a). The response speed to 8000 ppm H$_2$ of the Pd/TiO$_2$(700)/Ti sensor in air was typically fast, but the serious problem was too large over-shooting behavior. Currents both in air and in 8000 ppm H$_2$ balanced with air observed with the Pd/TiO$_2$(900)/Ti sensor were extremely low and it showed no response to H$_2$, probably because of the formation of an extremely thick TiO$_2$ film on the surface of the Ti plate. On the other hand, the Pd/TiO$_2$(800)/Ti sensor showed much better non-linear I-V characteristics under a forward bias, based on the Schottky barrier at the Pd/TiO$_2$ interface, among the Pd/TiO$_2$(n)/Ti sensors tested. It also showed the most stable H$_2$ response among them, but the H$_2$ sensing properties (especially, H$_2$ response and recovery behavior) was inferior to those of the H$_2$ sensors fabricated with anodized TiO$_2$ films (Pd/anodic-TiO$_2$(n)/Ti) reported in our previous studies (the magnitude of sensor response (I_g-I_b): ca. 5 x 10$^{-2}$ mA even at 250°C) [7-12]. The fast response and recovery of the anodized TiO$_2$ film is undoubtedly attributed to its porous structure which facilitates H$_2$ gas diffusion into the interface between Pd and TiO$_2$. And therefore slow response and recovery behavior of the Pd/TiO$_2$(800)/Ti is then considered to arise from its dense TiO$_2$ film.

3.2 Characterizations of Nb$_2$O$_5$(n)/Nb and H$_2$ sensing properties of Pd/Nb$_2$O$_5$(n)/Nb sensors

Nb metal was generally less stable in air at elevated temperatures than Ti metal. Thus, a Nb$_2$O$_5$ film on the Nb plate was prepared by heating at lower temperatures for shorter times than the conditions necessary for the formation of a TiO$_2$ film from a Ti plate as described above. Figures 5 and 6 show XRD patterns and SEM photographs of thermally oxidized Nb$_2$O$_5$ films in air at 400-550°C for 1 h (Nb$_2$O$_5$(n)/Nb). Nb$_2$O$_5$(400)/Nb showed no diffraction peaks except for those of Nb metal (Fig. 5(a)), but a little amount of products (submicron-size agglomerates with submicron-size particles) were observed at the surface of the Nb plate (Fig. 6(a)). Clear diffraction peaks expected for Nb$_2$O$_5$ were confirmed after the Nb metal was heat-treated in a temperature range between 450°C and 550°C. Their
surface morphology was extremely rough and little dependent on their annealing temperature. In addition, it was largely different from that of an anodized Nb2O5 film with disordered macropores (ca. 1–3 μm in diameter), as reported previously [13].

Figure 7 shows I-V characteristics in air and in 8000 ppm H2 balanced with air of the Pd/Nb2O5(n)/Nb sensors at 200°C. Response transients of these sensors to 8000 ppm H2 in air at a forward bias voltage of 0.1 V at 200°C are shown in Fig. 8. Pd/Nb2O5(400)/Nb could not be used as a diode-type gas sensor, because its resistance was too low. However, Pd/Nb2O5(450)/Nb showed a non-linear I-V characteristic and a large current in 8000 ppm H2 under forward bias conditions, while the current in air was extremely small even at a forward bias voltage of 2.0 V, as shown in Fig. 7(a). As a result, a large response to 8000 ppm H2 was induced at a forward bias voltage of 1.0 V, as shown in Fig. 8(a). On the other hand, Pd/Nb2O5(500)/Nb and Pd/Nb2O5(550)/Nb also showed clear difference in I-V characteristics between in air and in 8000 ppm H2 balanced with air, as shown in Figs. 7(b) and 7(c), but the heat-treatment above 500°C resulted in too high sensor resistance and too small magnitude of response, as shown in Figs. 8(b) and 8(c). Figure 9 shows cross-sectional SEM photographs of Nb2O5(n)/Nb (n = 450, 500 and 550). The Nb2O5 films consisted of stacked layers with a thickness of several μm, and the thickness of the Nb2O5 films (i.e., the number of stacked layers) increased with an increase in heating temperature. The resistance of diode-type gas sensors is generally dependent only on the magnitude of Schottky barrier formed at the metal/oxide interface. However, the resistance of Pd/Nb2O5(n)/Nb sensors seems to be largely influenced by the thickness of the Nb2O5 film. Therefore, strict thickness-control of the Nb2O5 film is indispensable in order to utilize the Nb2O5 as a diode-sensor material, but the thermal instability of the Nb metal apparently prohibits the improvement on the electrical and gas-sensing properties of Pd/Nb2O5(n)/Nb sensors.

3.3 Characterizations of Nb2O5(n)/Ti and H2 sensing properties of Pd/Nb2O5(n)/Ti sensors

A Nb film was deposited on a Ti plate by rf magnetron sputtering at 300 W for 5 min, and then heat-treated at 450°C for 6 h in air, to fabricate a thin Nb2O5 film on the thermally stable Ti plate. SEM photographs of the thin Nb2O5 film fabricated on the Ti plate are shown in Fig. 10. The dense Nb2O5 film with a relatively smooth surface and a well-controlled thickness (ca. 0.7 μm) was observed on the Ti plate, in comparison with Nb2O5(n)/Nb (see Figs. 6 and 9). The Pd/Nb2O5(450)/Ti sensor showed excellent nonlinearity of I-V curves at 100°C and 250°C as well as a large difference in sensor current between in air and in 8000
ppm H₂ balanced with air under a forward bias condition, as shown in Fig. 11, and thus it was expected that such I-V characteristics would guarantee much better responses to H₂. H₂ response transients of the Pd/Nb₂O₅(450)/Ti sensor at 100°C and 250°C in air are shown in Fig. 12. The sensor exhibited a much larger H₂ response and faster response and recovery speeds at 250°C than Pd/TiO₂(n)/Ti and Pd/Nb₂O₅(n)/Nb sensors. In addition, a clear H₂ response was confirmed even at 100°C, while the response and recovery speeds at 100°C became slower than those at 250°C, probably because H atoms dissolved in the Pd metal were not easily released to air at 100°C. H₂ sensing properties of the Pd/Nb₂O₅(450)/Ti sensor in N₂ were also measured at 100°C and 250°C, as shown in Fig. 13. The magnitude of H₂ responses in N₂ was more than ten times larger than that in air both at 100°C and 250°C, while the recovery speed in N₂ was much slower than that in air. Our previous study showed that the recovery speed of Pd/anodic-TiO₂(n)/Ti sensors under N₂ atmosphere was terribly slower than that under air atmosphere, probably because the H atoms absorbed in the Pd metal under N₂ atmosphere were slowly desorbed as H₂ molecules from the Pd surface and those absorbed in the Pd metal under air atmosphere were quickly desorbed as H₂O molecules from the Pd surface after reacting with O₂ [12]. The difference of such H₂-desorption behavior between in air and in N₂ may also have a great influence on the recovery behavior of the Pd/Nb₂O₅(450)/Ti sensor, as shown in Figs. 12 and 13.

Figure 14 shows variations of H₂ response of the Pd/Nb₂O₅(450)/Ti sensor with H₂ concentration in air and in N₂. The logarithm of H₂ response of the sensor operated under a forward bias voltage of 0.4 V was almost proportional to the logarithm of H₂ concentration in the wide range of H₂ concentration (10~8000 ppm) in air. In addition, a clear H₂ response (ca. 2 μA) and fast response and recovery behavior (not shown here) were confirmed even to 10 ppm H₂ in air. This may promise that the sensor can detect H₂ in the concentration range of ppb level in air. In contrast, the responses to more than 500 ppm H₂ in N₂ were much larger than those in air, even under an extremely low applied voltage of 0.01 V, but the responses to H₂ less than 100 ppm in N₂ were not confirmed at all. In addition, the H₂ sensitivity (the slope of the linear relationship between log(Iₐ-Iₐ) and log(H₂ concentration)) in N₂ was also smaller than that in air. The mechanism of such incomprehensible behavior in N₂ is not clear at present, but the surface reactivity and the solubility of H₂ into Pd and the variation in work function of Pd as a function of H₂ concentration in N₂ may be involved in such behavior.

4. Conclusion
H₂ sensing properties of Pd/MO(n)/M (MO: TiO₂ or Nb₂O₅, M: Ti or Nb, n: annealing temperature (°C)) as a diode-type gas sensor were investigated under air or N₂ atmosphere. The H₂ responses of Pd/TiO₂(n)/Ti sensors fabricated in this study were inferior to those of Pd/anodic-TiO₂(n)/Ti sensors reported in our previous studies, under air atmosphere [7-12]. On the other hand, Pd/Nb₂O₅(n)/Nb sensors, which were operated under a high forward bias voltage of +1.0 V, showed better H₂ sensing properties in air than Pd/TiO₂(n)/Ti sensors. However, the resistance of the Nb₂O₅ film was too high and the Nb metal was thermodynamically instable at elevated temperatures for gas-sensor applications. A Pd/Nb₂O₅(450)/Ti sensor showed the largest H₂ response and relatively fast response and recovery speeds in air among the sensors tested. The H₂ response of the Pd/Nb₂O₅(450)/Ti sensor in air was much lower than that in N₂ in the concentration range of more than 500 ppm, but it showed a clear H₂ response with relatively fast response and recovery speeds in a wide H₂ concentration range of 10~8000 ppm in air.

References


Biographies

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**Figure Captions**

Fig. 1. XRD patterns of Ti plates thermally oxidized in air at 600–900°C for 6 h (TiO$_2$(n)/Ti, n: (a) 600, (b) 700, (c) 800 and (d) 900).

Fig. 2. SEM photographs of thermally oxidized TiO$_2$ films of TiO$_2$(n)/Ti (n: (a) 700, (b) 800 and (c) 900).

Fig. 3. I-V characteristics of Pd/TiO$_2$(n)/Ti sensors (n: (a) 700, (b) 800 and (c) 900) in air (solid line) and in 8000 ppm H$_2$ balanced with air (dashed line) at 300°C. *: the bias voltage applied when the response behavior of the sensors was measured.

Fig. 4. Response transients to 8000 ppm H$_2$ in air of Pd/TiO$_2$(n)/Ti sensors (n: (a) 700, (b) 800 and (c) 900) at 300°C.

Fig. 5. XRD patterns of Nb plates thermally oxidized in air at 400–550°C for 1 h (Nb$_2$O$_5$(n)/Nb, n: (a) 400, (b) 450, (c) 500 and (d) 550).

Fig. 6. SEM photographs of thermally oxidized Nb$_2$O$_5$ films of Nb$_2$O$_5$(n)/Nb (n: (a) 400, (b) 450, (c) 500 and (d) 550).

Fig. 7. I-V characteristics of Pd/Nb$_2$O$_5$(n)/Nb sensors (n: (a) 400, (b) 450, (c) 500 and (d) 550) in air (solid line) and in 8000 ppm H$_2$ balanced with air (dashed line) at 200°C. *: the bias voltage applied when the response behavior of the sensors was measured.

Fig. 8. Response transients to 8000 ppm H$_2$ in air of Pd/Nb$_2$O$_5$(n)/Nb sensors (n: (a) 400, (b) 450, (c) 500 and (d) 550) at 200°C.

Fig. 9. Cross-sectional SEM photographs of Nb$_2$O$_5$(n)/Nb (n: (a) 450, (b) 500 and (c) 550).

Fig. 10. SEM photographs of Nb$_2$O$_5$(450)/Ti fabricated by rf magnetron sputtering of Nb on a Ti plate, followed by heat-treatment at 450°C for 5 h.

Fig. 11. I-V characteristics of a Pd/Nb$_2$O$_5$(450)/Ti sensor in air (solid line) and in 8000 ppm H$_2$ balanced with air (dashed line) at 100 and 250°C. *: the bias voltage applied when the response behavior of the sensors was measured.

Fig. 12. Response transients of a Pd/Nb$_2$O$_5$(450)/Ti sensor to 8000 ppm H$_2$ in air under a
forward bias voltage of 0.4 V at 100 and 250°C.

Fig. 13. Response transients of a Pd/Nb$_2$O$_5$(450)/Ti sensor to 8000 ppm H$_2$ in N$_2$ under a forward bias voltage of 0.01 V at 100 and 250°C.

Fig. 14. Relationship between H$_2$ response of a Pd/Nb$_2$O$_5$(450)/Ti sensor and H$_2$ concentration in air and in N$_2$ at 250°C.
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