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Proceeding Paper

Gas Sensitive Properties of β-Ga_2O_3 Thin Films Deposited and Annealed at High Temperature †

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Abstract: The gas-sensitive properties of thin films of β-Ga_2O_3 deposited by RF magnetron sputtering with heating of the substrate to 650 °C were studied. Some of the samples were subjected to additional high-temperature annealing at a temperature of 900 °C. As a result, for samples subjected to additional annealing, the response when exposed to 1% H_2 increased by 5 once, sensitivity to hydrogen-containing gases appeared. These samples are also characterized by good long-term stability compared to samples without high-temperature annealing. The improvement in gas-sensitive characteristics is explained by a decrease in oxygen vacancies and a decrease in current density by 4 orders of magnitude.

Keywords: β-Ga_2O_3 thin films; gas sensors; high temperature annealing; magnetron sputtering

1. Introduction

Active development of resistive gas sensors based on β-Ga_2O_3 began in the 80–90 s of the last century [1,2]. Thanks to advances in the synthesis of semiconductor materials, resistive gas sensors based on β-Ga_2O_3 have been widely developed. Compared to many metal oxide semiconductors (SnO_2, In_2O_3, WO_3 and ZnO), the using of Ga_2O_3 as a sensitive layer makes it possible to create gas sensors that are stable at high operating temperatures and low oxygen concentrations, weakly affected by environmental humidity and characterized by high stability of characteristics [3–5]. These advantages are key in the development of gas analytical systems for extreme operating conditions (elevated ambient temperatures, high concentrations of water vapor, changes in oxygen concentration over a wide range) [4,5].

When developing resistive gas sensors based on metal oxide semiconductors, it is important to reduce the contribution of bulk conductivity. For this reason, thin-film technology is promising for creating sensors. The magnetron sputtering method is widely used to form thin films of metal oxide semiconductors. In particular, thin films of Ga_2O_3 are formed using RF magnetron sputtering. RF magnetron sputtering has several advantages over other methods: low cost, ease of control, good adhesion, wide variety of materials and high sputtering speed. To improve the crystallinity of films obtained by this method, it is necessary to anneal at T > 800 °C. When annealing T < 800 °C, amorphous and a mixture of Ga_2O_3 phases are observed [6,7]. Another way to obtain crystalline films is by heating the substrate during deposition. This method is poorly widespread and researched. In a number of works [8–10], crystalline layers are obtained at a substrate temperature from 300 to 700 °C. The authors also note that the crystallinity of the film also depends on other factors: the presence of oxygen in the reactor, magnetron power,

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pressure in the reactor, etc. The gas-sensitive properties of Ga_2O_3 thin films obtained by high-temperature magnetron sputtering have not yet been studied. In this work, β-Ga_2O_3 samples obtained by RF magnetron sputtering at a substrate temperature of 650 °C and subsequent high-temperature annealing of 900 °C were studied.

2. Materials and Methods

β-Ga_2O_3 with a thickness of 300 nm was deposited by radio frequency magnetron sputtering of a (5N) oxide target in an argon plasma onto sapphire with a thickness of 0.43 mm. The substrate temperature during film deposition was 650 °C. This series was designated GO-650. The plate with the Ga_2O_3 film was divided into two parts, the second part was subjected to additional annealing at a temperature of 900 °C for 30 min in an air atmosphere. These samples are designated GO-650+900. Pt contacts of various topologies were formed on the surface of the films.

To measure the electrically conductive and gas-sensitive properties, platinum plane-parallel contacts were deposited on the surface of a thin GO-650 film through a shadow mask. The interelectrode distance was 600 μm. Interdigitated contacts with an interelectrode distance of 315 μm were deposited on the surface of a thin GO-650+900 film using vacuum deposition and photolithography.

Measurements of the current-voltage (I-V) characteristics and time dependences of the sample current when exposed to various gases were carried out with a Keithley 2636A source-meter in a sealed Nextron MPS-CHH microprobe station. This microprobe station allows to measure the electrically conductive characteristics of films in the temperature range from room temperature to 750 °C with an accuracy of T ± 0.1 °C. The measurements were carried out in dark conditions, in a flow of clean dry air or in a gas mixture of pure dry air + target gas. As the target gases H_2, CO_2, CO, NO_2 and O_2 were chosen. To study the effect of oxygen on the properties of thin Ga_2O_3 films, a mixture of N_2 and O_2 gases was pumped through the chamber. The flow rate of gas mixtures through the measuring chamber (volume 100 cm^3) was maintained at 1000 cm^3/min. A special generator served as a source of pure dry air. The concentration of the target gas in the mixture was controlled by a gas mixture generator with Bronkhorst mass flow regulators. The relative error of gas flow did not exceed 1.5%. The applied voltage to the sample electrodes was 5 V.

3. Gas-Sensitive Properties of Ga_2O_3 Thin Films

Main Samples GO-650 and GO-650+900 have high resistance even at T < 300 °C, the current in the samples at 5 V is no more than pA. The current increases with increasing temperature from 300 to 600 °C, and from 400 to 750 °C for samples GO-650 and GO-650+900 by 3 orders of magnitude, respectively.

In Figure 1 shows the dependence of responses to fixed H_2 concentrations on temperature for GO-650 and GO-650+900 thin films. Exposure to reducing gases H_2, CH_4, NH_3 and CO results in a reversible increase in current through the samples.

The following relationship was chosen as a reaction to reducing gases:

$$S_g = I_g/I_{air}, \tag{1}$$

where I_g is the current of a thin film in a gas mixture of pure dry air + reducing gas; I_{air}— thin the film current in pure dry air. Exposure to O_2, NO_2 leads to a reversible decrease in the current through the GO-650 and GO-650+900 samples. The following relationship was used to response to these gases:

$$S_{ox} = I_{air}/I_{ox}, \tag{2}$$

where I_{ox} is the current of a thin film in a gas mixture of pure dry air + oxidizing gas. The curves in Figure 1 are characterized by the presence of maxima S_{MAX} at a certain temperature T_{MAX}. It is recommended to select T_{MAX} as the operating temperature.

The response of GO-650 films when stored in a sealed bag after exposure to H_2 changes significantly. This results in a significant increase in response. Such a drift of gas-sensitive characteristics over time is typical for thin films of metal oxides and semiconductors. For samples GO-650+900 such a pattern is not observed, the response deviates from the average value in small areas (Figure 2).

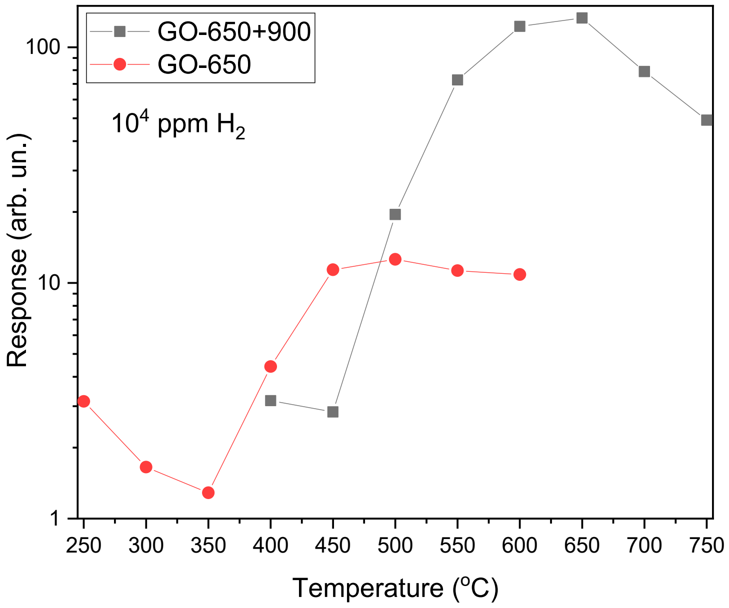

Figure 1. Dependence of the response of GO-650 and GO-650+900 at 10^4 ppm H_2 on the operating temperature.

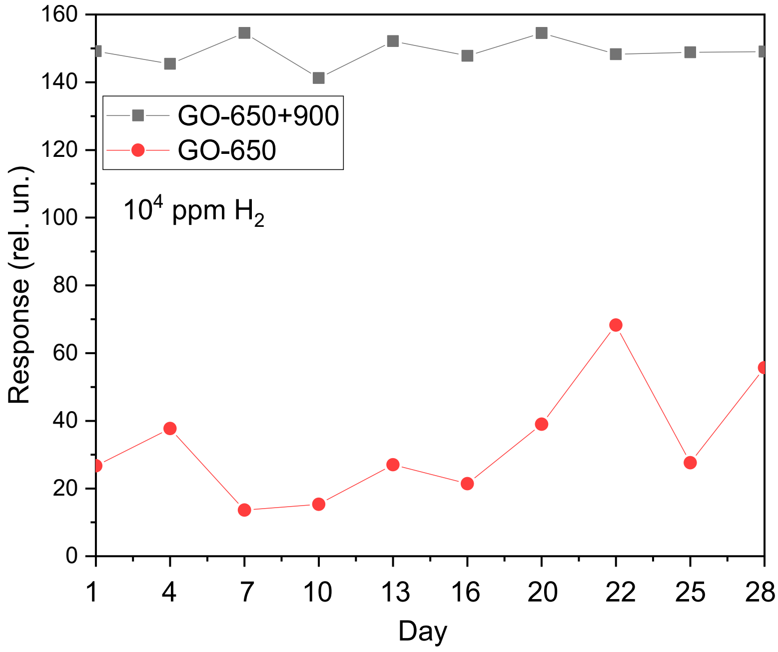

Figure 2. Long-term stability under the exposure to a fixed hydrogen concentration.

Despite the poor long-term stability of the GO-650 samples, all samples have good temporary stability over the course of a single experiment. Figure 3 shows the time dependences of the current under 5-fold exposure to 1% of H_2.

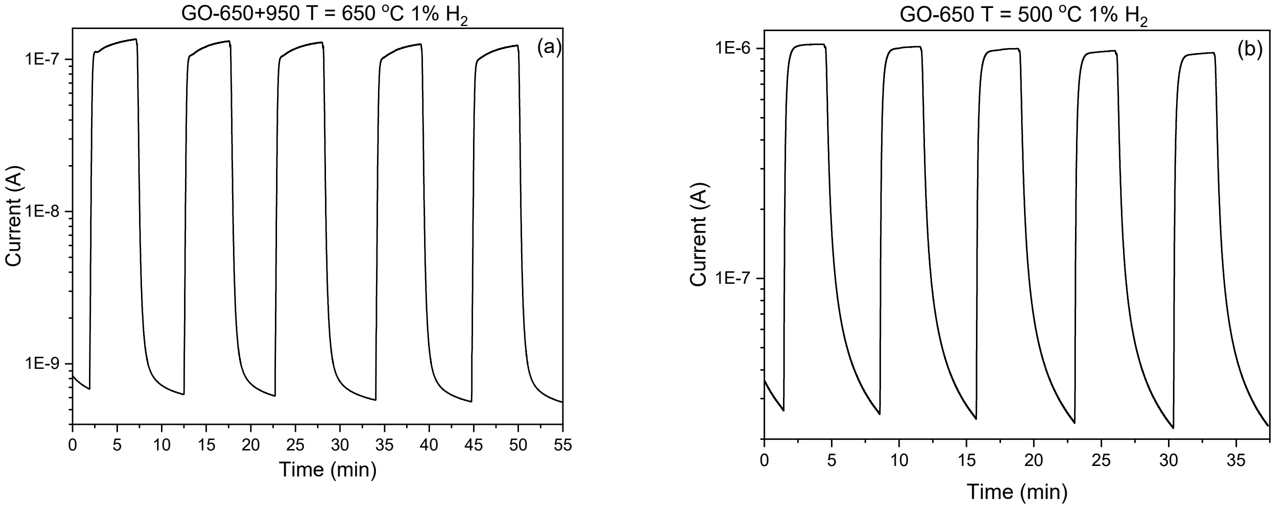

Figure 3. Time dependences of the current through the samples under fivefold exposure to 1% of H_2.

The selectivity of thin films was measured. The temperature dependences of the response for various gases for GO-650+900 thin films are presented in Figure 4.

The concentration of CH_4, CO_2 and O_2 was 1 vol. %, the concentration of CO and NH_3 was 0.2 vol. %. GO-650 thin films do not respond well to other gases. GO-650+900 samples have a high response to H_2, NH_3 and CH_4.

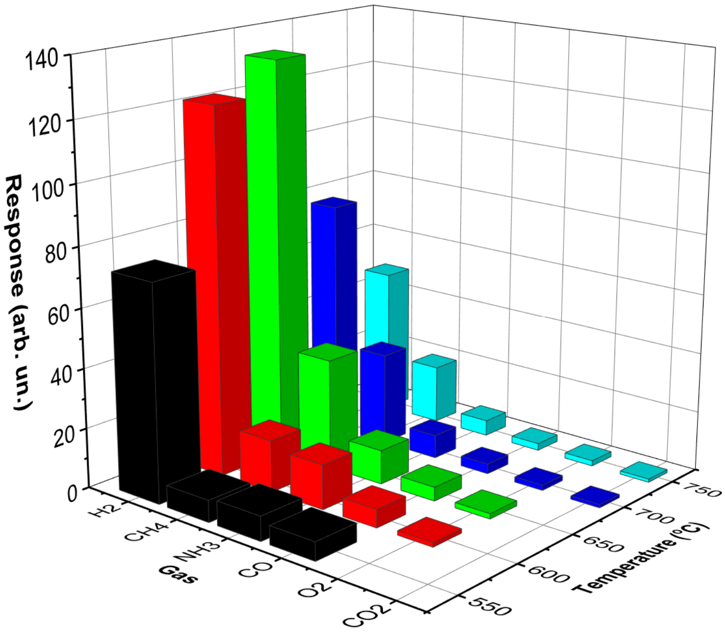

Figure 4. Temperature dependences of the response to various gases and for thin films GO-650+900.

The improvement in the gas-sensitive characteristics of GO-650+900 thin films is mainly due to annealing in an air atmosphere. As a result of annealing, the number of oxygen vacancies decreased, as evidenced by a decrease in the current density. The current density of the GO-650 samples is 0.10 A/cm², the current density of the GO-650+900 samples is 6.27*10–5 A/cm². The current density was calculated at T = 500 °C. The stability of the GO-650+900 samples was also affected by the formation of interdigitated contacts.

4. Mechanism of Gas Sensitivity

In the air, oxygen is chemisorbed on the surface of gallium oxide, which captures electrons from the conduction band of gallium oxide, forming in the near-surface region of the semiconductor a layer depleted of major charge carriers, electrons. Oxygen chemisorbed on the surface of β-Ga_2O_3 films is presented in molecular O_2^-, atomic O^- and O^{2-} forms. The atomic form of chemisorbed oxygen O^- is the most reactive when interacting with molecules of reducing gases. In the temperature range of 200–650 °C, O^- predominates on the surface of β-Ga_2O_3.

Chemisorption of oxygen can be described by the following expression:

$$O_2 + 2e \rightarrow 2O^-_{ch}, \tag{3}$$

where O^-_{ch} is a chemisorbed oxygen ion. Superstoichiometric gallium atoms Ga^{3+} on the surface of β-Ga_2O_3 can as adsorption centers for oxygen. In the region of selected operating temperatures, when reducing gases appear in the air, their molecules interact with previously chemisorbed O^-_{ch}. These interactions on the surface of β-Ga_2O_3 can be described by the following reactions:

$$H_2 + O^-_{ch} \rightarrow H_2O\uparrow + e, \tag{4}$$

$$2NH_3 + 3O^-_{ch} \rightarrow N_2\uparrow + 3H_2O\uparrow + 3e, \tag{5}$$

$$CH_4 + 4O^-_{ch} \rightarrow CO_2\uparrow + 2H_2O\uparrow + 4e, \tag{6}$$

When the surface of a semiconductor is exposed to oxidizing gases NO_2 and NO, the following reactions may occur:

$$NO_2 + e^- \rightarrow NO_2^-, \tag{7}$$

$$NO_2 + O^-_{ch} \rightarrow NO_3^-, \tag{8}$$

Reactions (7) occur without the participation of $O\text{-}_{ch}$ ions, NO_2 and NO molecules are chemisorbed onto a free adsorption center and capture electrons from the conduction band of β-Ga_2O_3. An additional negative charge on the surface of β-Ga_2O_3 leads to a greater increase in $e\varphi_s$, and, consequently, to a decrease in conductivity and charge carrier current in β-Ga_2O_3.

5. Conclusions

For the first time, the gas-sensitive properties of β-Ga_2O_3 structures obtained by RF magnetron sputtering with heating of the substrate and subsequent high-temperature annealing have been studied. Thin films of β-Ga_2O_3 without subsequent high-temperature annealing had a 3–4 times lower response to hydrogen and had a long drift of characteristics compared to β-Ga_2O_3 samples with subsequent high-temperature annealing. As a result of high-temperature annealing and the formation of interdigitated contacts, GO-650+900 thin films became more stable, and the responses increased several times. As a result of annealing in air at T = 900 °C in samples followed by high-temperature annealing, the number of vacancies decreases, the current density decreases by 4 orders of magnitude, and stability increases.

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References

1. Fleischer, M.; Hanrieder, W.; Meixner, H. Stability of semiconducting gallium oxide thin films. *Thin Solid Films*. **1990**, *190*, 93–102. https://doi.org/10.1016/0040-6090(90)90132-W.
2. Fleischer, M.; Giber, J.; Meixner, H. H_2-Induced changes in electrical conductance of β-Ga_2O_3 thin-film systems. *Appl. Phys.* **1992**, *A54*, 560-566. https://doi.org/10.1007/BF00324340.
3. Afzal, A. β-Ga_2O_3 nanowires and thin films for metal oxide semiconductor gas sensors: Sensing mechanisms and performance enhancement strategies. *J. Mater.* **2019**, *5*, 542–557. https://doi.org/10.1016/j.jmat.2019.08.003.
4. Hoefer, U.; Frank, J.; Fleischer, M. High temperature Ga_2O_3-gas sensors and SnO_2-gas sensors: A comparison. *Sens. Actuators B Chem.* **2001**, *78*, 6–11. https://doi.org/10.1016/S0925-4005(01)00784-5.
5. Lampe, U.; Fleischer, M.; Meixner, H. Lambda measurement with Ga_2O_3. *Sens. Actuators B Chem*. **1994**, *17*, 187–196. https://doi.org/10.1016/0925-4005(93)00880-8.
6. Pech, S.; Kim, S.; Kim, N.H. Magnetron Sputter-Deposited-Ga_2O_3 Films on c-Sapphire Substrate: Effect of Rapid Thermal Annealing Temperature on Crystalline Quality. *Coatings* **2022**, *12*, 140. https://doi.org/10.3390/coatings12020140.
7. Singh, A.K.; Gupta, M.; Sathe, V.; Katharria, Y.S. Effect of annealing temperature on β-Ga_2O_3 thin films deposited by RF sputtering method. *Superlattices Microstruct.* **2021**, *156*, 106976. https://doi.org/10.1016/j.spmi.2021.106976.
8. Ramana, A.K.B.C.V. Mechanical Properties of Nanocrystalline and Amorphous Gallium Oxide Thin Films. *Adv. Eng. Mater.* **2018**, *20*, 1701033. https://doi.org/10.1002/adem.201701033.
9. Saikumar, A.K.; Nehate, S.D.; Sundaram, K.B. Review—RF Sputtered Films of Ga_2O_3. *ECS J. Solid State Sci. Technol.* **2019**, *8*, Q3064–Q3078. https://doi.org/10.1149/2.0141907jss.
10. Vega, E.; Isukapati, S.B.; Oder, T.N. Microstructure and optical properties of sputterdeposited Ga2O3 films. *J. Vac. Sci. Technol. A* **2021**, *39*, 033412. https://doi.org/10.1116/6.0000938.