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Oxygen Sensors Based on Thin Films of Gallium Oxide Modified with Silicon †

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Abstract: The results of investigation of the electrical resistivity of Ga_2O_3 thin films modified with silicon under the influence of oxygen in the range of O_2 from 9 to 100 vol. % and changes in the heating temperature of structures from 25 to 700 °C were presented. Thin films of Ga_2O_3 were obtained by RF magnetron sputtering of Ga_2O_3 targeted with pieces of Si on the target's surface in oxygen–argon plasma. The possibility of developing of selective oxygen sensors based on thin films Ga_2O_3 modified with silicon with a temperature of maximum response 400 °C was shown. Oxygen influence leads to a reversible increase in the samples' resistance due to the the chemisorption of oxygen on the surface of thin Ga_2O_3 films. An increase in the response of sensors based on the thin polycrystalline films of gallium oxide modified with silicon is caused an increase in the adsorption centers for O^- due to an increase in the surface inhomogeneity and the appearance of additional adsorption centers Si^{4+}.

Keywords: Gallium oxide; thin films; RF-magnetron sputtering; oxygen

1. Introduction

It is offered to use high-temperature oxygen sensors based on polycrystalline films and single-crystal wafers of β-Ga_2O_3 in a number of papers [1–5]. In the range of working temperatures T from 700 to 1100 °C, oxygen penetrates into the bulk of Ga_2O_3, where it interacts with the oxygen vacancies V_O. It was experimentally shown that with increasing oxygen concentration in a mixture of O_2 + N_2 from 20 to 100 vol.% sensor's resistance increases 1.04 ÷ 1.6 times. The disadvantages of such sensors are high power consumption and relatively weak sensitivity to O_2. High operating temperatures make it difficult to develop sensors compatible with other elements of gas analytical systems.

The possibility of creating low-temperature O_2 sensors based on Ga_2O_3 nanowires was considered in [6]. The sensitivity of the structures to gas was explained by the chemisorption of O_2 particles on the semiconductor surface. The authors excluded bulk effects involving of interaction between O_2 and V_O. The sensor response increased with oxygen concentration according to a power law with an index of 0.57 at a temperature of 300 °C that corresponds to the maximum sensitivity.

The high sensitivity to gas at low temperatures was explained by the increase in the ratio between the surface area of a semiconductor and its bulk. In this research, the selective detection of O_2 has been experimentally established. The sensitivity of the structures to O_2 was investigated in a limited range of oxygen concentration from 0.5 to 5 vol.%.

Currently, many studies are devoted to silicon doped gallium oxide. Such material is of interest to power electronics. However, the gas-sensitive properties of gallium oxide with the addition of silicon have not been studied. The purpose of this work is to research the gas-sensitive characteristics of Ga_2O_3 thin films modified with silicon with exposure to O_2. In this work, we denote gallium oxide modified with silicon as Ga_2O_3–Si.

2. Materials and Methods

Ga_2O_3 thin films were formed by the RF magnetron sputtering of a gallium oxide target (99.999 % purity, made in the USA) in oxygen-argon plasma using the Edwards A-500 installation. Polycrystalline polished sapphire wafers were used as a substrate. The substrate was not specifically heated. Working chamber pressure and the installation's power capacity were 7×10^{-3} mbar and 70 W, respectively. Oxygen concentration in Ar+O_2 mixture remained at 56.1 ± 0.5 vol.%. Distance between the target and the substrate was 70 mm. It took 20–24 min to sputter one film onto a sapphire substrate. Pieces of Si (99.999 % purity) placed on the surface of the target to modify samples. The ratio of the surface areas of the Si pieces and the sputtered part of the target was 3×10^{-3}. After deposition of Ga_2O_3 films, the obtained structures were annealed in an Ar atmosphere for 30 min at a temperature of 900 °C to form the β-phase of Ga_2O_3 [7]. The film thickness was 160–180 nm and was measured by means of a Solver HV atomic force microscope of NT-MDT.

To measure the resistance of the sensors, a metallic chamber with 600cm^3 volume was used. There were two gas sensors into the metallic chamber. A mixture of nitrogen and oxygen of high purity was pumped through the chamber. The content of the gas mixture components was control by Bronkhorst gas flow meters. The gas mixture flow was maintained at a constant 1800 cm^3/min level. Concentration of 0 vol. % of O_2 corresponds to pumping only nitrogen through the chamber. Measurements of the resistance of the structures were carried out using a Keithley 2636A source – meter. The applied voltage to the samples was 5 V. The sensors were heated using a laboratory power source.

The morphology of the surface of the films was studied using a Solver HV atomic force microscope of NT-MDT. The determination of the elemental composition of gallium oxide thin films was carried out using specially manufactured samples of a large area. XPS was conducted on the analytic complex of the Surface Science Center (Riber). To excite X-ray spectra, AlKα radiation was used (hv = 1487 eV). XPS spectra were obtained in an ultrahigh vacuum (~ 10^{-9} Torr) using a two-stage cylindrical mirror analyzer. The energy resolution for the XPS spectra was ~ 0.1 eV. The structure and phase composition of gallium oxide films was determined by X-ray diffraction analysis using a high-precision Shimadzu XRD-6000 unit (Shimadzu Corporation, Japan).

3. Results and Discussion

Using atomic force microscopy, it was found that the surface of the Ga_2O_3–Si thin films was a more developed surface of Ga_2O_3 films and represented by grains of the same shape in the form of thin flakes oriented in the same direction with the characteristic dimensions of 145 and 100 nm. The surface roughness of the Ga_2O_3–Si films was 0.2345 microns. The surface structure of Ga_2O_3 films without additives was represented by irregularly shaped grains with an average characteristic size of 100 nm. The roughness of such films was 0.0783 microns. It should be noted that an increase in grain size was observed for thin films of Ga_2O_3 films obtained by RF magnetron sputtering and upon doping with Nb and W [8,9]. From our results it follows that modifying of films with silicon promoted the formation of larger grains of Ga_2O_3. However, in general, the surface of the film was more embossed, i.e., the specific surface area in contact with oxygen increases.

According to XRD analysis the samples consisted of β-phase gallium oxide polycrystals (Figure 1) [10]. Also, according to XRD, there were two intense peaks associated with sapphire [10,11]. For the Ga_2O_3–Si films, there were peaks corresponding to SiO_2 (114) and (222).

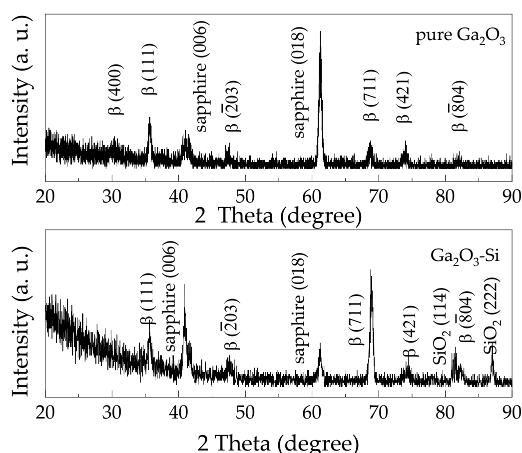

Figure 1. XRD pattern of the pure Ga_2O_3 and Ga_2O_3–Si thin films.

XPS analysis of the samples of the pure Ga_2O_3 and Ga_2O_3–Si showed that spectra contain followings lines: gallium Ga 2p – 1118 eV, the Ga LMM Auger transition – 598–370 eV, Ga 3p – 105 eV, Ga 3d – 20 eV, oxygen O 1s – 530 eV, the O KLL Auger transition – 1000–960 eV. The energy position of the Ga 2p and Ga 3d lines indicated that the thin films correspond in composition to Ga_2O_3. The analysis of silicon in Ga_2O_3 was difficult due to the overlap of the Si 2p and Ga 3p lines. However, in the spectrum of the sample of Ga_2O_3–Si after annealing, there was a slight increase in the signal intensity in the Si 2p region. In this case, silicon was probably in the oxidized state of SiO_x ($1< x <2$). It was not possible to determine the concentration of silicon in the samples because of its low value. It was previously noted that when doping Ga_2O_3 films obtained by magnetron sputtering with Si, silicon oxide was not formed [12]. In this research, annealing was carried out under other conditions.

Quantitative XPS analysis of the samples showed that for the pure Ga_2O_3 thin films an O/Ga ratio was 1.37. Stoichiometric Ga_2O_3 possess an O/Ga ratio of 1.5. The O/Ga ratio in the Ga_2O_3 films depends on the sputtering conditions [13]. It should be noted that the obtained films of the pure Ga_2O_3 were close to stoichiometric. The Ga_2O_3–Si thin films were characterized by an O/Ga ratio of 1.06. That is, gallium oxide films are characterized by a lack of oxygen. The oxygen content in the films mainly depends on the annealing conditions. We believed that a significant deviation from stoichiometry for the Ga_2O_3–Si thin films towards a decrease in the oxygen content was caused by an increase in the specific surface of the films upon modified with silicon. Under conditions of high-temperature annealing in an argon atmosphere, the probability of desorption of lattice oxygen O_O rose with an increase in the specific surface of the films.

Figure 2 shows the change in the electrical resistance of the two sensors based on the Ga_2O_3–Si thin films at exposure to 44.5 vol.% of oxygen and at T = 600 °C. Sensors were initially located in a nitrogen atmosphere. Differences in the characteristics of sensors, their kinetics, response values, response and recovery times were caused by the disadvantages of magnetron sputtering technology of thin films. However the regularities for the sensors obtained on one plate were 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. Oxygen influence on sensors led to reversible changes in their resistance. It was discovered that in the 300–700 °C temperature range after pumping oxygen out of the chamber the resistance of the samples was fully recovered. At $T \leq 300$ °C accuracy of measuring instruments' readings was significantly impacted by noises due to high resistance of the sensors. At higher temperature ranges (300–700 °C) the sensors have significant reproducibility of the characteristics.

To evaluate the performance of sensors the response and recovery times were estimated. The response time t_{res} is the time period during which sensor resistance reaches $0.9R_{Sst}$ level after the

beginning of oxygen exposure, where R_{Sst} is sensor resistance stationary value at 44.5 vol.% of oxygen concentration. The recovery time t_{rec} denotes the time interval during which sensor resistance reaches level $1.1R_{0st}$, where R_{0st} is sensor's stationary resistance value in the nitrogen atmosphere. The shortest response time for sensors was observed at T = 600 °C and was 11–13 s. The recovery time was ~ 70–80 s.

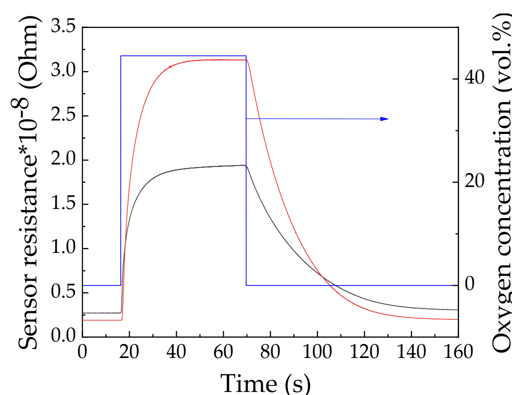

Figure 2. Time dependence of resistance of sensors based on the Ga_2O_3–Si thin films at exposure to 44.5 vol.% of O_2 and at T = 600 °C.

The following relation was chosen as the sensor response S to oxygen:

$$S = R_s(C)/R_N, \quad (1)$$

where C is the oxygen concentration; $R_s(C)$ is the electrical resistance of the samples in the gas mixture O_2 + N_2; R_N is the electrical resistance of the samples in the nitrogen atmosphere. The samples were not practically subjected to oxygen exposure in the temperature range from room temperature to 200 °C. Starting from a temperature of 200 °C, Ga_2O_3–Si exhibited sensitivity to O_2. Temperature dependences of the sensor response to oxygen concentrations 44.5 and 100 vol. % in the temperature range from 200 to 700 °C are shown on Figure 3. There was a pronounced maximum of the sensor response to oxygen on the curves at T = 400 °C. Such temperature of the maximum response is much lower than in [1–5] but higher than in [6]. The response of the sensors decreased with a further increase in temperature. However at T = 700 °**C**, for all oxygen concentrations, a slight increase in the response of the Ga_2O_3–Si structures was observed.

The response of sensors with increasing oxygen concentration rose according to the power law $S \sim C^m$ at all temperatures chosen for research (Figure 4). The value of the index m depends on the temperature. At a temperature 400 °C m = 0.86±0.02 and at T = 500 ÷ 700 °C m = 0.61±0.04.

Evaluation of the effect of H_2 and CO on the resistance of Ga_2O_3-Si was carried out at a temperature corresponding to the maximum response to oxygen. A mixture containing 21 vol. % of O_2 and 79 vol. % of N_2 was chosen as the initial medium. Impact of 1.55 vol. % of H_2 and 160 ppm of CO led to a slight decrease in R_s by 1.9 and 1.1 times, respectively. Exposure to 71 ppm nitrogen dioxide led to an increase in film resistance by 10 times. It follows from this that under the established conditions, the Ga_2O_3-Si thin films react poorly to the exposure to high concentrations exceeding the maximum permissible limits of reducing gases. However, the resistance of the Ga_2O_3–Si thin films increased sharply when oxidizing gases appear in the atmosphere.

The obtained dependence of the sensor response on the oxygen concentration can be explained by the chemisorption of oxygen on the surface of thin Ga_2O_3 films. In the temperature range from 300 to 700 °C oxygen was chemisorbed on the Ga_2O_3 surface mainly in atomic form and captured an electron from the conduction band of gallium oxide [14]. According to XPS analysis, the Ga_2O_3–Si films were characterized by a significant deviation from stoichiometry. The surface and bulk of Ga_2O_3-Si thin films were saturated with superstoichiometric gallium atoms Ga^{3+}. In addition, superstoichiometric silicon atoms Si^{4+} were present on the surface of the Ga_2O_3 thin films. Superstoichiometric gallium Ga^{3+} and Si^{4+} atoms on the surface of a gallium oxide film acted as adsorption centers for oxygen atoms and molecules. An increase in the index m and the sensor

response at temperature range 350 ÷ 500 °C was caused by the influence of Si^{4+} and a reaction with oxygen at these temperatures. A decrease in the response of sensors at temperatures above 500 °C (Figure 3) was caused by the formation of a SiO_2.

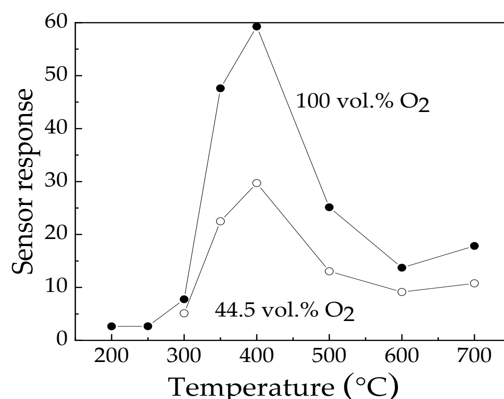

Figure 3. Temperature dependence of the sensor response to oxygen.

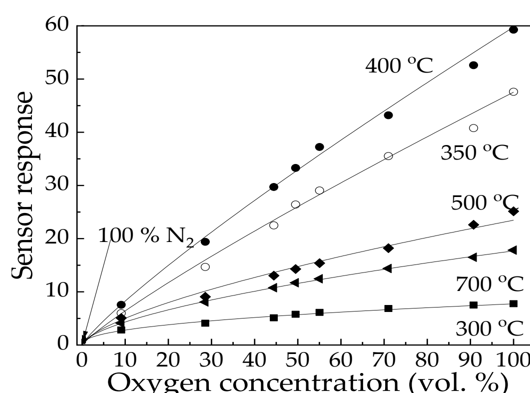

Figure 4. Dependence of the sensor response on the oxygen concentration.

The negative charge of oxygen ions on the Ga_2O_3 surface, which, due to the high concentration of intrinsic and introduced defects, is an n-type semiconductor, caused the energy bands to bend upward. In this case, a space charge region was formed, depleted in the main charge carriers—electrons. The energy band bending $e\phi_s \sim N_i^2$, where N_i is the surface density of oxygen ions O^- chemisorbed on gallium oxide films. In this case, the resistance and response of the sensors to oxygen are proportional to $e\phi_s$. An increase in N_i during oxygen chemisorption leads to an increase in $e\phi_s$ and a corresponding increase in resistance. An increase in the sensor response upon the modification of thin gallium oxide films by silicon is caused by an increase in the adsorption centers for O^- due to an increase in the surface inhomogeneity and the appearance of additional adsorption centers Si^{4+}.

4. Conclusion

Thus, the possibility of creating oxygen sensors based on Ga_2O_3–Si thin films prepared by the method of RF magnetron sputtering is shown. It was discovered that the obtained films correspond to β-phase of gallium oxide. The studied structures demonstrate sensitivity to oxygen from 9 to 100 vol.%. The maximum response of the structures is observed at 400 °C. Oxygen influence leads to a reversible increase in the samples' resistance due to chemisorption of oxygen O^- on the surface of thin Ga_2O_3 films. An increase in the response of sensors based on the thin polycrystalline films of gallium oxide modified with silicon is caused an increase in the adsorption centers for O^- due to an increase in the surface inhomogeneity and the appearance of additional adsorption centers Si^{4+}. The oxygen reaction with Si^{4+} is took place in the temperature range 350–500 °C.

Author Contributions: conceptualization, software, validation, formal analysis, data curation, writing—original draft preparation, writing—review and editing, supervision, project administration, funding acquisition, A.V.A.;

methodology, A.V.A., E.V.C., and B.O.K.; investigation, A.V.A., N.N.Y., P.M.K., and S.N.N.; resources, A.V.A., and E.V.C.; visualization, A.V.A., and N.N.Y.; X.X.;

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