Hydrogen Sensing Properties of Anodized TiO_2 Film Sensors Equipped with Pd and Pt Electrodes in Different Structure

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Abstract

H_2 sensing properties of diode-type gas sensors fabricated with anodized TiO_2 films equipped with Pd and Pt electrodes in different structure have been investigated. In air atmosphere, the H_2 response of a TiO_2 sensor with Pd-Pt alloy electrodes fabricated by simultaneous sputtering of Pd and Pt (Pt-Pd/TiO_2) was larger than those of sensors with layered electrodes of Pd(upper layer)/Pt(lower layer) or Pt(upper layer)/Pd(lower layer), which will be referred to be Pd/Pt/TiO_2 and Pt/Pd/TiO_2, respectively, fabricated by successive sputtering of constituent metals. On the other hand, all sensors showed much larger H_2 responses in N_2 than those in air, and the magnitude of H_2 response was quite comparable to each other among three kinds of sensors in N_2. These result show that adsorbed oxygen and/or thin oxide layers on the surface of Pd have a great influence on the H_2 sensing behavior.
Keywords: Anodic oxidation; TiO_2; Diode-type sensor; H_2

Introduction

Our previous studies have revealed that a TiO_2 thin film having sub-micron pores could be fabricated by anodic oxidation of a Ti plate and that the anodized TiO_2 thin film equipped with a Pd top electrode and the Ti plate bottom electrode exhibited high H_2 response in a wide range of H_2 concentration as a diode-type sensor under flowing both air and N_2 atmospheres (1, 2). In this study, H_2 response properties of three kinds of sensors equipped with Pd-Pt electrodes, but in different structure, fabricated by r.f. magnetron sputtering were studied to evaluate the role of each noble metal.

Experimental

A half part of a Ti plate (5.0 × 10.0 × 0.5 mm) was anodically oxidized in a 0.5 M H_2SO_4 aqueous solution at 20°C for 30 min at a current density of 50 mA cm^{-2}. A pair of electrode (3.0 × 3.0 mm) was fabricated on the TiO_2 thin film and the Ti plate by radio-frequency magnetron sputtering of Pd (300 W, 7 min) and Pt (200 W, 7 min) simultaneously (Pd : Pt = 36 : 64 (wt%)) or successively (See Fig. 1 and Table 1). The electrical contact to Au lead wires was achieved by application of a Pt paste and then was ensured by subsequent firing at 600°C for 1 h in dry air. A dc voltage of 1 mV was applied to the sensors under forward bias conditions, and the H_2 sensing properties were measured at 250°C to 8000 ppm H_2 balanced with air or N_2. The H_2 response properties of the sensor subjected to the additional treatment in dry N_2 at 600°C for 1 h were also measured. For easy comparison, air- and N_2-treatments are expressed as T_{air} and T_{N2}, respectively, and

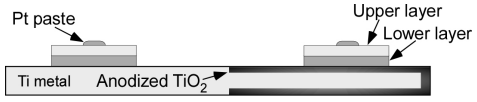

Fig. 1 Schematic sensor structure.

Table 1 Electrode structure of sensors.

No.	Sensor	Electrode	
		Upper layer	Lower layer
1	Pd-Pt/TiO_2	Pd-Pt (single layer)	
2	Pt/Pd/TiO_2	Pt	Pd
3	Pd/Pt/TiO_2	Pd	Pt

measurements in air and in N_2 atmosphere are indicated as M_{air} and M_{N2}, respectively.

Results and Discussions

Figure 2 shows response transients of three kinds of sensors to 8000 ppm H_2 at 250ºC. Under the T_{air}-M_{air} conditions, the H_2 response of Pd-Pt/TiO_2 was the largest among the three kinds of sensors, probably due to the largest amount of dissolved H species into the alloy electrode. On the other hand, the H_2 response of Pt/Pd/TiO_2 was extremely smaller than those of Pd/Pt/TiO_2 and Pd-Pt/TiO_2. This phenomenon may arise from higher H_2 oxidation activity of Pt than Pd, leading to a smaller amount of H_2 molecules capable of reaching at the surface of the under-laying Pd, especially in the case of Pt/Pd/TiO_2. In contrast, all sensors showed much larger H_2 responses under the T_{N2}-M_{N2} conditions than those observed under the T_{air}-M_{air} conditions. This fact indicates that less amounts of oxygen adsorbate at the electrode surfaces as well as in oxygen-free environment facilitate the dissolution of H species into the electrodes. In addition, Pt/Pd/TiO_2 showed faster response speed in comparison with Pd-Pt/TiO_2 and Pd/Pt/TiO_2 in air. This result can be explained by the less oxidative nature of Pt than Pd, namely the shorter time necessary for reducing the oxidized electrode surface. Actually, all sensors showed fast response speeds in N_2. However, recovery speeds of all sensors in N_2 were terribly slower than those observed in air. This result implies that the existence of gaseous oxygen in the environment is essential for achieving fast extraction of H species dissolved into the electrodes, and therefore it takes a longer time for the complete extraction in N_2.

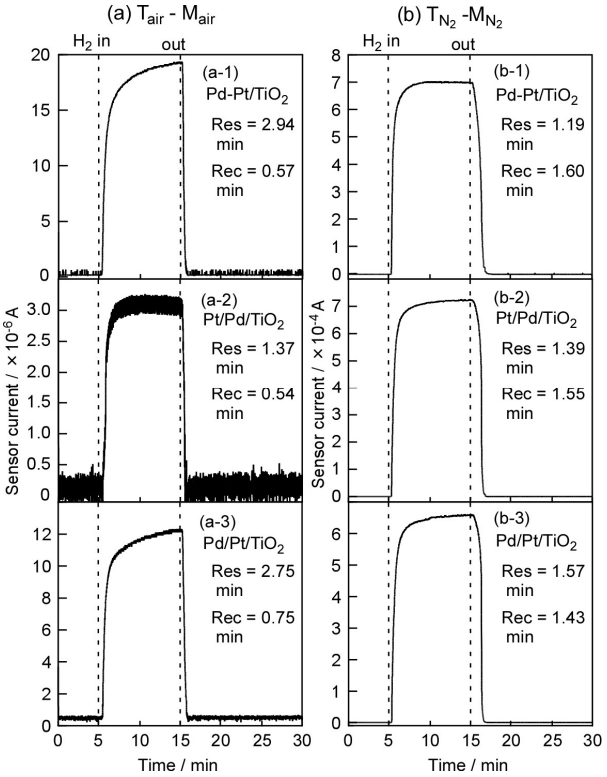

Fig. 2 Response transients of three kinds of sensors to 8000 ppm H_2 in (a) air and (b) N_2 at 250ºC. The sensors were pretreated at 600ºC for 1 h in (a) air and (b) N_2.

Conclusions

H_2 sensing properties of diode-type gas sensors of Pd-Pt/TiO_2, Pt/Pd/TiO_2 and Pd/Pt/TiO_2 have been investigated. The magnitude of H_2 response and the response speed were largely dependent on the structure of the electrodes in air. On the other hand, the magnitude of H_2 response in N_2, which was much larger than that in air, and H_2 response and recovery speeds were almost independent of the electrode structure. These results reveal that the adsorbed oxygen and/or thin oxide layers have a great influence on the H_2 sensing behavior.

References

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