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TiO_2 thin film gas sensor for monitoring ammonia

B. Karunagaran [a], Periyayya Uthirakumar [a], S.J. Chung [a], S. Velumani [b], E.-K. Suh [a,*]

[a] *Semiconductor Physics Research Center and Department of Semiconductor Science and Technology, Chonbuk National University, Jeonju 561 756, Republic of Korea*

[b] *Departamento de Fisica Aulas 2, cub 111, ITESM - campus Monterrey, Garza-Sada 2501, Monterrey, N.L. C.P.64849 México*

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Abstract

Systematic development and mechanistic studies of sensing materials are critical to the design of higher performance gas sensing elements and arrays. Polycrystalline metal-oxide semiconductors such as SnO_2 and TiO_2 are among the most widely used materials for thin film-based conductometric gas sensors. The mechanistic steps responsible for the gas-induced conductance changes of polycrystalline metal-oxide sensors have been investigated. Results are presented for TiO_2 gas sensing films. The TiO_2 films experience an increase in conductance upon exposure to ammonia. Reduction of surface oxygen is proposed as the dominant mechanism for the increase in conductance in TiO_2 sensing films upon exposure to ammonia. Here TiO_2 films of low thickness prepared using DC magnetron sputtering were employed for sensing applications. A suitable operating temperature, sensitivity, response and recovery time of the TiO_2 thin film gas sensor was studied for sensing ammonia.

Keywords: TiO_2; Thin films; Gas Sensor; Sputtering; Ammonia sensor

1. Introduction

There is a general opinion in both scientific and engineering communities that there is an urgent need for the development of cheap, reliable sensors for control and measuring systems, for automation of services and microelectronics with an excellent performance, reliability and low price. For the development of sensors, interest has increased to study the transduction principle, simulation of the systems and structural investigations of the materials and choice technology [1–7]. In many aspects of today's life, the use of gas sensors becomes increasingly important. These devices are not suited to make high precision measurements of gas concentrations but to detect the presence of target gases and give a warning if several threshold values are attained.

It is well known that reducing gases to be detected remove some of the adsorbed oxygen and modulate the height of the potential barriers, thus changing the overall conductivity and creating the sensor signal. Among the metal oxides that undergo appreciable change in electrical conductivity when exposed to a gas atmosphere, the most studied material have been SnO_2, ZnO, V_2O_5 [8,9]. This implies that the sensitivities are critically dependent on having reproducible grain boundaries [10], which require keeping the preparation parameters for the sensitive material within an extremely tight tolerance. This situation is better in the case of novel gas sensors based on metal oxides that are stable at high temperatures, so permitting an operating

* Corresponding author. Tel.: +82 63 270 3928; fax: +82 63 270 3585.
E-mail addresses: bojkarun@yahoo.com (B. Karunagaran), eksuh@chonbuk.ac.kr (E.-K. Suh).

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temperature between 500 and 1000 °C [11,12]. Because of the high temperature sintering of the sensor material, the preferred conduction mechanisms are those in which the grain boundary resistance do not have significant effect on conductivity. Such metal oxides, which can withstand a high operating temperature are $SrTiO_3$, Ga_2O_3, Fe_2O_3 and TiO_2. Many reports are available on $SrTiO_3$, Ga_2O_3 [12], Fe_2O_3 [13] gas sensors. Even though many reports are available on the physical characterization of TiO_2 films prepared by different methods, the gas sensing properties of this promising material is still unexploited. Recently, Egashira et al. [14] have studied the gas sensing properties of TiO_2 thin films deposited by anodic oxidation, but no report is available on the gas sensing property of DC magnetron sputtered TiO_2 thin films. Hence the present investigation has been focused on the deposition of TiO_2 films using DC magnetron sputtering and the characterization of the films for gas sensing applications.

2. Experimental

2.1. Film preparation

Titanium oxide thin films were deposited onto well-cleaned silicon substrates using a home built DC magnetron system. 99.999% pure titanium of 110 mm diameter and 2 mm thickness has been used as the sputtering target. High purity argon and oxygen were used as the sputtering and reactive gases respectively. Rotary and diffusion pump combination was used to get the desired vacuum. The base pressure of the system is better than 10^{-5} mbar. After attaining the base pressure the oxygen partial pressure was set using a needle valve. Later on, argon was let in and the sputtering pressure was maintained. In order to check the stability of the partial pressure, after each deposition the argon flow was stopped and the oxygen partial pressure was checked and it was found to be at the value set before. Such a practice is generally followed in reactive sputtering processes. Before each run the target was pre-sputtered in an Ar atmosphere for 5–10 min in order to remove the surface oxide layer from the target. All the depositions were carried out at a total pressure of 1×10^{-3} mbar. The distance between the target and substrates was kept at 80 mm. The surface roughness and thicknesses of the films were measured by an α-step stylus profilometer. The compositions of the films were analyzed using Auger electron spectroscopy (AES). The structure and microstructural parameters of the prepared films were investigated using a Philips X-ray diffractometer (XRD) with Cu K_α radiation at 40 kV and 30 mA at scanning angles (2θ) from 5° to 60° and also using Atomic Force Microscope (PSI, Auto probe CP Model).

2.2. Sensor design

State of the art gas sensors based on semiconductor metal oxides usually have a planar structure, with a film of sensitive material being supported by a substrate equipped with electrodes. In the present study a planar structure thin film gas sensor was fabricated with TiO_2 as the sensing layer. A thin sensitive TiO_2 film was deposited by a DC reactive magnetron sputtering technique onto a well-cleaned silicon substrate equipped with interdigitated comb shaped electrodes (electrode spacing = 2 mm).

2.3. Characterization set-up for gas sensors

Normally, gas sensors are characterized by two methods i) using a dynamic system and ii) a static system [2], in the present study a static system is employed. The static system consists of a practically airtight chamber (vacuum tight bell jar, vacuum ≈ 1.333×10^{-5} mbar) in which the sample, heater and temperature sensors are arranged with electrical connections. The gas inlet and the air admittance valves are made at the base plate in order to inject the test gas and air. A known volume of the chamber is chosen as the gas chamber. A heater made of kanthal wire, a Cr–Al thermocouple and the gas sensors are arranged inside the chamber. The gas injection is carried out by a hypodermic syringe.

In a static system, the sensor is tested for gas sensing in the following sequence. The temperature of the sensor is controlled by varying the current flow through the heater and measured with an accuracy of ±1 °C using a temperature indicator. The test gas is injected inside the bell jar through a needle valve. The electrical characteristics of the sensor are observed by changing its temperature from room temperature to 500 °C in air ambient and this response is considered as a reference response for the calculation of sensitivity. In order to inject the gas easily the chamber is evacuated slightly (≈ 1.133×10^{-1} mbar) using a rotary pump. After injecting the test gas, all the valves are closed to avoid the test gas leakage during the experiment. Then the resistance of the sensor is measured by changing the sensor temperature in air and in the injected gas ambient. After completing the temperature scan, the gas is leaked out, the other cycles are carried out by injecting fresh gas into the chamber.

2.4. Experimental circuit

The sensitivity factor of the TiO_2 thin film sensor is measured by using the circuit shown in the Fig. 1. The conductance G of the film in air and test gas is calculated using the formula:

$$G = \frac{V_s}{R_s(V - V_s)}$$

where V is the voltage applied to the planar sensor, V_s is the voltage drop across the standard resistance (R_s).

The sensitivity factor (S_F) of the sensors were evaluated from the relation:

$$S_F = \frac{|\Delta G|}{G_a} = \frac{G_a - G_g}{G_a}$$

where G_a is the conductance of the sensor measured in air and G_g is the conductance of the sensor in the presence of the test gas.

3. Results and discussions

3.1. Structure and microstructure

Structure and the structure-related parameters of this material have been discussed in detail in one of our earlier paper [15], in which we reported that the grain size increases with the annealing temperature and it approaches a constant value at about 873 K, confirming the fully-crystallized state of the film. An X-ray diffraction pattern of the film annealed at 873 K is shown in the Fig. 2. The pattern reveals a polycrystalline structure with tetragonal symmetry. Such a film with a fully-crystallized state is a requisite for a gas sensor where the sensing is based on the change in conductivity during the exposure of the sensing layer to the gas. The microstructure of the film is analyzed using atomic force microscope (AFM); Fig. 3 shows the large-scale 2D AFM image of the film annealed at 873 K, which also supports the highly-crystalline state of the films.

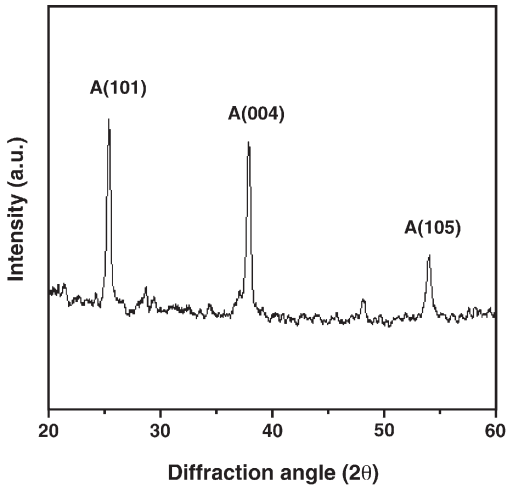

Fig. 2. XRD pattern of the TiO_2 thin film annealed at 873 K.

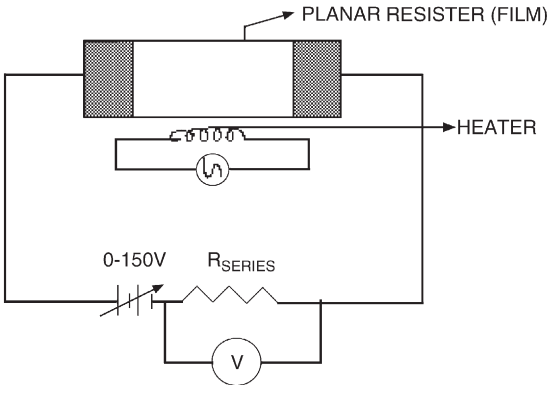

Fig. 1. Measurement configuration employed for the measurement of conductance.

3.2. Ammonia sensing

The as-deposited titanium dioxide thin film does not show a satisfactory response to the presence of ammonia (NH_3). Hence we have used films annealed at 873 K for the gas sensing applications. Such films showed an appreciable decrease in their resistance, which gives a higher sensitivity factor (S_F), when exposed to concentrations higher than 500 ppm of NH_3. This is because, in

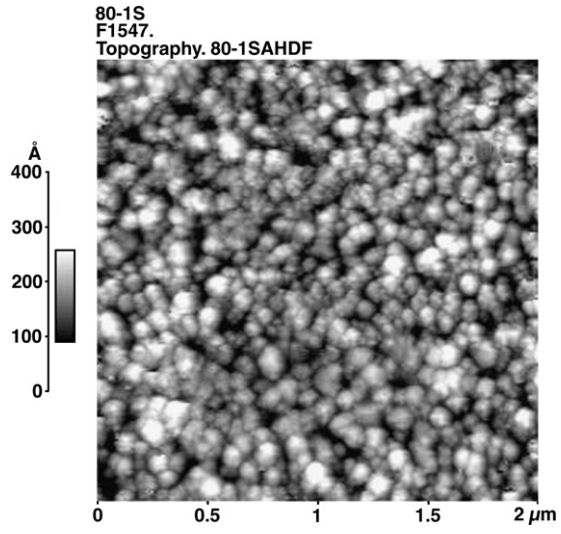

Fig. 3. Large-scale 2-dimensional AFM image of the TiO_2 film.

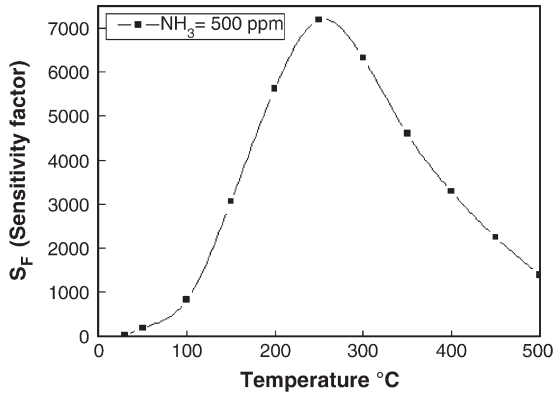

Fig. 4. Variation of sensitivity factor of TiO_2 sensor as a function of temperature (NH_3 concentration 500 ppm).

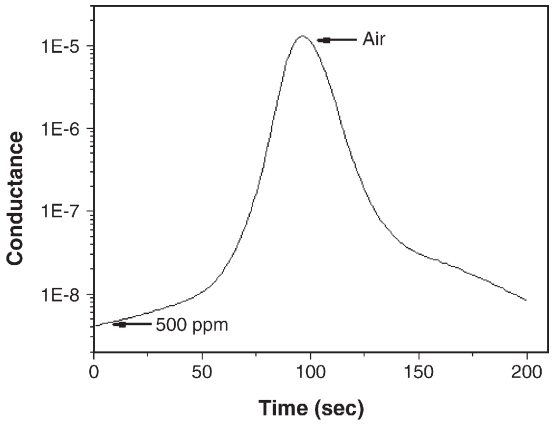

Fig. 6. Variation of conductance with the flow of ammonia (response time) and air (recovery time).

the stationary condition, ammonia acts as a reducing agent for all the metal-oxide semiconductors. Fig. 4 shows the sensitivity factor of annealed TiO_2 films to 500 ppm of ammonia gas as a function of the working temperature. As is evident from the graph (Fig. 4) the sensitivity factor increases with the temperature and reaches a maximum value at about 523 K. If the temperature is increased again, the sensitivity factor decreases. This behaviour can be explained with the analogy to that of the mechanism of gas adsorption and desorption on ZnO [16,17], ITO [18] and SnO_2 [19,20] films.

A metal oxide can adsorb oxygen from the atmosphere both as the O_2^- and O^- species. The adsorption of O^- is more reactive and thus makes the material more sensitive to the presence of a reducing gas, in the present case NH_3. Now at relatively low temperature the surface preferentially adsorbs O_2^- and the sensitivity of the material is consequently very small. As the temperature increases the dominant process becomes the adsorption of O^- and hence the sensitivity of the material increases. If the temperature increases too much, then desorption of all the oxygen ionic species adsorbed previously occurs and the sensitivity decreases. Fig. 5 shows the variation of sensitivity factor with respect to the ammonia gas concentrations at an operating temperature of 250 °C. It was found that the sensitivity factor increases with increasing gas concentration. The repeatability of the ammonia sensing was performed and it was found to be selective at the temperature 523 K showing a maximum sensitivity.

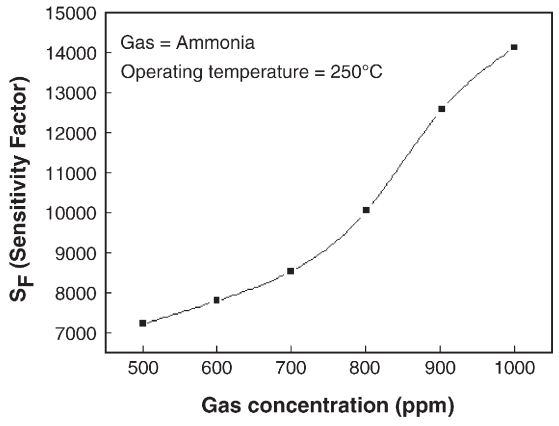

Fig. 5. Variation of sensitivity factor of a TiO_2 sensor as a function of the NH_3 concentration at an operating temperature of 250 °C.

3.3. Response and recovery time

Fig. 6 shows the response curve of an annealed titanium oxide film following a step change in composition from air to 500 ppm NH_3 in air at the critical working temperature. In this way we have measured the response and recovery times. The response time represents the time required by the sensitivity factor to undergo 90% variation with respect to its equilibrium value following a step increase in the test gas concentration and it was found to be 90 s in the case of ammonia. Likewise, the recovery time represents the time required by the sensitivity factor to return to 10% below its equilibrium value in air following the zeroing of the test gas ammonia and it was found to be around 110 s.

4. Conclusions

A planar structure thin film gas sensor was fabricated with TiO_2 as the sensing layer. A thin sensitive TiO_2

film was deposited by a DC reactive magnetron sputtering technique onto a well-cleaned silicon substrate equipped with interdigitated comb shaped electrodes. A static gas sensing mechanism was employed to analyse the sensing ability of the prepared sensors. As-deposited films were not sensitive to the ammonia gas. However, films annealed at 873 K, with good crystallinity were found to exhibit a good sensing property and selectivity for ammonia gas and it showed the highest sensitivity to ammonia at an operating temperature of 250 °C. The TiO_2 films experience an increase in conductance upon exposure to ammonia. We are proposing reduction of surface oxygen as the dominant mechanism for the increase in conductance in TiO_2 sensing films upon exposure to ammonia. Response and recovery times of this sensor for a flow of 500 ppm of ammonia were evaluated as 90 and 110 s respectively.

Acknowledgments

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