

Gas Sensing with Titania Thick Films

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A TiO₂-based gas sensor fabricated from TiO₂ thick films with the rutile structure was sensitive to CO and other reducing gases. The negative temperature coefficient behavior of the films was examined at various temperatures and different CO concentrations. Scanning electron microscopy (SEM) and XRD analysis were used to study the microstructure and the phases developed. At temperatures above 500°C, response times of less than 1 minute were characteristic of this sensor.

1. Introduction

The growing attention to environmental problems has increased the need for reliable and selective solid-state sensors for air quality monitoring, automotive industries and general combustion controlling systems. Due to the high associated toxicity of CO, low levels of detection are necessary, even down to 100 ppm, for general purpose applications.

A chemical sensor is a device that converts information from a chemical species (the input) into a physical signal (the output).⁽¹⁾ Sensors must have physicochemical features that promote both sensitivity and selectivity. Under ideal conditions, a selective sensor must be able to distinguish different gases from one another by eliminating similar responses from interfering components. The commonly used lean burn oxygen sensors are ionic pumping cells made of zirconia.⁽²⁾ An alternative sensor with a high potential for cost reduction is the semiconductor oxygen sensor, which offers a very attractive means of sensing different gases. Semiconductor gas sensors detect reducing gases from changes in their electrical conductivity. The lack of long-term reliability has prevented the widespread use of these devices.⁽³⁾

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In this regard, the stability of materials becomes of paramount importance. Ceramics appear to be more convenient as active materials for these sensors. Gas-sensitive resistors based on semiconductor ceramic oxides are simple and robust devices, which owe their response to changes in charge carrier concentration within a depletion layer at the solid-gas interface, which is in turn caused by a change in the surface density of electron trap states.⁽⁴⁾ Oxygen chemistry at oxide semiconductor surfaces plays a key role in the operation of these ceramic gas sensors.⁽⁵⁾ The surface of these sensors acts as the adsorption site for oncoming gases. This causes a resultant ionization and/or diffusion of charged species into the bulk or along grain boundaries.⁽⁶⁾ The reducing gas depletes the coverage of adsorbed oxygen ions on the sensor surface and supplies electrons to the conduction band.⁽⁷⁾ The use of high quality oxide powders is thus required for the preparation of reliable devices. The effects of the microstructure, namely, the ratio of surface area to volume and the pore size of the powders used, are also important.

Titanium dioxide is a common ceramic material for the manufacturing of gas sensors, and a considerable amount of current research activity has been devoted to the development of stable pure or doped titanium dioxide sensors.⁽⁸⁻¹⁰⁾ These sensors based on TiO_2 are well known and have been investigated for use as oxygen sensors in different environments. They are used in monitoring some minor constituents of air due to their stability at high temperatures.⁽¹¹⁻¹⁷⁾ This material has also been proved to be the effective for detection of nitrogen oxides in environmental monitoring.⁽¹⁸⁾ These benefits are due to the simple structure of such oxides and the low cost of the resulting combustion control.^(11,12) Materials are conveniently prepared in the form of porous bodies or layers and measurements are easily made with such devices.⁽³⁾ For better sensing performance and selectivity, the surface may be treated with a variety of additives. Semiconductor gas sensors made of porous TiO_2 ceramics utilize their resistance changes to detect inflammable gases. Electrical conductivity in this intrinsic wide band-gap n-type semiconductor (> 3 eV) is vastly enhanced in an atmosphere with low oxygen pressure.

Titania (TiO_2) is known for its polymorphism. The most common forms are rutile and anatase; brookite and $\text{TiO}_2(\text{B})$ are less common.⁽¹⁹⁾ Recent activities have been focused on the electrical behavior and conduction mechanisms of anatase.

Ceramic sensors are typically fabricated as sintered porous pellets, thick films or thin films. Thick- and thin-film oxygen sensors have the advantage of small volume and fast response to atmospheric changes due to their shorter diffusion paths. Deposition parameters play a key role in the microstructure of the film and consequently can have a strong influence on gas sensing properties.

On the other hand, in the case of sintered blocks the grain size of the powder used has been suggested to be the controlling factor.⁽²⁰⁾ In this paper we report the results obtained using semiconductor rutile-based thick-film gas sensors in tests which have been less emphasized by other researchers. Devices were prepared from commercially synthesized titania powders.

2. Experimental

2.1 Materials

Titanium dioxide (rutile) was obtained from Hapkins & Williams (#867600, Chadwell Heath, Essex, England). This type of titania was selected because of its crystallographic nature and its uniform particle size and shape. The powder was preheated at a rate of 20°C/min and held at 750°C for 3 h within alumina heating crucibles in a power-controllable electric kiln in air and then was sieved in a 400-mesh sieve. This powder was used as the main starting raw material. The powder was analyzed for impurities using inductively coupled plasma emission spectroscopy (ARL 3410, Ecublens CH-1024, Switzerland), and the analytical grade of the powder was confirmed. Nb₂O₅ and P₂O₅ were observed as the major impurities of the prepared powder. A nickel-filtered CuK α X-ray, before and after heating, was used to determine the presence of rutile phase via diffraction (XRD) using a D-500, SIEMENS (D-7500, Karlsruhe, Germany) at 30 KV and 25 mAmp for 2 θ between 15° and 80°. The scan rate was 5°/min. No major changes developed in the phases during the preheating process.

Particle size (PSA) and surface area were then measured. The surface area of the powder was 25 m²/g (as measured by a Gemini Micromeritics, Norcross, GA, 30093, U.S.A.) using the BET technique. The microstructural features were ascertained by scanning electron microscopy (SEM). Although the mean particle size measured by PSA (Fritsch, Analysette 22) was estimated to be more than 5 μ m, the SEM observations reveal no particles above 0.3 μ m in size (Fig. 1). This contradiction is due to the unsuccessful dispersion of titania particles in the aqueous medium used by PSA caused by using ultrasonic baths at different durations even in the presence of adequate peptisizers. Due to the suitable particle size of the material selected and to avoid unwanted contamination, no extra milling was applied to the powder. Prepared powders were then used to fabricate sample sensors.

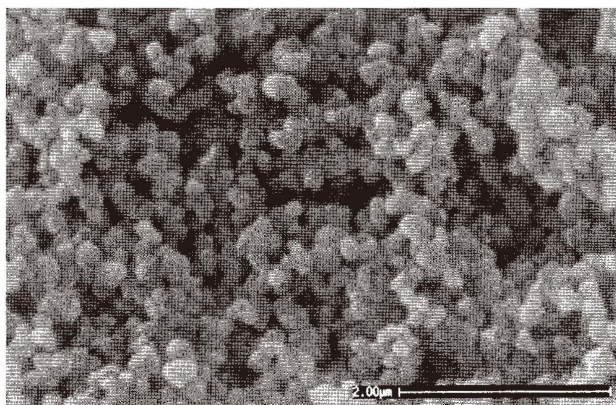


Fig. 1. SEM image of titania powder used.

2.2 Device preparation

The TiO₂ sensor was fabricated by screen-printing conductive pastes (Heraeus, GG1032, 63450 Hanau, Germany) as conductive strips on a dense alumina substrate. The printed substrate was air-dried and then fired at 780°C to remove organic materials and stabilize the conductive precious metals on the ceramic surface. At room temperature the prepared base was assessed to insure the resistance of the gold strip was less than 0.1 Ω/cm. To insure that no current leakage occurred, the electrical resistance between two conductive electrodes on the base was measured; a usable sample needs to have values higher than 50 MΩ at 750°C. This requirement was balanced with the results obtained for titania in subsequent experiments.

Gold wires 0.07 mm long were connected as the DC probes on the gold-coated area on the surface. To ensure the integrity of the attachment of the gold wires to the bulk surface of the sensor commercial conductive paste (Heraeus, RP2003-237) was used and the assembly was heated to 700°C. Figure 2 shows a schematic diagram of the sensor. The two other ends of the gold wires were connected to an amp meter and a power supply to measure electric resistance. A thermocouple was mounted on the base of the device to measure temperature. The selected powder was mixed with deionized water and was coated onto the prepared base by dipping and then was dried for 24 h. The thickness of the layer was estimated to be 100 μm. All samples were electrically aged under normal operating conditions for 2 days before any test.

2.3 Sensitivity

The dc conductivity of the samples and their response time to the gases were measured with a system consisting of a gas reaction area, a heating stage, an apparatus for controlling the temperature, and instruments for measuring the electrical behavior. The sensor was placed within a gas reactor comprising quartz tubes contained within a tube furnace. Gases were passed through the tube. A gas mixing system based on mass flow controllers provided the testing atmosphere. The rate and ratio of the gases were controlled by mass flow controllers (Brooks Instrument Division, SK62SR, U.K.). Before starting the sensing measurements, the device was kept in 1% CO balanced with N₂ for 1 h to allow for sample equilibrium. Then sensing measurements were carried out at 200–700°C ± 1°C.

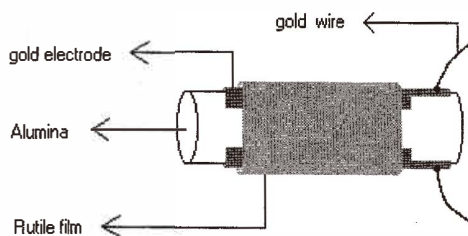


Fig. 2. Schematic of the sensor configuration and setup.

Prior to entry into the furnace, the CO was passed through columns of out-gassed molecular sieves and silica gel. Parameters were evaluated based on the average of at least 5 samples to examine the reproducibility and precision of the results. These evaluations were repeated several times for each sample to test the reproducibility of the characteristics of the device. Before being used in a subsequent experiment, the sensor was allowed to recover in air. To explore the reversibility of sensor response, measurements were carried out as a function of gas concentration in both increasing and decreasing modes. All containers and sample holders were rinsed in distilled and deionized water. SEM was used to observe the microstructure of the deposited film.

3. Results

Systematic heat treatments of the commercial powders were performed. The bulk samples prepared at different firing temperatures were analyzed by XRD analysis. The curves reveal our TiO_2 to be rutile. Rutile has a stable arrangement of atoms at room temperature; anatase is slightly different in energy and thus exists in a metastable form, which transforms to rutile on heating.⁽¹⁹⁾ No brookite or other phases were observed in our powder (Fig. 3). Thermodynamically, no transformation in the duration of our experiment occurred, which is in agreement with the theoretical predictions for the working temperatures selected.

Figure 4 shows an SEM image of the samples fired at 870°C. The samples were made of spherically shaped particles approximately 200 nm in size. The SEM images show grain size on the nanometer level, while working at elevated temperatures induced significant grain growth. Because the size of particles increased and the density changed during firing,

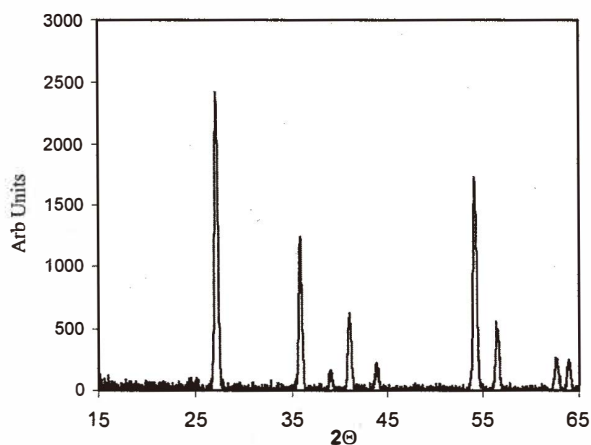


Fig. 3. XRD pattern of titania samples fired at 870°C.

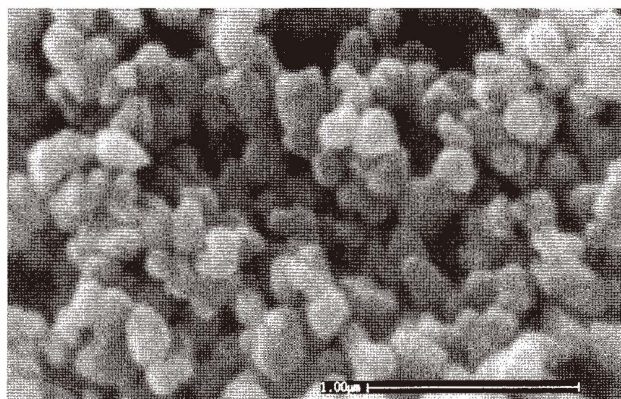


Fig. 4. SEM image of the samples fired at 870°C.

a maximum working temperature needed to be selected. The shrinkage of the bodies during firing was also cited to support selection of the optimum firing temperature (Fig. 5). Shrinkage begins at approximately 900°C and, accordingly, 750°C was the maximum possible working temperature.

The samples were biased at a constant voltage of 10 V dc, and conductivity was determined on the basis of the electrical current that passed. Figure 5 shows the conductivity variations against working temperature. The resultant specimen proved sensitive to the gases of interest, exhibiting signal variations and fast response times.

No major increase in conductivity was observed at less than 300°C. Although this temperature is higher than that reported for tin oxide, a lower threshold electrical current can produce a higher precision device.

Figure 6 shows the relationship between the changes in the electric current as a function of gas concentration with temperature variations under different conditions of sensor operation. The logarithmic effect and the key role of the working temperature on the appliance are also observable.

Figure 7 shows the sensitivity profiles of the device as functions of operating temperature at different concentrations. It has been observed that increases and decreases in conductance are influenced by CO and depend on the working temperature. As the temperature increases, the sensitivities increase up to approximately 600°C. According to Fig. 6, the working temperature of titania gas sensors lie in the range of 300–700°C.

The sensitivity (S) is defined as the ratio of the electrical conductance of the device in CO to that in a CO-N₂ gas mixture as,

$$S = (I_g - I_0) / I_0 \quad (1)$$

The term I_g is the sensor conductance in the presence of the target gas, and I_0 is the conductance in carrier gas. Figure 8 shows the response, that is, the dynamic variation of

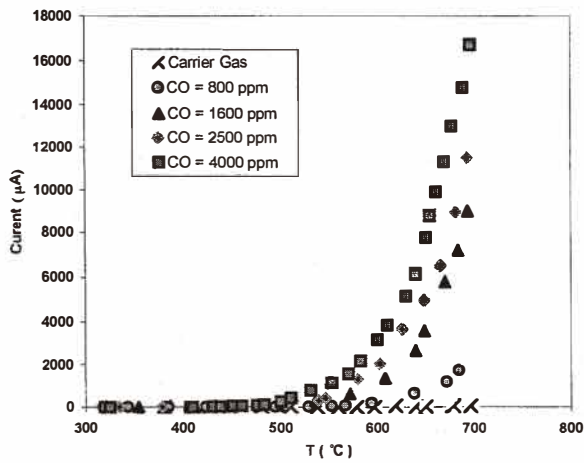


Fig. 5. NTC behavior of sample.

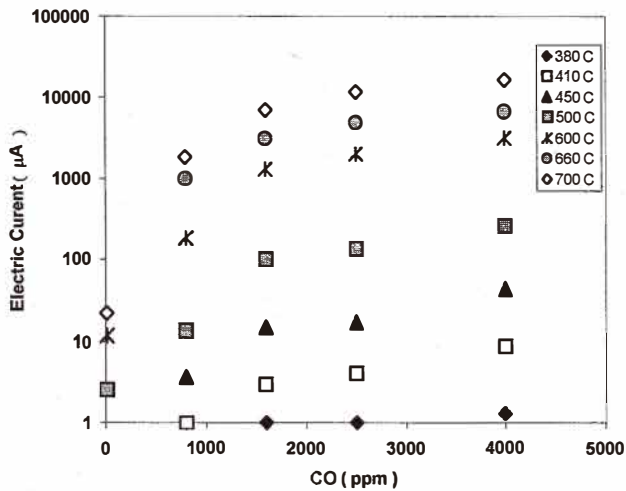


Fig. 6. Effect of gas concentration on conductivity of device.

the sensor over a 2 h working period in the test chamber at 660°C. This result shows the electrical response of the described sensors and the typical sensing characteristics for 400 ppm CO gas in an N₂ atmosphere. The time dependence and response of the sensitivity during the successive injection of the CO was less than one minute.

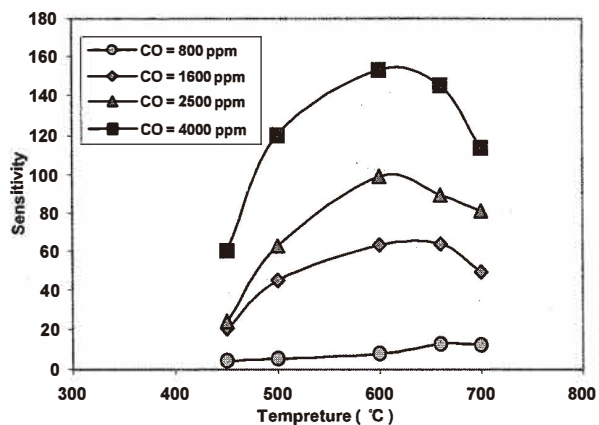


Fig. 7. Effect of working temperature on sensitivity.

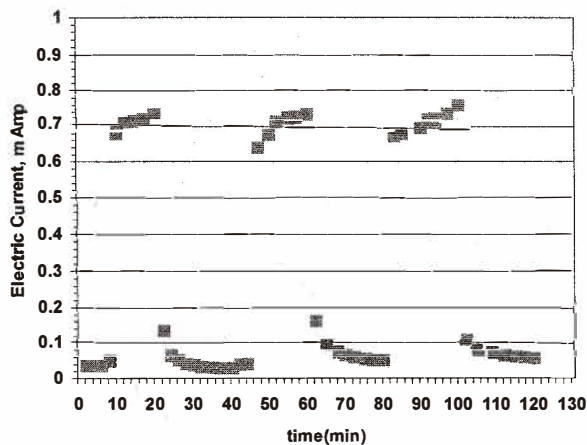


Fig. 8. Dynamic response of sensor.

The maximum tolerable concentration of CO in a work place is 50 ppm, and the alarm CO at 50 ppm at approximately 600°C. The measurements highlight that these films are stable and that the recovery of the signal is complete when the carrier gas flux is restored after the gas test. The response and recovery times are both approximately 1 min. Similar times are obtained at other concentrations, although the minimum threshold CO level varies with the working temperature and is between 800 at 320°C to 300 at 420°C. When the sensor is used at higher temperatures, a lower level of detection is observed.

4. Conclusion

TiO₂ thick films with the rutile structure were sensitive to CO and oxygen reducing gasses. The gas response dynamics for rutile thick films was observed. Due to the high operating temperatures, this sensor shows a fast recovery time. The rutile-based sensors have a combination of electrical and chemical properties that make them useful as high temperature CO sensors.

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