Effect of oxygen on the properties of Ga$_2$O$_3$:Si thin films

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Abstract. The results of studies of electrical and gas-sensitive characteristics of thin films Ga$_2$O$_3$:Si on exposure to oxygen in the range from 0 to 100 vol. % and operating temperatures from 25 to 700 °C were presented. Samples were obtained by HF magnetron sputtering. The possibility of developing low-temperature oxygen sensors was shown. A model of oxygen interaction with Ga$_2$O$_3$:Si films was proposed. The mechanism of Si influence on gas-sensitive properties of thin films of gallium oxide was proposed.

1. Introduction

Interest in the research of the effect of oxygen on the properties of gallium oxide is caused by the prospects of developing miniature sensors based on this material for analysis of the composition of exhaust gases of internal combustion engines, monitoring the concentration of reagents in the chemical industry and metallurgy.

In papers [1-6] it is proposed to use high-temperature oxygen sensors based on thin films (1 µm) of β-phase gallium oxide. The oxygen vacancies V$_{O}$ present in the structure of gallium oxide are electron donors and determine the n-type conductivity of the material [7]. The working principle of these sensors is based on the interaction of gaseous oxygen with the oxygen vacancies in the structure of Ga$_2$O$_3$. The resistance of gallium oxide increases with the oxygen concentration $C$ according to the power law. As the sensor response was taken the ratio of the Ga$_2$O$_3$ resistance at the set value $C$ and at $C = 20$ vol. %. The sensor response increases to 1.04 – 1.6 times at the changing of $C$ in a mixture of O$_2$+N$_2$ from 20 to 100 vol. %. The authors argue that high-temperature oxygen sensors have selectivity due to the impossibility of chemisorption of extraneous gas particles on the surface of gallium oxide at the high temperatures. Additional experimental studies are necessary to confirm this fact. The disadvantages of such sensors are high power consumption and relatively low sensitivity to O$_2$. High operating temperatures $T = 700 – 1100$ °C make difficulties to develop devices compatible with gas analysis systems.

The possibility of developing low-temperature oxygen sensors based on Ga$_2$O$_3$ nanowires is considered in [8]. The sensitivity of structures to gas is explained by the chemisorption of O$_2$ particles on the surface with the participation of oxygen vacancies V$_{O}$, the authors exclude volume effects. The response of the structure at $T=300$ °C, which corresponds to the maximum sensitivity, rises with increasing of oxygen concentration $C$ according to the power law with an exponent – 0.57. The high
response at low temperatures is explained by the increasing in the ratio between the surface area of the semiconductor and its volume. In this paper, the selective detection of oxygen was experimentally established, but the authors do not explain what this is due to. The sensitivity of structures to O\textsubscript{2} was investigated in a limited range of C from 0.5 to 5 vol. %.

The sensitivity of metal oxides to the gases can be increased and shifted to the low-temperature region by modifying with various additives. In this paper the gas-sensitive and electrical characteristics of thin films Ga\textsubscript{2}O\textsubscript{3} doped by Si on exposure to O\textsubscript{2} in the range C from 0 to 100 vol. % and T from 25 to 700 °C are investigated. Ga\textsubscript{2}O\textsubscript{3}:Si is researching widely for electronics applications [7], however, the gas-sensitive properties of such material have not been studied.

2. Experiment
Thin films of Ga\textsubscript{2}O\textsubscript{3}:Si were formed by high-frequency magnetron sputtering of gallium oxide target (99.999 %, USA) in oxygen-argon plasma by means of Edwards Auto-500. Wafers of the polycrystalline sapphire with a thickness of 150 microns and a diameter of 30 mm were used as substrates. Substrates were not specifically heated at the sputtering process. The total pressure in the chamber was 7·10\textsuperscript{-1} mbar, the power of the installation – 70 W. The oxygen concentration in the mixture Ar + O\textsubscript{2} was maintained at 56.1 ± 0.5 vol. %. The distance between the target and the substrate was 70 mm. Pieces of Si (99.999 %) were placed on the surface of the target to dope the samples. The ratio of the surface areas of the Si pieces and the sprayed part of the Ga\textsubscript{2}O\textsubscript{3} target was 3·10\textsuperscript{-3}. The deposition time of Ga\textsubscript{2}O\textsubscript{3} thin films was 24 minutes. After deposition of Ga\textsubscript{2}O\textsubscript{3} films, the obtained structures were annealed in Ar atmosphere for 30 minutes at a temperature of 900 °C. Under these annealing conditions, β-phase Ga\textsubscript{2}O\textsubscript{3} is formed [9]. The sensitive elements of a given shape and size were formed by photolithography. Before the deposition of gallium oxide films the platinum contacts to the layer of Ga\textsubscript{2}O\textsubscript{3} and the heater on the reverse side of the substrate were formed by sputtering followed by photolithographic engraving. After cutting, sensors 1.5x1.5 mm\textsuperscript{2} in size with the area of the sensitive layer of 0.78x0.6 mm\textsuperscript{2} were assembled into TO-8 cans. The thickness of the prepared films was about 160 – 180 nm.

The element composition of formed thin films was determined by Auger electron spectroscopy using specially manufactured large-area samples. To measure the resistance of the sensors used a metal chamber which housed two sensors. A mixture of nitrogen of high purity (99.999 %) and technical oxygen (99.7%) was pumped through the chamber. The content of the components of the gas mixture was controlled by the gas flow meters Bronkhorst. Oxygen concentration of 0 vol. % corresponds to the pumping through the chamber of nitrogen only. Resistance measurements of structures at the various conditions were carried by means of source–meter Keithley 2636A characterized by high accuracy and capable of measuring the resistance of the order of 10\textsuperscript{13} Ω. The applied voltage to the structures was 5 V. The sensors were heated by means of a laboratory DC power supply.

3. Results and discussions
Analysis of the temperature dependence of the resistance of samples in a gas mixture containing 21 vol. % of O\textsubscript{2} and 79 vol. % of N\textsubscript{2} showed that in the Ga\textsubscript{2}O\textsubscript{3}:Si band gap there are two donor levels located 0.036 and 1.37 eV below the conduction band bottom. The first level is caused by doping by Si, the second is due to the presence of oxygen vacancies in the Ga\textsubscript{2}O\textsubscript{3} structure. Starting on 200 °C, the samples demonstrate sensitivity to oxygen. Figure 1 shows that the maximum response is observed at T=400 °C. The sensor response S is the ratio of resistance at a given value C and resistance at 100 % N\textsubscript{2} in a chamber. The S with increasing oxygen concentration increases according to the power law S~C\textsuperscript{b} (Figure 2). An exponent b depends on temperature (Table 1).

The sensitivity of samples to hydrogen, carbon monoxide and nitrogen dioxide was analyzed to determine the selectivity of oxygen detection. The influence of hydrogen and carbon monoxide on the resistance of Ga\textsubscript{2}O\textsubscript{3}:Si films was evaluated at a temperature corresponding to the maximum response to oxygen. A mixture containing 21 vol. % of O\textsubscript{2} and 79 vol. % of N\textsubscript{2} was selected as the initial atmosphere. After the establishment of the stationary values of R the appropriate gas was launched.
into the chamber. Effect of 1.55 vol. % of hydrogen and 160 ppm of CO leads to a slight decrease in resistance of 1.87 and 1.1 times, respectively. Exposure to 71 ppm nitrogen dioxide leads to an increase in film resistance by 10 times. It follows from this that under the established conditions, thin Ga$_2$O$_3$:Si films react poorly to the exposure to high concentrations exceeding the maximum permissible limits of reducing gases. However, the resistance of the thin Ga$_2$O$_3$:Si films increases sharply when oxidizing gases (nitrogen dioxide, oxygen) appear in the atmosphere.

**Table 1.** The temperature dependence of the exponent b of thin Ga$_2$O$_3$:Si films.

| $T$, °C | 300   | 400   | 500   | 600   | 700   |
|---------|-------|-------|-------|-------|-------|
| b       | 0.44±0.03 | 0.86±0.02 | 0.67±0.03 | 0.60±0.05 | 0.61±0.01 |

**Figure 1.** Temperature dependencies of the response at different concentration of O$_2$.

**Figure 2.** The concentration dependencies of response to oxygen.

The response time $t_{res}$ and recovery time $t_{rec}$ were determined to estimate the operation speed of sensors. However, the gas flow rate and the time required for the formation and transmission of the gas mixture into the measuring chamber effect on $t_{res}$ and $t_{rec}$. Therefore as the $t_{res}$ was chosen the time from the beginning of the sensor resistance change, initially placed in an oxygen-free environment, to the time of establish of $0.9 \cdot R$ at $C=44.5$ vol. % (Figure 3). The shortest response time for sensors was observed at $T=600$ °C and was $110 \sim 130$ s. Response time at exposed to 71 ppm of nitrogen dioxide at a temperature of 400 °C amounted to 213.2 s. After exposure of all gases the resistance of the sensor recovered to the initial values. As a recovery time for oxygen sensors was chosen the time between the beginning of the resistance reduction and the establishment of 1.1 of the stationary resistance of sensor placed in an oxygen-free environment. The recovery time was ~ 800 s. It should be borne in mind that the times $t_{rec}$ and $t_{rec}$ were determined at exposed to relatively high concentrations of oxygen on the sensors.

Figure 3 shows the change in resistance of the two sensors based on the thin Ga$_2$O$_3$:Si films at exposure to 44.5 vol. % of oxygen. Differences in the characteristics of sensors, their kinetics, response values, response and recovery times are caused by the disadvantages of magnetron sputtering technology of thin films. However the regularities for the sensors obtained on one plate are the same. The sources of differences of samples can be heterogeneous distribution of silicon, different concentration of local defects, minor differences in the area and thickness of films, etc.
Figure 3. The time dependence of sensor resistance at exposure to 44.5 vol. % of oxygen.

The curves of increase of the sensor resistance at exposed to oxygen (Figure 3) are satisfactorily approximated by the difference of two decreasing exponential functions. The time-constants are $11 \sim 30$ s and $57 \sim 71$ s. The curves of decay of the sensor resistance after the oxygen exposure are satisfactorily approximated by the sum of two decreasing exponential functions and the time-constants are $58 \sim 95$ s and $232 \sim 288$ s.

It is necessary to estimate the ratio between the grains size $d_s$ of Ga$_2$O$_3$ and the Debye length $L_D$ in this material to establish the mechanism of oxygen influence on the electrical resistance of the films. The Debye length was calculated according to

$$L_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{e^2 n}},$$

where $\varepsilon_r = 10.2$ [10] is the relative permittivity of the Ga$_2$O$_3$; $\varepsilon_0$ is the electrical constant; $k$ is Boltzmann constant; $e$ is the electron charge; $n$ is the electron concentration in Ga$_2$O$_3$. For the researched films $n = n_F + n_d$, where $n_F$ is the electron concentration due to ionization oxygen vacancies; $n_d$ is the electron concentration due to ionization donor level of Si. The resistance of films at $T = 600$ °C and the electron mobility $\mu_n = 0.44$ cm$^2$/V·s [10,11] were used to calculate $n$. The electron concentration in Ga$_2$O$_3$:Si films at $T = 600$ °C and placed in an oxygen-free environment is $(2 \sim 4) \times 10^{16}$ cm$^{-3}$ and on exposure to 44.5 vol. % of oxygen $n \approx (2 \sim 3.5) \times 10^{15}$ cm$^{-3}$. Estimates have shown that the Debye length is greater the characteristic grains sizes of the thin Ga$_2$O$_3$:Si films which are 145 and 100 nm. Consequently barriers at the interface of Ga$_2$O$_3$ grains do not affect the transport of charge carriers. The conductivity of the films has a semiconductor character. Oxygen molecules have acceptor properties and during chemisorption on the Ga$_2$O$_3$ surface capture electrons from the conduction band of the semiconductor forming a layer depleted by electron in the near-surface region of the semiconductor. However, the absence of the saturation of concentration dependences of the oxygen sensor resistivity, the presence of two time constants during the rise and fall of the resistance during the supply and pumping of oxygen and low responses to reducing gases indicate that a significant role is played by the interaction of oxygen molecules and oxygen vacancies according to the reaction $O_0 \leftrightarrow V_0^{\delta^+} + pe^{-} + 1/2 O_2^g$, here $O_0$ is lattice oxygen; $O_2^g$ is gaseous oxygen, $p=1$ for $V_0^{\delta^+}$ and $p=2$ for $V_0^{\delta^+}$. The presence of the maximum in figure 2 is explained by the dependence on the temperature of the ratio between the processes of adsorption and desorption of oxygen molecules. The increase of the sensor response at $T=700$ °C is caused by the increasing role of the bulk processes with the participation of $V_0$.

Auger electron spectroscopy study had shown that the Si concentration in the samples is less than 0.5 at. % and there is a deviation from stoichiometry. The concentration of Ga atoms is 42.3 at. %, the
oxygen atoms – to 57.1 at. %. Atomic force microscopy research had shown that the surface roughness of the Ga$_2$O$_3$:Si is 0.2345 microns. This value for the Ga$_2$O$_3$ is 0.0783 microns. The gain of the sensor response for the Ga$_2$O$_3$:Si thin films is caused by the formation of a more extended surface of the samples resulting in an increase in the surface density of the adsorption centers for oxygen molecules and a changing of the stoichiometry of structures towards an increase in the concentration of Vo in the bulk of Ga$_2$O$_3$.

4. Conclusion
The possibility of developing low-temperature oxygen sensors based on thin films Ga$_2$O$_3$:Si was shown. There are two donor levels in the band gap of the Ga$_2$O$_3$ due to the impurity of Si (0.036 eV) and oxygen vacancies (1.37 eV). The temperature of the maximum response to O$_2$ is 400 °C. The increasing of the resistance of thin films according to the power law with an increasing of the oxygen concentration at $T\leq$700 °C is caused by the chemisorption of O$_2$ and interaction with oxygen vacancies. The growth of sensor response at $T>700$ °C is caused by the increasing role of the bulk processes involving oxygen vacancies. Si stimulates the formation a more extended surface of Ga$_2$O$_3$ and increase concentration of oxygen vacancies in the bulk of films.

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