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<tbody>
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<tr>
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Hydrogen Sensing Properties of Anodized TiO₂ Film Sensors Equipped with Pd and Pt Electrodes in Different Structure

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Abstract

H₂ sensing properties of diode-type gas sensors fabricated with anodized TiO₂ films equipped with Pd and Pt electrodes in different structure have been investigated. In air atmosphere, the H₂ response of a TiO₂ sensor with Pd-Pt alloy electrodes fabricated by simultaneous sputtering of Pd and Pt (Pt-Pd/TiO₂) 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/TiO₂ and Pt/Pd/TiO₂, respectively, fabricated by successive sputtering of constituent metals. On the other hand, all sensors showed much larger H₂ responses in N₂ than those in air, and the magnitude of H₂ response was quite comparable to each other among three kinds of sensors in N₂. These result show that adsorbed oxygen and/or thin oxide layers on the surface of Pd have a great influence on the H₂ sensing behavior.

Keywords: Anodic oxidation; TiO₂; Diode-type sensor; H₂

Introduction

Our previous studies have revealed that a TiO₂ thin film having sub-micron pores could be fabricated by anodic oxidation of a Ti plate and that the anodized TiO₂ thin film equipped with a Pd top electrode and the Ti plate bottom electrode exhibited high H₂ response in a wide range of H₂ concentration as a diode-type sensor under flowing both air and N₂ atmospheres (1, 2). In this study, H₂ 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 H₂SO₄ 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 TiO₂ 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 H₂ sensing properties were measured at 250°C to 8000 ppm H₂ balanced with air or N₂. The H₂ response properties of the sensor subjected to the additional treatment in dry N₂ at 600°C for 1 h were also measured. For easy comparison, air- and N₂-treatments are expressed as T_air and T_N₂, respectively, and
measurements in air and in N\textsubscript{2} atmosphere are indicated as M\textsubscript{air} and M\textsubscript{N2}, respectively.

**Results and Discussions**

Figure 2 shows response transients of three kinds of sensors to 8000 ppm H\textsubscript{2} at 250\textdegree C. Under the T\textsubscript{air}-M\textsubscript{air} conditions, the H\textsubscript{2} response of Pd-Pt/TiO\textsubscript{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\textsubscript{2} response of Pt/Pd/TiO\textsubscript{2} was extremely smaller than those of Pd/Pt/TiO\textsubscript{2} and Pd-Pt/TiO\textsubscript{2}. This phenomenon may arise from higher H\textsubscript{2} oxidation activity of Pt than Pd, leading to a smaller amount of H\textsubscript{2} molecules capable of reaching at the surface of the under-laying Pd, especially in the case of Pt/Pd/TiO\textsubscript{2}. In contrast, all sensors showed much larger H\textsubscript{2} responses under the T\textsubscript{N2}-M\textsubscript{N2} conditions than those observed under the T\textsubscript{air}-M\textsubscript{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\textsubscript{2} showed faster response speed in comparison with Pd-Pt/TiO\textsubscript{2} and Pd/Pt/TiO\textsubscript{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\textsubscript{2}. However, recovery speeds of all sensors in N\textsubscript{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\textsubscript{2}.

**Conclusions**

H\textsubscript{2} sensing properties of diode-type gas sensors of Pd-Pt/TiO\textsubscript{2}, Pt/Pd/TiO\textsubscript{2} and Pd/Pt/TiO\textsubscript{2} have been investigated. The magnitude of H\textsubscript{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\textsubscript{2} response in N\textsubscript{2}, which was much larger than that in air, and H\textsubscript{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\textsubscript{2} sensing behavior.

**References**