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Sensitivity of β Ga_2O_3 Thin Film Oxygen Gas Sensors at High Temperature

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Ga_2O_3 thin film sensors in various thicknesses from 300 nm to 900 nm approximately, were fabricated on Si substrate using RF sputtering technology. The oxygen gas sensing characteristics were evaluated as a function of film thickness in N_2/O_2 gas stream mixture at high temperature, 1000°C. It was found that both the response time and sensitivity of β-Ga_2O_3 sensors to oxygen gas are not influenced by increasing in film thickness. The relation between oxygen gas sensing properties and film thickness was discussed on the basis of reactivity on the film at high temperature, from 750°C to 1000°C.
Key words: gallium oxide, oxygen sensor, sensitivity, high temperature

1. INTRODUCTION:

Oxygen sensors are widely used as exhaust gas sensors in automobile industries and incinerators plants. Recently, every new car which is using the gasoline engine is equipped at least two oxygen sensors to control engine operation.

One of the most important materials as gas oxygen sensor at high temperature is β-Ga_2O_3 because of it melting point of about 1800°C. At high temperature the sensing properties of binary oxides are usually determined by an oxygen deficit inside the material, which makes them to behave like *n*-type semiconductors. Another advantage of using β-Ga_2O_3 is that it has only one stable structural modification, β-monoclinic one that can be easily obtained by thermal annealing at 800°C [1]. Hence, this structure is stable in the whole temperature range up to melting point. It was proved that gallium oxide is sensitive to reducing gases such as CO, H_2, CH_x on the basis of surface reactions below 700°C [2]. On the other hand, over 900°C it can be used as oxygen sensor based on the existence of the oxygen vacancies inside the material [3, 4].

In our previous research work [5], it was proved that using β-Ga_2O_3 thin films deposited by RF sputtering using a powder target and single crystal with various electrode geometries the response times were in the same range of 10 seconds at 1000°C but the sensitivities were shown different behavior, 150% for sputtered thin film and 103 % in the case of single crystal.

In this paper, we analyze the oxygen sensitivity of β-Ga_2O_3 sensors on the dependence of the oxygen partial pressure as a function of the film thickness when they were operated at high temperature from 750°C to 1000°C. In order to get a well-defined stoichiometry of gallium oxide thin-films an annealing process at 1100° C for 2 hours was performed.

2. EXPERIMENTAL:

Gallium oxide thin films were deposited on a Si substrate by RF magnetron sputtering, using an ANELVA L 210 FHS system. For this purpose a 4 –inch target was prepared from pure Ga_2O_3 (99.999 %) powder. Ar was used as sputtering gas at a pressure of 2 Pa. During sputtering process Si-substrate temperature was kept at 200°C. Deposition time was varied from 1 h 30 min to 6 h in order to get films with various thicknesses from 270 nm to 900 nm, approximately (Fig. 1).

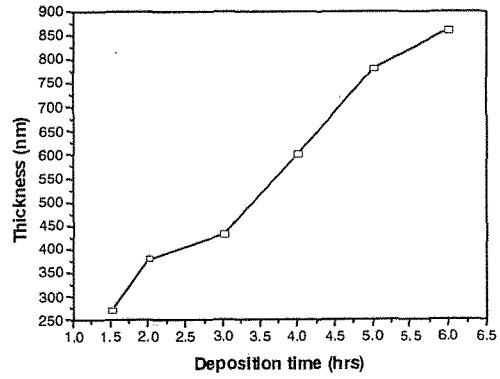


Fig. 1: Dependence of the film s thickness on the deposition time and electrical resistance.

Pt interdigital electrodes with 50 μm spacing made by the lift-off method have been deposited on the top of the samples. The test samples were placed in a quartz tubular furnace that can be operated at high temperatures over 1000°C. The response characteristics for oxygen gas were measured in a high purity controlled stream of O_2/N_2 mixture flowing continuously through the quartz tube. This system allowed us to change separately the oxygen and/or the nitrogen content in the gas mixture stream and then to mix them in various ratios at operating temperature. Electrical resistance measurements were recorded using a digital multimeter which was connected with a computer.

3. RESULTS AND DISCUSSION:

The X-ray diffraction patterns (using Cu $K\alpha_1$ with wave length λ = 1.54056 Å) of β-Ga_2O_3 samples are presented in Fig. 2 (a) and (b).

Apart from the strong diffraction peaks of the Si substrate, a diffraction peak of Ga_2O_3 material with α (202)/β $(\bar{6}01)$ phase or a combination of these two phases was obtained for our as-deposited films (Fig. 2 (a)). Therefore, we suppose that these as-deposited films contain very small crystallites.

In order to get a well-defined stoichiometry of gallium oxide thin-films an annealing process at 1100° C for 2 hours was performed. This process ensured the transformation of α –phase into β –phase polycrystalline monoclinic phase of gallium oxide (Fig. 2 (b)) and also could improve the stability of the sensor at the operating temperature. After annealing process, the peaks of pure β phase as: (110), $(\bar{4}01)$, (002), (111), (401), $(\bar{6}01)$, (600) and (403) were identified in XRD patterns of Ga_2O_3 films deposited by RF magnetron sputtering method with various thicknesses (Fig. 2 (b)).

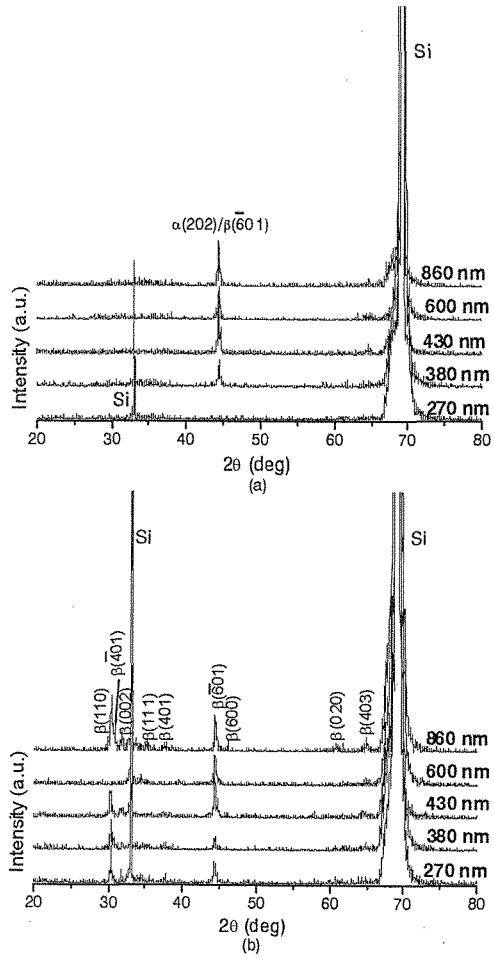
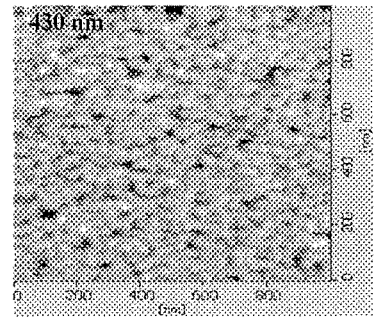


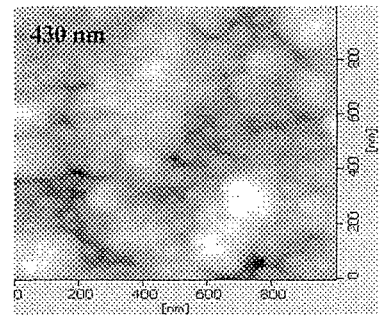
Fig. 2: XRD patterns of as-deposited (a) and annealed (b) Ga_2O_3 films deposited by rf sputtering.

The intensity of some diffraction peaks, (110) and $(\bar{6}01)$, is higher then other diffraction peaks. In this case, we assumed that the intensity was increased by the improvement in the crystallinization of Ga_2O_3 films and the increasing of grain size, respectively.

Surface morphology investigations performed by AFM revealed a surface grain-like structure for as-deposited Ga_2O_3 thin films with crystallites of 35 nm in the diameter.



(a)



(b)

Fig. 3: AFM images of Ga_2O_3 sputtered thin film with various thicknesses (a) as-deposited and (b) after annealing process, respectively.

As can be seen in Fig. 3 (a), tiny crystallites of gallium oxide were stacked densely to cover the surface Si substrate, even when the sample was sputtered only 1 and half hour. Moreover, we have found that the morphology of Ga_2O_3 thin film surfaces remained the same irrespective of the deposition time for the sputtering process, in good agreement with the result of XRD analysis just mentioned. After annealing process at 1100°C in air, we have found that the grain size was increased to 70 nm (Fig. 3 (b)). By increasing the crystallite size, we assume that surface area for the exposure at oxygen gas is increasing the depletion layer at the surface could decrease and increase the electrical conductivity of thin film.

On the other hand, by a sputtering technique the films are usually prepared with a grain-like compact surface structure and no clear limitation of individual grain. In order to analyze the oxygen sensing mechanism for the sensors the ration of the outer surface to the volume of the sensing layer has to be maximized by choosing a proper morphology of the sensing material.

It is known that the oxygen sensing properties of polycrystalline metal-oxide semiconductor strongly

depends on grain boundaries which can contain a high density of surface defects. In general, these defects are commonly accepted to be oxygen vacancies. They can appear as active surface states leading to the formation of depletion layers. These states can trap or release free negative carriers, generating potential barriers and determine the electrical conductivity. When the oxygen partial pressure in the atmosphere changes, the transient behavior of a resistive gas sensor is determined by the rate of the several processes which can occur at the surface of thin film, at the grain boundaries or/and in the bulk of the material [6]. In the intrinsic region the balance charge will give a dependence of electrical resistance on the oxygen partial pressure according to a power law:

$$R \propto P_{O_2}^{-m} \qquad (1)$$

where m is a coefficient and it was found to be -0.24 for all our sensors which is very close to that obtained from single crystal by Cojocaru et al. in ref. [7].

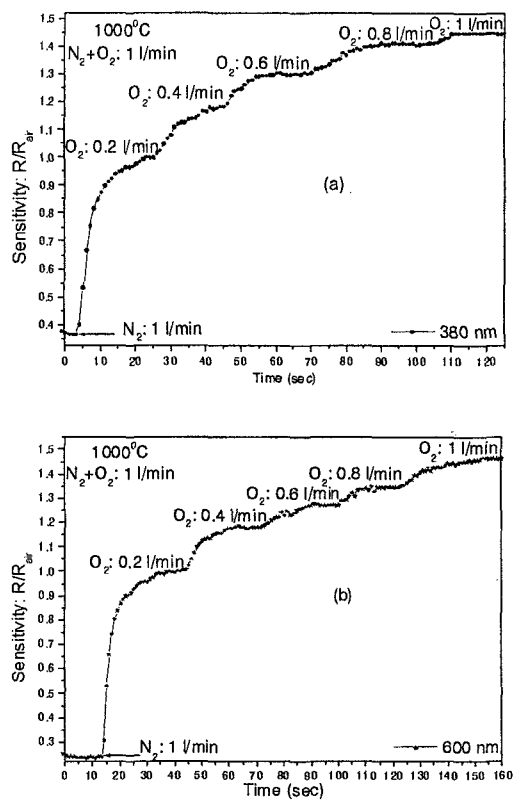


Fig. 4: Sensitivity of β-Ga_2O_3 sensors films with thickness of (a) 380 nm and (b) 600 nm by varying the oxygen content from 0 to 100% in the gas stream of N_2 and O_2 at 1000°C.

In Fig. 4 (a) and (b), the β-Ga_2O_3 thin film sensors prepared with various thicknesses were exposed to oxygen gas. Their sensitivity at oxygen gas is compared at 1000°C. The sensitivity was defined as the ratio between the resistance (R) when the oxygen gas is presented in various flow ratios and the resistance in surrounding standard atmosphere (R_{air}) when the gas stream has the composition 20 % oxygen and 80 % nitrogen. The value of R/R_{air} increases as the oxygen partial pressure in the gas mixture increases from 0 to 100 %. The β-Ga_2O_3 polycrystalline thin films show the sensitivity (R/R_{air}) of about 150% and it is not dependent upon the film thickness. These results lead to that the sensitivity behavior of β-Ga_2O_3 thin films is not a function of the film thickness but could be rather determined by oxygen vacancies concentration in whole deposited film. In this case, the amount of oxygen vacancy could be a characteristic of the preparation technique. We assumed that defects concentration is an important parameter of the Ga_2O_3 thin films and could be a property of the material deposited with sputtering technique and can make a thin film to behave a homogeneously distribution of oxygen vacancy concentration on the surface.

On the other hand, the maximum sensitivity of 145% was achieved for the sensors that work at 1000°C (fig. 5). In this case oxygen sensitivity is depended on the thermal activity of oxygen vacancy on/into film thickness at different operating temperatures. For our devices suitable operating temperature to use them as oxygen gas sensors in maximum working range is at 1000°C.

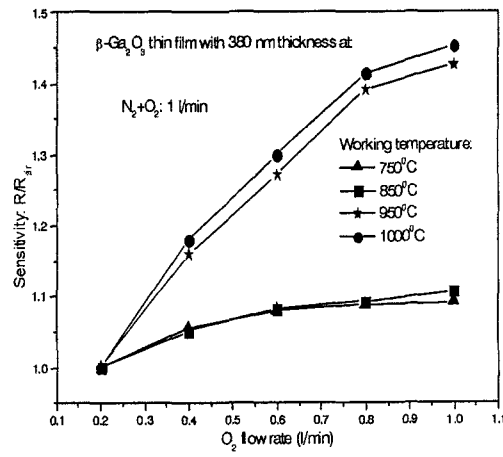


Fig. 5: Sensitivity of β-Ga_2O_3 thin film as a function of the oxygen content of the gas stream of N_2 and O_2 at different operating temperatures.

The dynamic response of the β-Ga_2O sensors with various thicknesses to sudden changes of the oxygen content from 0 to 20 % with as a function of time is presented in Fig. **6**. We have calculated the normalized sensitivity 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 when oxygen flow rate is 20 %. The response time of the sensors was measured as the time necessary for the sensor resistance to increase to 90 % of its saturation value.

At 1000°C, a response time (t_{90}) of about 9 sec was gotten for Ga_2O_3 sensors with 600 and 780 nm and for those with thickness in a range of 270 nm and 380 nm about 10 sec after a sudden change in the oxygen content from 0 to 20 % of the gas mixture stream (N_2+O_2) as is

shown in Fig. 6. Total flow rate was kept constant at 1 l/min by balancing N_2 and O_2 gases.

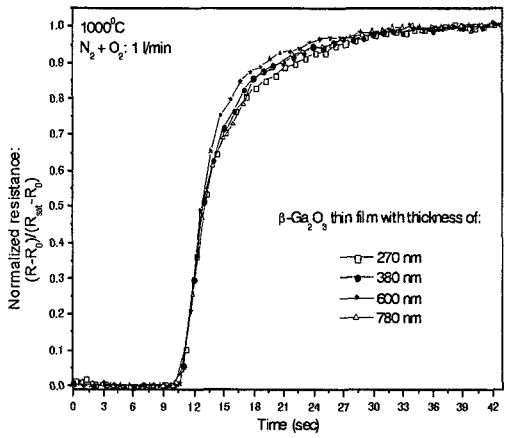


Fig. 6: Dynamic response of Ga_2O_3 sensors at 1000°C. Oxygen concentration in the gas stream is changed from 0 to 20 %.

A significantly influence of the deposited film thickness on the response times could not be observed. This result is quite natural if the sensor kinetics are controlled by diffusion process at surface, hence by the surface-to-volume ratio for the thin film. In this case, the response time should vary with grain size. By changing the crystallite diameter the value of response time is changed. For larger grain size where the surface-to-volume ratio is bigger, respectively making the sensors to behave at the oxygen gas faster a response at high temperature 1000°C. To support this presumption, the response time must be determined by the oxygen diffusion length at film surface in accordance with the relation:

$$t_{90} \propto \frac{\phi^2}{D} \qquad (2)$$

where ϕ is grain diameter and D is the diffusion coefficient. The processes as the reaction and diffusion of oxygen vacancy at the grain boundaries [6] may also play an important role among the processes that can influence the value of the response time, making the effect of grain boundaries to be less marked in films with bigger grains due to the increasing of the exposure area.

4. CONCLUSIONS:

The oxygen sensing characteristics were investigated for β-Ga_2O_3 sensors thin-films deposited by sputtering technique using a powder target. All these sensors show response times in the range of seconds which can not be dependent on the film thickness because of the similar surface morphology. In this paper, we have analyzed the oxygen sensitivity of β-Ga_2O_3 sensors at various oxygen gas flow rate. It was found that for the same film thickness of sensor the sensitivity increased as operating temperature was increased from 750°C to 1000°C. We supposed that the higher oxygen sensitivity could be obtained in the case of the sensors that can operate at high temperature 1000° C and have a constant oxygen vacancy. Moreover, the amount of oxygen vacancies could depend on the fabrication methods for the sensor devices and is not a function of film thickness. For our β-Ga_2O_3 sensor the surface processes mostly influence the modifications of the resistance getting an oxygen sensitivity of 150 % and makes it to be suitable for using in the automobile industry and incinerators plans.

5. REFERENCES:

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