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Design of anodically oxidized Nb_2O_5 films as a diode-type H_2 sensing material

Takeo Hyodo [a,*], Junji Ohoka [b], Yasuhiro Shimizu [a], Makoto Egashira [a]

[a] *Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan*
[b] *Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan*

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Abstract

H_2 sensing properties of an anodically oxidized Nb_2O_5 film coupled with a noble metal electrode (M/Nb_2O_5, M: Au, Pt and Pd) have been investigated under various operating conditions. Among the sensors tested, Pd/Nb_2O_5(S), which was prepared by anodic oxidation in an aqueous solution of 0.5 M H_2SO_4 and coupled with a Pd electrode, showed the highest H_2 response, and the logarithmic sensor current under a forward bias was proportional to the logarithmic H_2 concentration in the whole range tested (10–8000 ppm). The current–voltage characteristics of the Pd/Nb_2O_5(S) sensor at 100 °C apparently showed a typical rectifying function of a metal–semiconductor junction, which was formed between the Pd electrode and the Nb_2O_5 thin film. Addition of water vapor in measurement atmosphere enhanced the magnitude of response to H_2 in air. On the other hand, the magnitude of the CO response was relatively smaller than that to H_2. It was confirmed that the sensor could also respond to H_2 in dry air, even at 28 °C. In addition, the response to N_2-diluted H_2 was much larger than that to air-diluted H_2. Based on AC impedance spectra of the Pd/Nb_2O_5(S) sensor, it is considered that variations in activation energy of two conductance components in air and 8000 ppm H_2 balanced with air with forward bias voltages are well correlated with those in the *I–V* characteristics in air.
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1. Introduction

Semiconductor H_2 gas sensors have already been used in various application fields such as fire alerts, gas leakage detectors and industrial process control systems. However, numerous efforts are still being directed to developing a high performance H_2 sensor [1–5], because the use of H_2 gas as a clean energy source is significantly expanding into various fields. We recently found that a TiO_2 thin film having well-developed pores of submicron size could be fabricated by anodic oxidation of a Ti plate, and that the TiO_2 thin film coupled with Pd and Ti electrodes showed diode-type current (*I*)–voltage (*V*) characteristics and then exhibited high and reversible response to H_2 in both air and N_2 atmospheres [6–9]. These properties are considered to arise from much lower Schottky barrier height at the boundary between the Pd electrode and the TiO_2 film in H_2 than that in air, due to dissociative adsorption of H_2 molecules and then dissolution of H atoms into the Pd electrode. Such interesting results prompted us to investigate the possibility of other anodic oxide films as a diode-type H_2 sensing material.

An anodically oxidized Nb_2O_5 thin film has attracted attention as a dielectric material for solid-type electrolytic capacitors, because of its higher dielectric constant and durability than those of anodically oxidized Al_2O_3 and Ta_2O_5 [10]. However, no information is available about the ability of the anodically oxidized Nb_2O_5 thin film as a gas sensor material in the literature, while the Nb_2O_5 thick films prepared by conventional methods have been used as a resistive-type oxygen sensor [11] and a varistor-type hydrogen sensor [12,13].

In the present study, therefore, we investigated the H_2 sensing properties of anodically oxidized Nb_2O_5 films coupled with noble metal electrodes prepared under different conditions. In addition, the H_2 sensing mechanism of the films was also studied by using AC impedance technique [13–15].

* Corresponding author. Tel.: +81 95 819 2645; fax: +81 95 819 2643.
E-mail address: hyodo@net.nagasaki-u.ac.jp (T. Hyodo).

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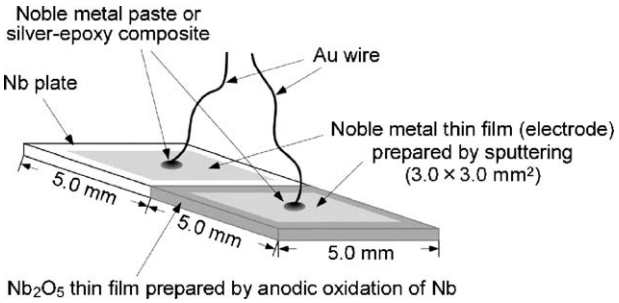

Fig. 1. Schematic drawing of an M/Nb_2O_5 sensor.

2. Experimental

A half of a Nb metal plate (5.0 mm wide, 10.0 mm height and 0.5 mm thick) was anodically oxidized in an aqueous solution of 0.5 M NaOH, H_3PO_4 or H_2SO_4 (10–30 °C) at a current density of 10–100 mA cm^{-2} for 10–30 min. Microstructure of the films obtained was observed by a scanning electron microscope (SEM; Hitachi, S-2250N).

A noble metal (Pd, Pt or Au) was sputtered on the surface of both the anodically oxidized thin film and the bare metal plate, and then Au wires were attached with a noble metal paste (Au: Tokuriki Chemical Lab., 8556; Pd: Tanaka Kikinzoku Kogyo, T60; Pt: Tanaka Kikinzoku Kogyo, TR-7905) or a conductive silver-epoxy composite (Chemtrinics, CW2400), as shown in Fig. 1. Thereafter, these sensors were fired at 200 °C for 30 min (silver-epoxy composite) or 400 °C for 1 h (noble metal pastes) in air. The anodically oxidized Nb_2O_5 thin film coupled with a noble metal electrode is denoted as M/Nb_2O_5(L) (M: Au, Pd or Pt; L: aqueous solution used for the anodic oxidation, i.e. N for NaOH, P for H_2PO_4 and S for H_2SO_4, respectively).

A DC voltage of +0.5 or +1.0 V was applied to the sensors, and transient changes in current flowing through the sensors upon exposure to 10–8000 ppm H_2 balanced with dry air or nitrogen were monitored at 28–300 °C. The response measurement was conducted in a flow apparatus at a gas flow rate of 100 ml/min, unless otherwise noted. The volume from the switch valve for changing 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. Effect of water vapor (2.8%) on the H_2 response was also examined by employing the flow gas humidified by bubbling through liquid water in a vessel at room temperature. In addition, response of the sensors to 0.15% CO was also tested. *I–V* characteristics of the sensors were also measured in a range of −1.2 to 1.2 V at a sweep rate of 10 mV s^{-1}. AC impedance measurement of the sensors was carried out in the frequency range of 1 Hz–32 MHz with an oscillation amplitude of ±100 mV. These electrochemical measurements were conducted by employing a potentiostat/galvanostat (Solartron, 1278) equipped with an impedance gain/phase analyzer (Solartron, 1260) and the measurement software supplied by Scribner Associates (Corrware and Zplot).

3. Results and discussions

3.1. Effect of electrode materials and surface morphology of Nb_2O_5 films

Fig. 2 shows SEM photographs of the Nb_2O_5 films anodically oxidized at a current density of 100 mA cm^{-2} at 20 °C for 30 min in three kinds of electrolytes. Some amount of submicron-size pores existed irregularly on the surface of the Nb_2O_5 film prepared in the NaOH solution, while the film prepared in the H_3PO_4 solution had a small quantity of pores larger than 3 μm in diameter. On the other hand, many disordered micropores (diameter: ca. 1–3 μm) were observed on the surface of the film prepared in the H_2SO_4 solution. The appearance of the Nb_2O_5 film prepared in H_2SO_4 was very similar to that observed for the anodically oxidized TiO_2 film [6–9] prepared in our previous studies, but the size of pores in the Nb_2O_5 film was about 10 times as large as that of the TiO_2 film. Fig. 3 shows *I–V* characteristics of the Pd/Nb_2O_5 sensors prepared in three different electrolytes. The *I–V* characteristics were measured at 100 °C. In fabricating these sensors, Au lead wires were fixed to the Pd electrodes with the silver-epoxy composite. Pd/Nb_2O_5(N) showed nearly ohmic *I–V* behavior in both air and 8000 ppm H_2 balanced with air, as shown in Fig. 3a, although larger current was clearly observed in 8000 ppm H_2 than in air. In the case of Pd/Nb_2O_5(P), non-linear *I–V* characteristics were observed in both environments due to the formation of a typical rectifying junction at the interface between the Pd electrode and the Nb_2O_5 thin film. However, it was not suitable for a H_2 sensor, since the *I–V* characteristic in 8000 ppm H_2 was comparable to that in air, and therefore no H_2 response appeared. On the other hand, Pd/Nb_2O_5(S) showed a non-linear *I–V* characteristic and large current in 8000 ppm H_2 under forward bias conditions, while the

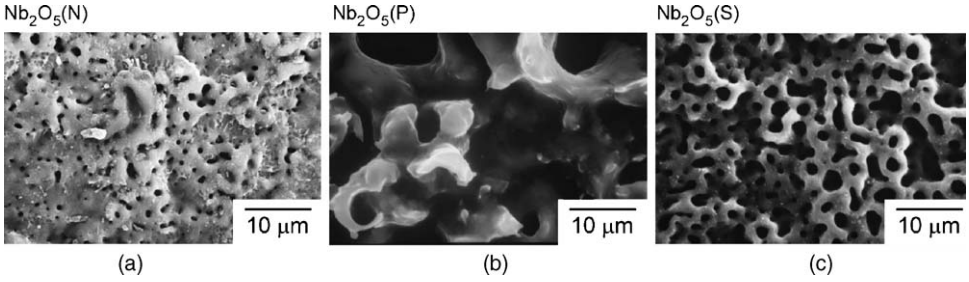

Fig. 2. SEM photographs of Nb_2O_5 films anodically oxidized at a current density of 100 mA cm^{-2} at 20 °C for 30 min in aqueous solutions of 0.5 M (a) NaOH, (b) H_3PO_4 and (c) H_2SO_4.

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