

OXYGEN SENSOR BASED ON Ga₂O₃ FILMS OPERATING AT HIGH TEMPERATURE

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In this paper oxygen sensors based on gallium oxide thin films were analyzed. The gallium oxide thin films have been prepared by rf magnetron sputtering from a powder target using Ar as the sputtering gas. At high temperatures gallium oxide thin films behaves like an n-type semiconductor due to an oxygen deficit. The thin films obtained by this method have a higher electrical conductivity due to a higher oxygen vacancy concentration. Two sensors with different geometries were investigated, one using interdigital electrodes and one using a sandwich structure with a mesh type electrode on the top of Ga₂O₃. The sensing characteristics (stability, sensitivity and response time) of the oxygen sensor were investigated at 1000 °C. Response times of about 10 seconds can be achieved for low oxygen concentrations using first type sensor and about 20 seconds for the second type. The mechanism of oxygen sensing in sputtered gallium oxide films is also discussed.

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1. Introduction

In recent years resistive gas sensors based on metal-oxide semiconductors have been investigated intensively, for sensing oxygen or harmful gases in a wide range of temperatures from room temperature up to 1000 °C in an attempt to produce fast and highly sensitive sensors especially for automobile industry and environmental pollution control [1].

At high temperatures the defects in metal oxides are in equilibrium with the surrounding atmosphere. This equilibrium is attained by creation or destruction of the oxygen vacancies and as a consequence the electrical conductivity depends on the oxygen partial pressure [2]. Below 700-800 °C the defect equilibrium is frozen and gas sensitivity is achieved through surface reactions.

Gallium oxide is one of the most suitable materials for high temperature gas sensing, due to a high melting point and stable structure. Below 700°C gallium oxide exhibits sensitivity to reducing gases (CO, H₂, CH_x) [3] on the basis of reactions at the surface of the material. Over 900 °C gallium oxide can be used as oxygen sensor [4,5]. At high temperatures the sensing properties of Ga₂O₃ are due to a deficit in the oxygen content of the material, which makes it to behave like an n-type semiconductor.

In this paper we are investigating the sensitivity and response time of two oxygen sensors, with different geometries, based on Ga₂O₃ thin films sputtered from a powder target, operating at 1000°C. For one sensor we used a structure with Pt interdigital electrodes and for the second one a Pt-Ga₂O₃-Pt sandwich structure with a mesh type electrode on the top. We are also discussing some aspects of the mechanism of oxygen sensing in sputtered gallium oxide films.

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2. Experimental

Gallium oxide thin films (about 1 μm thickness) were deposited by rf magnetron sputtering, using an ANELVA L-210-FHS system. For this purpose a 4-inch powder target was prepared from pure Ga_2O_3 (99.999 %). The samples were prepared at different substrate temperatures using Ar (at 2Pa pressure) as the sputtering gas.

Sensors with two different geometries (denoted type A and type B) were fabricated. For the type A sensor we used $\text{Al}_2\text{O}_3/\text{SiO}_2$. The silicon oxide layer with a thickness of about 0.8 μm was also obtained by sputtering from a SiO_2 target and it was used as a barrier layer to prevent the diffusion of aluminum into gallium oxide film. These substrates were provided with Pt interdigital electrodes with 50 μm spacing made by the lift-off method and after that covered with Ga_2O_3 . For the type B sensor (Fig. 1) we used silicon substrates. First a Ga_2O_3 layer was sputtered on silicon to ensure a good insulation of the substrate and the adherence of the bottom Pt layer. Over this Pt electrode another Ga_2O_3 layer was sputtered, playing the role of the sensing layer. On the top a mesh type platinum electrode was deposited using the lift-off method. The mesh electrode consists of 100 μm Pt lines with 100 μm space between them.

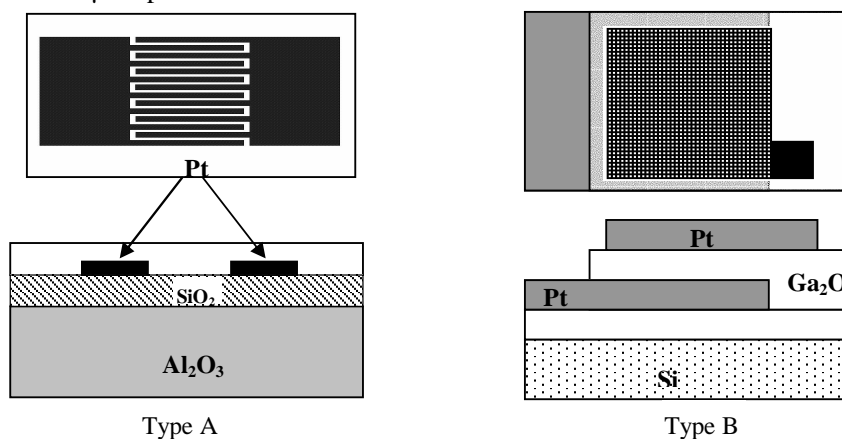


Fig. 1. Schematic representation of the sensors

The structure, composition and surface morphology of the films was investigated by means of XRD, AES and AFM measurements.

The samples were connected on the measurement circuit by bonding 0.1 mm Pt wires on the Pt electrodes. The electrical resistance was measured with a digital multimeter connected to a computer where the data were recorded. The specimens were placed in a quartz tube and introduced in a cylindrical furnace that can operate up to 1100 $^{\circ}\text{C}$. The temperature inside the furnace was controlled with a Pt/Pt-Rh thermocouple.

The sensing characteristics were measured in a controlled stream of oxygen and nitrogen mixture flowing continuously through the quartz tube, while the temperature of the furnace was kept constant at 1000 $^{\circ}\text{C}$. This system allows us to change the oxygen content of the gas stream from 0 % to 100 % while maintaining a constant gas flow rate, which in our experiments was 1 l/min. The percentages are related to the oxygen flow rate and represent only an approximation for the oxygen partial pressure in the measuring chamber. The sensitivity and response time of the gallium oxide specimen sensors were measured at 1000 $^{\circ}\text{C}$.

3. Results and discussion

X-ray diffraction investigations of our Ga_2O_3 films show that as-deposited samples are amorphous. In order to ensure the transformation of amorphous phase into a polycrystalline monoclinic phase of Ga_2O_3 and the stability of the sensor at the operating temperature, after

deposition the samples were annealed in air for 1h at 1050 °C. The surface morphology and grain structure of the films were investigated by AFM.

Previously [6] using AES measurements, we have shown that the oxygen vacancy concentration in Ga₂O₃ films sputtered from a powder target is higher than in the films sputtered from a ceramic target. Thus films with a higher electrical conductivity can be obtained which is a desirable property for sensors based on metal oxides which are insulators and can have high resistances even at high temperatures. The temperature dependence of electrical conductivity was typical as for semiconductor materials, i.e. its conductivity increases as the temperature is increased.

A typical dynamical response for Type A sensors subjected to several changes of the oxygen content in the gas stream between 20% and 0% is presented in Fig. 2. The behavior of the sensor resistance when the oxygen content in the surrounding atmosphere is changed indicates that the electrical conduction is due to electrons. If the oxygen concentration in the surrounding atmosphere is reduced oxygen vacancies are formed due to a diffusion of oxygen out of the film, releasing electrons and decreasing the resistance.

As can be observed from Fig. 2 the response of the gallium oxide films is stable and reproducible.

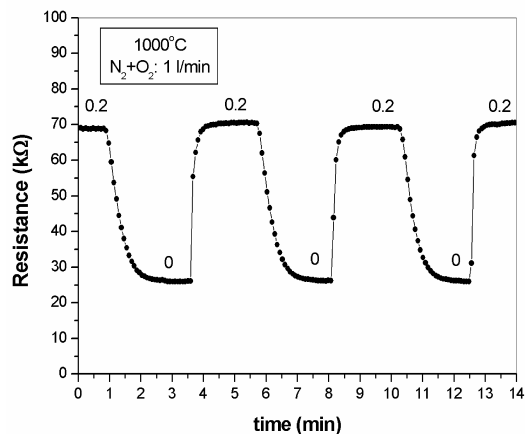


Fig. 3. Dynamical response of Type A sensor to a change of the oxygen flowing rate from 0.2 to 0 l/min.

The type B sensor also has good sensitivity to oxygen in the whole concentration range as can be observed from Fig. 3.

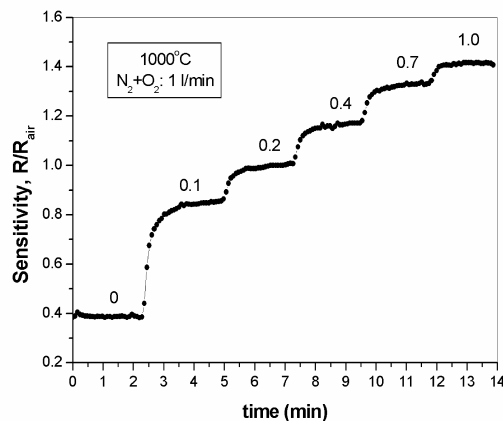


Fig. 3. Sensitivity of Type B sensor to different changes in the oxygen flowing rates

The response time, t_{90} , of the sensors was calculated as the time necessary for the sensor resistance to increase to 90 % of its saturation value. For the Type A sensor a response time of 10 s was achieved while for the Type B sensor the response time was about 20 s.

The oxygen sensing properties of metal oxides at high temperatures are usually explained considering the basic reaction between the oxygen molecules in the gas phase and oxygen vacancies



Here $p = 1$ or 2 if the oxygen vacancies are single or doubly ionized. According to the law of mass action the equilibrium constant is given by

$$K_p(T) = P_{O_2}^{1/2} [V_o^{(p)}] n^p. \quad (2)$$

In the intrinsic region the charge balance can be written as

$$p[V_o^{(p)}] = n \quad (3)$$

given a dependence of the electrical conductivity on the oxygen partial pressure according to eqn.

$$\sigma \propto P_{O_2}^m \quad (4)$$

where $m = -1/2(p+1)$. In this case $m = -1/4$ for single ionized oxygen vacancies and $-1/6$ for doubly ionized oxygen vacancies.

In the extrinsic domain the charge balance is due to different charged defects concentration

$$[A'] \approx [V_o^{**}] \quad (5)$$

where $[A']$ is the concentration of the negative charged acceptors and oxygen vacancies are considered doubly ionized. In this case the oxygen vacancy concentration is fixed by the charged acceptor concentration given a dependence of the electrical conductivity on the oxygen partial pressure according to eqn. (4) where $m = -1/4$.

For Ga_2O_3 it was found that $m = -1/4$ both in crystals [7,8] or thin films [4,9]. For our sensors we found that $m = -0.22$ (Fig. 4) which is close to theoretical value $m = -1/4$. Since the interpretation using single oxygen vacancies is not common for metal oxide sensors this means that for our result we have to consider the extrinsic region. The dependence of the sensitivity on the oxygen content in the oxygen/nitrogen mixture stream with a total flowing rate of 1 l/min is presented in Fig. 4 for both Type A and Type B sensors.

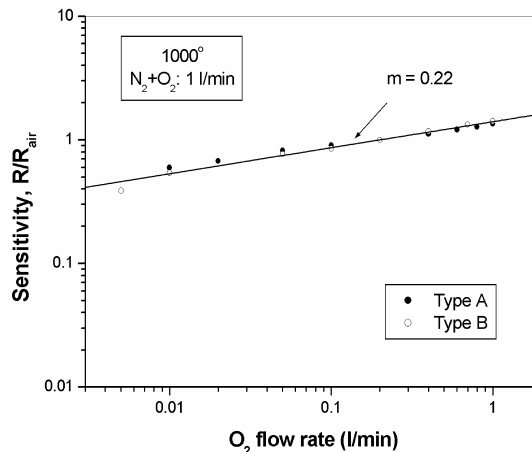


Fig 4. Sensitivity of Type A and B sensors as a function of the oxygen content of O_2/N_2 mixture.

When the oxygen partial pressure is increased the oxygen molecules adsorbed at the surface split into two atoms that will occupy the oxygen vacancies, near the surface. A diffusion process of oxygen inside the film, across the grain boundaries, will reestablish equilibrium with the gas phase. Practically the response time can be influenced by the surface reactions rate or/and the diffusion rate.

The different response times for Type A and Type B sensors suggest that the reaction at the sensor surface is not the rate-limiting step in this case it is expected to obtain the same result.

For obtaining information on the sensing mechanism we investigated the dependence of response time on the grain size for Type A sensor. Samples with different grain size were obtained by modifying the substrate temperature during sputtering. These samples were simultaneously annealed after deposition to avoid misinterpretations due to different annealing time or annealing temperature. For the samples obtained on substrate at room temperature a response time of about 35 sec. was achieved while for samples obtained at a substrate temperature of 300 °C the response time was about 14 sec. This result is shown in Fig. 5 for a change in oxygen content of O₂/N₂ mixture from 0% to 20%. Normalized sensitivity was calculated as $(R-R_0)/(R_{sat}-R_0)$ where R_0 is the resistance before introducing the oxygen and R_{sat} is the saturation value. Previously [6] we observed the same effect for samples obtained at different sputtering pressure. At lower sputtering pressure films with higher grain size are obtained due to a lower sputtering rate. The difference in the grain size was observed in the AFM images. The response for a sample obtained at 2Pa was about three times faster than that corresponding to samples sputtered at a pressure of 10Pa. This indicates that the processes taking place at the grain boundaries play an important role among the processes that can influence the value of the response time. The result can be explained by the fact that sputtered films are compact with no open pores, making the effect of grain boundaries to be more pronounced in films with smaller grains.

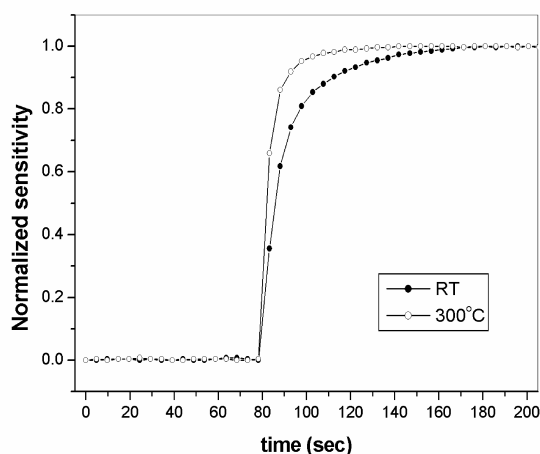


Fig. 6. Normalized sensitivity of Type A sensor for samples obtained at different substrate Temperatures.

The response time was found to increase with decreasing temperature. For example for one sensor obtained at 300 °C substrate temperature the response time increases from 14 sec. at 1000 °C to 21 sec at 950 °C and 30 sec. at 900 °C. The result can be due to the temperature variation of either diffusion coefficient or surface reaction coefficient at grain boundary. The Arrhenius plot of this dependence suggests that there is no change in the sensing mechanism in this temperature range.

4. Conclusions

Using Ga₂O₃ thin films sputtered from a powder target, stable, fast, low cost oxygen sensors operating at 1000 °C can be produced. The films have good electrical conductivity and are sensitive in the whole oxygen concentration range. We proposed a sensor geometry based on Pt-Ga₂O₃-Pt sandwich structure with a mesh type electrode on the top. This sensor also shows good sensitivity to oxygen. Grain boundaries play an important role in determining the value of the response time in sputtered gallium oxide films. The sensitivity of both studied sensors is higher for low oxygen concentrations, making this sensor suitable for applications in incinerator plants or in automobile industry.

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