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CO sensing performance in micro-arc oxidized TiO_2 films for air quality control

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Abstract

Porous TiO_2 films were prepared by the micro-arc oxidation (MAO) of Ti plates, and their CO sensing properties at low concentrations (5–100 ppm) were investigated as an application for an air quality control sensor. The obtained rutile films exhibited the maximum CO gas response at 350 °C, which is typical for semiconductor-type gas sensors, and the R_a/R_g was ~1.6 for 10 ppm CO (R_a: resistance in air, R_g: resistance in a sample gas). The magnitude of the gas response increased almost linearly with increasing the CO concentration from 5 to 100 ppm. The CO sensing performance of the TiO_2 sensor in the presence of humidity was investigated and compared with that of a SnO_2 sensor.

Keywords: CO sensor; TiO_2; Micro-arc oxidation; Air quality control

1. Introduction

There is an increasing demand for the air quality control in automobile cabins. An automated ventilation system, which requires the gas sensors that can monitor the air quality both inside and outside the vehicle, has been suggested for this purpose [1,2]. The major pollutants flowing into the cabin are the exhaust gases such as CO, hydrocarbons (HCs), and NO_x emitted from the foregoing cars. At the intake, the pollutant gases are diluted with ambient air. Accordingly, at least, 30 ppm CO and 2 ppm NO_x should be detected to find out the presence of gasoline and diesel vehicles ahead [1]. Moreover, the concentration limit of gas detection is being lowered to improve the automated ventilation system.

Tin-dioxide (SnO_2)-based semiconductor type gas sensors have been used as air quality control sensors. In the literature, the SnO_2-based air quality sensor exhibited a gas response of $R_a/R_g \sim 1.25$ for 10 ppm CO and $R_a/R_g \sim 1.6$ for 30 ppm CO [2]. However, SnO_2-based sensors are known to be quite susceptible to humidity and temperature change accompanying with gas flow rate change, which influence the reference resistance in air (R_a) in addition to the gas response [1,3,4]. For the reliable and reproducible sensor operations, the gas response of SnO_2-based sensors should be further improved [5,6] or other sensor materials with less susceptibility to humidity are highly required.

TiO_2 has been studied as a CO sensor, which works at high temperatures (>400 °C) due to its thermal stability. However, the magnitude of the gas response was generally low ($R_a/R_g < 2$) even toward several hundreds ppm CO gas [7,8]. Several attempts have been made to improve the CO gas sensing performance of the TiO_2 sensor, including synthesis of nano-sized powders [8,9] and/or incorporation of various metals or metal oxides such as Au, Nb, Ta, Nb_2O_5, La_2O_3, CuO [7,8,10–12]. The CO sensing properties were greatly enhanced by these approaches, but most studies were limited to high CO concentrations (>50 ppm). Recent reports have shown that a hydrogen sensor with an extremely high gas response can be achieved using TiO_2 with various nano-dimensional architectures [13–16]. Based on these results, it was speculated that the CO sensing performance of the TiO_2 sensor at low concentrations (<30 ppm) could be improved by employing these nano-architectures even though this sensor still exhibits the higher H_2 sensing performance.

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In this study, TiO_2 films containing submicron-sized pores were prepared by micro-arc oxidation and their CO sensing properties were characterized at concentrations as low as 5 ppm in order to use them in air quality control sensors. In addition, the effect of humidity on the CO sensing performance was examined and the comparison was made to the SnO_2 sensor. Special focus was placed on the low concentration limit of CO detection and signal stability against humidity.

2. Materials and methods

Commercially pure titanium plate (99.7%, Aldrich) was cut into the rectangular specimens sized 10 mm × 10 mm × 2 mm. The specimens were ground with #1200 abrasive paper and the surface was cleaned with acetone and distilled water. The Ti plates were micro-arc oxidized in an electrolytic solution containing 0.5 M H_2SO_4 at an applied voltage of 200 V for 10 min. After the MAO treatment, the samples were thermally oxidized at 600 °C for 1 h in air at a heating rate of 5 °C/min. The phase of the oxidized layer was analyzed by X-ray diffraction (XRD) and the microstructure was observed using scanning electron microscopy (SEM).

A circular Pt or Pd electrode of 5 mm diameter was sputtered on both sides of the oxidized specimens (MAO + thermal oxidation) and Pt lead wires were attached to them using Pt or Pd paste, respectively. Thereafter, all the sensors were fired at 600 °C for 1 h in order to make the electrical contact between the paste and the Pt lead wires. The sensor element was placed in a quartz test chamber located inside the tube furnace and stabilized at the predetermined temperature for about 30 min with flowing air. The total gas flow rate was kept constant at 160 sccm and various CO concentrations were produced by adjusting the mixing ratio of CO gas and air. After stabilization, air was switched to the test gas. The CO sensing property was obtained by measuring the changes of electric resistance between fresh air and 30 ppm CO balanced with air at temperatures ranging from 200 to 400 °C. The electrical resistance was measured using a multimeter (2000 multimeter, Keithley). In this study, the magnitude of the gas response (sensitivity) was defined as the ratio (R_a/R_g) of the resistance in air (R_a) to that in a sample gas (R_g). The response time ($t_{90\%}$) was defined as the time required for the sensor to reach 90 % of the final signal. The concentration dependence of the CO gas response was checked by exposing the sensor to various CO concentrations (5–100 ppm) at 350 °C. The gas response was also measured in a wet atmosphere, which was obtained by flowing the gases through the bubbler kept at 50 °C. The relative humidity was 70% at the outlet of the sensing equipment measured at room temperature. For comparison, a SnO_2 gas sensor was prepared by screen-printing a commercial SnO_2 powder (99.9%, Aldrich) on an alumina substrate with a Pd electrode.

3. Results and discussion

The as-prepared MAO specimen was an almost single phase of rutile (TiO_2) (Fig. 1(A)) and a very weak peak of anatase phase was detected contrary to the previous work [13]. The dominant rutile phase can be attributed to the relatively higher applied voltage in this study [17]. The subsequent heat treatment increased the peak intensity of rutile relative to the Ti peak (Fig. 1(B)).

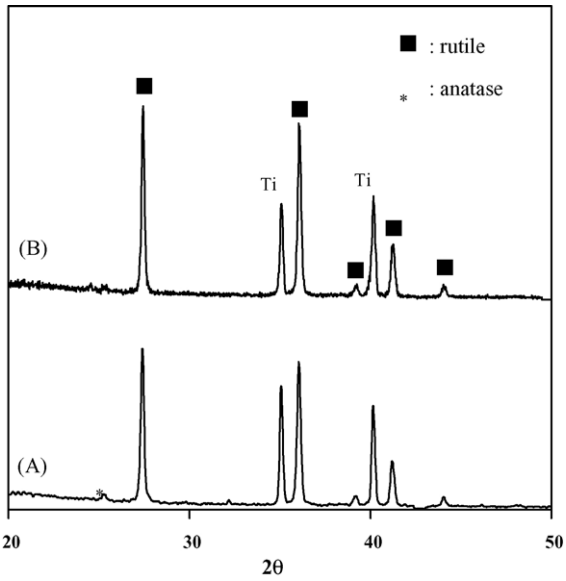

Fig. 1. XRD patterns of the micro-arc oxidized samples; (A) as-prepared and (B) heat-treated at 600 °C for 1 h.

The surface morphology and cross-sectional view of the oxidized layers are shown in Fig. 2. The oxide film had a porous microstructure with sub-micron and nano-sized spherical pores (Fig. 2(A)). These pores were well separated and distributed homogeneously over the samples. From the cross-sectional view, there was no obvious discontinuity between the oxide film and the underlying substrate, and the thickness of the oxide film was estimated to be ∼4 μm (Fig. 2(B)). No specific change in surface morphology or oxide film thickness was observed after the subsequent oxidation at 600 °C (Fig. 2(C) and (D)). However, the increase of the rutile peak intensity in XRD patterns indicated that additional oxides might be formed unnoticeably during heat treatment or the as-prepared MAO specimen might be fully crystallized if they were partially crystallized after the MAO treatment.

Fig. 3(A) shows a response transient of the TiO_2 sensor with Pd electrode to 30 ppm CO balanced with air measured at 350 °C. Upon injecting a sample gas, the resistance decreased rapidly by factor of ∼3. The recovery was similar to the gas response and the sensing signal was quite stable and reversible even after the gases had been switched several times. The magnitude of gas response (R_a/R_g) was estimated to be 2.68 and the response time ($t_{90\%}$) was 200–400 s. The sensor response was significantly enhanced but the response was rather slow compared with SnO_2-based sensor [2]. In the TiO_2 sensor, anatase phase is reported to have better CO sensing properties than rutile phase [10,11]. Thus, it is expected that the CO sensing performance of the TiO_2 films can be further improved through the realization of the anatase phase either by controlling the MAO conditions or adding the appropriate additives [10–12].

No CO gas response was observed in the sensor with Pt electrode. In addition, the MAO specimens were oxidized at higher temperatures (700–900 °C) and the sensors were also fabricated